# Non-innocence of the diiminepyridine ligand in 

 its cobalt complexesBy Di Zhu

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## Doctor of Philosophy

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#### Abstract

This thesis focuses on the properties of the diiminepyridine (DIP) ligand and its transition metal complexes, especially cobalt complexes.

Existing and new X-ray structures of five-coordinate DIP Fe and Co dihalide complexes have been analyzed with the assistance of the two-angle criterion $\omega$ and the potential energy surfaces for the distortion of first-row transition metal complexes have been explored by density functional theory (DFT). The steric hindrance of the DIP ligand showed some influence on the preference for SP over TBP. However, the small energy barrier (less than $6 \mathrm{kcal} / \mathrm{mol}$ ) indicated easy distortion of the metal centers. The metal effect seems to be small in terms of the structural preference. Further analysis of iron dialkyl complexes showed that the larger sterical bulkiness of the DIP ligand corresponds to the higher activity of their iron complexes in ethylene polymerization. However, there seems to be no direct correlation between structural preference and catalytic activity.

The effect of modification of DIP ligands was further studied by developing ligand parameters, which intend to measure the $\sigma$-donor and $\pi$-acceptor ability of the ligand, according to the assumption that the stabilization energy of the metal complexes can be decomposed using a linear energy relationship. The results showed that the standard DIP ligand is both a strong $\sigma$-donor and a strong $\pi$-acceptor, and inferior only to the bis(carbene)pyridine ligand. The strong $\pi$-acceptor ability of DIP plays a role in stabilizing cobalt(I) complexes that are intermediates en route to active catalysts.


A mild way to make (DIP)CoR using labile-ligand cobalt dialkyl precursors has been explored. The described procedure to synthesize $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in this thesis is simple and easy to reproduce. This compound is stable at room temperature and can be further converted to (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in high yield. The X-ray structure of the analogous $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}$ showed a structure similar to its iron analog. Application to DIP ligands indicates that the $\pi$-acceptor ability of the ligand determines whether cobalt(I) or cobalt(II) dialkyl will be obtained. However, steric protection is important in obtaining stable cobalt(I) alkyl complexes. Based on the above, the reactivity of the alkyl cobalt(I) complex of 2,6-[2,6-Me $\left.\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{C}\left(\mathrm{CH}_{3}\right)\right]_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ (L) ligand was explored in more detail. This ligand is less hindered than the often-used 2,6${ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ ligand and might induce more interesting chemistry. Hydrogenolysis of $\mathrm{LCoCH}_{2} \mathrm{SiMe}_{3}$ generated an unstable cobalt(I) hydride which was quickly converted to cobalt(0) dinitrogen complex in the presence of dinitrogen. When reacted with organic halides, especially aryl chlorides, this cobalt $\mathrm{N}_{2}$ complex broke the carbon-halogen bond through a binuclear oxidative addition mode to generate two cobalt(I) products. The radical mechanism proposed was supported by DFT studies. The resulting cobalt(I) aryl products can further react with activated alkyl halide to generate cross-coupled products through a radical mechanism. $\mathrm{LCo}\left(\mathrm{N}_{2}\right)$ can also be used to break the acyl carbon-oxygen bond of esters, although less efficiently.

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## Contributions of other Authors

The work in this thesis is mainly performed by the author, as supervised by Dr. Peter H.M. Budzelaar. The following parts are contributed by other people:

1) Andrew Chalaturnyk wrote part of the code for the "calcGeom" program in Chapter 3.
2) Dr. Peter H.M. Budzelaar did most of the DFT calculations in Chapter 6 and part of the single-crystal X-ray measurements in Chapter 3.
3) Dr. Bas de Bruin (University of Amsterdam, the Netherland) did EPR measurements in Chapter 7.
4) Dr. Kirk Marat did the low-temperature NMR experiment in Chapter 6.
5) Wayne Buchannon did all the GC/MS experiments in this thesis.
6) Mark Cooper assisted me in doing single-crystal X-ray diffraction measurements.

## List of Abbreviations

| Ac | Acetyl |
| :---: | :---: |
| B3LYP | Adiabatic connection method using Becke (1998) exchange functional |
|  | and Lee-Yang-Parr correlation functional |
| BP86 | Gradient corrected method using Becke 88 exchange functional and |
|  | Perdew 86 correlation functional |
| b-p | Gradient corrected method using Becke 88 exchange functional and |
|  | VWN(V) and Perdew 86 correlation functionals |
| b3-lyp | Becke (1998) exchange functional and VWN(V) (19\%) and Lee-Yang- |
|  | Parr (81\%) correlation functionals |
| BS | Broken symmetry |
| Bz | Benzoyl |
| $\operatorname{CCSD}(\mathrm{T})$ | Coupled cluster with single and double substitution operators |
| CSD | Cambridge Structural Database |
| COSY | Correlation Spectroscopy |
| Cp | Cyclopentadienyl |
| DFT | Density Functional Theory |
| ${ }^{\text {iPr }}$ ADIP | $2,6-(\mathrm{RN}=\mathrm{CMe})_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}, \mathrm{R}=\mathrm{CHMe}_{2}\left({ }^{i} \mathrm{Pr}\right)$ |
| DIP | Diiminepyridine |
| EPR | Electron paramagnetic resonance |
| FAA | Full angle analysis |


| GC/MS | Gas chromatography-Mass spectroscopy |
| :--- | :--- |
| HF | Hartree Fock |
| HMBC | Heteronuclear multiple-bond correlation spectroscopy |
| HSQC | Heteronuclear single-quantum correlation spectroscopy |
| KS | Kohn Sham |
| LDA | Local density approximation |
| MAO | Methylaluminoxane |
| MECP | Minimum energy crossing point |
| MO | Molecular orbital |
| MP2 | Møller-Plesset perturbation theory of order 2 |
| MP3 | Møller-Plesset perturbation theory of order 3 |
| NMR | Nuclear magnetic resonance |
| PhDIP | 2,6-Bis(phenyliminoethyl)pyridine |
| iPrDIP | 2,6 -Bis[1-(2,6-isopropylphenylimino)ethyl]pyridine |
| Py | pyridine |
| QM | Quantum mechanics |
| SP | Square pyramid |
| SVP | Split valence polarization |
| SQUID | Superconducting Quantum Interference Device bipyramid |
| TBP | TMEDA |

TMS
TZVP

VB
VWN

TZVPP Valence triple-zeta plus polarization
Tetramethylsilane
Triple Zeta Valence Plus Polarization

Valence bond
Vosko-Wilk-Nusai

## Chapter 1. Exploration of Diiminepyridine (DIP) Ligands

### 1.1 Brief introduction to olefin polymerization

Polymers can be found everywhere in our everyday life, such as plastic bags, rubber, plastic bottles used in cosmetics and so on. Polyolefins, specifically polyethylene, compose a major part of market polymers and millions of metric tons of polyethylene are produced every year.

The first industrial production of polyethylene was done by Imperial Chemical Industries in the 1930s, where the radical polymerization process was initiated by oxygen and the whole procedure required high pressure and high temperature. ${ }^{1}$ As they are highly branched, the polymers produced in this way are of low density, highly flexible and transparent. Later on, introduction of transition metal catalysts enabled the process to be done at much lower pressures. Although a variety of catalysts have been developed for polymerization, ${ }^{2}$ only three types of catalysts for ethylene polymerization are used today on a large scale in industry: the Phillips catalysts (chrome-on-silica), ${ }^{3}$ Ziegler-Natta catalysts ${ }^{4}$ and metallocene catalysts. ${ }^{5}$

The Phillips catalyst was first discovered by Hogan and Banks of Phillips Petroleum in the $1950 \mathrm{~s}:^{6}$ they found that chromium oxide on silica is able to catalyze ethylene polymerization at a pressure of 4 MPa , producing a highly branched polymer of low
density. ${ }^{7}$ The polymers produced are soft and easy to stretch. Now, polyethylenes produced by this method comprise half of the commercial polyethylenes.

The Ziegler-Natta catalyst is more well-known due to the fact that Ziegler and Natta were awarded the Nobel Prize in 1963 for the production of polyethylene and polypropylene. ${ }^{8}$ $\mathrm{TiCl}_{3}$ or $\mathrm{TiCl}_{4}$ supported on silica or $\mathrm{MgCl}_{2}$ was activated by alkyl aluminum reagents to catalyze ethylene polymerization at high efficiency but low pressure and temperature. ${ }^{4}$ The polymer produced has much higher density (due to much less branching of the polymer) and much narrower molecular weight distribution than that produced by the Phillips catalyst. Due to the easy manipulation of the Ziegler-Natta catalyst, the polymer produced has comprised nearly the other half of commercial polyethylene (this method is also good for the production of polypropylene).

A more recent development is the use of metallocenes, reported first by Natta and Breslow simultaneously in 1957: they used $\mathrm{Cp}_{2} \mathrm{TiCl}_{2}$ activated by $\mathrm{Et}_{3} \mathrm{Al}$ or $\mathrm{Et}_{2} \mathrm{AlCl} .{ }^{9}$ The discovery of MAO (methylaluminoxane) boosted the development of metallocene catalysts significantly. ${ }^{\text {I }}{ }^{10}$ These catalysts produce polymers with much narrower molecular weight distribution. The active species in homogeneous metallocene catalysis is a 14-e metallocene alkyl cation (e.g. $\mathrm{Cp}_{2} \mathrm{Ti}^{+}-\mathrm{R}$, Scheme 1.1 ), ${ }^{11}$ while we are less sure about the active species in the heterogeneous Ziegler-Natta and Phillips catalysts. ${ }^{12}$

[^0]

Scheme 1.1. Activation of metallocene dichloride precursors to active species

As we can see, all these catalysts used in the production of commercial polymers are based on early transition metals. An efficient late transition metal catalyst was first reported by Brookhart and coworkers ${ }^{13}$ in 1995, although there were a few scattered reports dating before that time. ${ }^{14}$ Bulky $\alpha$-diimine ligands were used to assist nickel and palladium in polymerizing ethylene, which clearly proves that late transition metals can also do ethylene polymerization. A big boost to the study of the late transition metals came from the application of the diiiminepyridine (DIP) ligand in this field. ${ }^{15 a}$ In 1998, Brookhart ${ }^{16}$ and Gibson ${ }^{17}$ independently reported that 2,6-bis(arylimino)pyridine iron(II) and cobalt(II) dihalide complexes (Figure 1.1), activated by MAO, are highly efficient in ethylene polymerization ${ }^{\text {II }}$. Since then, similar systems (Figure 1.1) have also been studied extensively.

[^1]

Figure 1.1. Series of Diiminepyridines

Although DIP ligands have gained tremendous attention mainly because of their use in olefin polymerization, they have been shown to support a variety of chemical reactions. ${ }^{15 b}$ In the present thesis, the focus is not on olefin polymerization. Rather, we are interested in understanding how DIP ligands can be used to modulate the electronic and steric properties of metal centers in order to improve their catalytic activity in oxidative addition and $\mathrm{C}-\mathrm{C}$ coupling reactions and so on.

### 1.2 Organization of the whole thesis

The current thesis is organized as follows: the background of the research in this thesis will be presented in the current Chapter 1, followed by the illustration of the methods used in the research (Chapter 2). The structure analysis of (DIP) $\mathrm{MX}_{2}$ (Chapter 3), ligand parameter studies of DIP type ligands (Chapter 4), synthesis exploration of the labileligand cobalt dialkyls (Chapter 5), their applications to the synthesis of DIP cobalt(I) monoalkyl complexes (Chapter 6), and binuclear oxidative addition of $\operatorname{Co}(0)$ to the aryl
halides and the further CC coupling study of the resulting DIP cobalt(I) aryl products (Chapter 7) will be subsequently presented. Finally, conclusions and outlook of the research in this thesis will be summarized in Chapter 8. Experimental sections for each chapter (Chapter 9), references and Appendixes for each Chapter can be found at the end of the thesis. The information (cif file) of X-ray structures that are not published is provided in the supporting information of the thesis; this material can be found in the end of the thesis or via the internet at http://mspace.lib.umanitoba.ca/

### 1.3 Introduction to diiminepyridine ligands

Catalytic reactions have received much attention during the past 100 years due to their milder reaction conditions and higher atom and energy efficiency. Catalysts play a major role by providing a new or modified reaction path with a lower activation energy. Ideally, the catalyst will participate in the generation of products and is reformed after the reaction without any loss or change. However, most "catalysts" used are in reality precatalysts which have to be "activated" by reaction with an activator, or go through certain initial reactions to generate the actual active species. In addition, due to side reactions of the catalyst, after a certain number of catalytic cycles, it typically deactivates. Because the actual active species is usually too reactive to be isolated, most studies in applied catalysis focus on modification of pre-catalysts to improve activity, selectivity or catalyst lifetime. Thus, understanding how the precatalyst is activated, and how changes in the
ligand affect activation and catalysis, are helpful to the optimization of catalytic reactions.

Normally, there are two ways to generate the active species: one is to generate it in situ by mixing metal salts, ligands and reactants together, which is common in organic chemistry; the other way is to activate a well-defined metal complex by one or two steps. As the active species generated by the former method is normally hard to track and the identity is not always clear, I am interested in the latter approach. Well-defined metal complexes consist of metal centers and ligands. Transition metals dominate catalysis, due to their characteristic valence d orbitals, variable oxidation states and high coordination numbers. As for the ligands, the coordinating atoms are mainly $\mathrm{P}, \mathrm{N}, \mathrm{O}, \mathrm{C}$ or S ; they play a big role in the properties of the resulting complex. They cannot only tune the catalytic activity of the metal centers, but also the stabilities of the metal centers by coordination. For example, $\mathrm{Co}^{3+}$ is not stable in water because it is a strong enough oxidant to oxidize water to oxygen (standard reduction potential of $\mathrm{Co}^{3+} / \mathrm{Co}^{2+}: 1.82 \mathrm{~V}$ ). After being coordinated by ammonia, $\mathrm{Co}^{3+}$ is very stable in water and indeed $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{2+}$ is a very strong reductant (reduction potential of $\left.\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+} / \mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{2+}: 0.1 \mathrm{~V}\right) .{ }^{18}$ Thus, modifying ligands to improve catalytic activity is a widely used strategy and a wide variety of ligands have been developed, e.g., phosphines, ${ }^{19}$ carbenes, ${ }^{20}$ cyclopentadienyls $(\mathrm{Cp}),{ }^{21}$ and diiminepyridines (DIP). Phosphine ligands are widely used in both laboratory research and industrial production. The development of phosphine ligands started from monophosphine, ${ }^{23}$ then bisphosphines and terphosphines, to polyphosphines. ${ }^{24}$ A wellknown application is palladium-catalyzed cross coupling; ${ }^{25}$ for this work, Suzuki,

Negishi, and Heck received the 2010 Nobel Prize in chemistry. ${ }^{26}$ Carbene ligands have become popular more recently, after people found that replacement of phosphines by carbenes can often lead to catalysts of similar selectivity but higher stability. ${ }^{27 \mathrm{a}} \mathrm{Cp}$ ligands are used mainly in metallocene or half-metallocene chemistry; ${ }^{5}$ the Cp ligand is a good ligand with strong $\sigma$-donor ability. DIP ligands (good $\pi$-acceptors) are receiving more and more attention due to high efficiency of their metal complexes in ethylene polymerization. As DIP ligand chemistry is the focus of this thesis, research on it will be covered here. General interactions between ligands and metal centers will first be illustrated, followed by analysis of the DIP ligand. After an illustration of the synthesis of the DIP ligands, the electronic structure of DIP ligands and the resulting properties such as coordination modes to metal centers, electron-accepting ability, and non-innocent behaviour in redox reactions will be described in detail. The study of four-coordinate DIP Co(I) complexes will subsequently be discussed. Finally, tuning light transition metals by DIP ligands to mimic heavy metals will be illustrated.

### 1.4 Metal-ligand interactions

When a ligand coordinates to a metal center, there are two common types of interactions between them: $\sigma$-interactions and $\pi$-interactions (Figure 1.2). $\sigma$-Interactions exist in any complex while $\pi$-interactions have to go together with $\sigma$-interactions (to the best of my knowledge, there is no report of systems with only $\pi$-interactions and without $\sigma$ interactions). In terms of the ligand, $\sigma$-interaction is usually $\sigma$-donation from ligand to
metal, while depending on the position of lone-pair electrons, the $\pi$-interaction can be $\pi$ donation (from ligand $\pi$-orbital to metal) or $\pi$-backdonation (from metal d non-bonding electrons to empty ligand $\pi^{*}$ orbital).


Figure 1.2. Interactions between a metal center (M) and a ligand (L)

A direct result of the ligand coordination to the metal center is the relative energy change of valence orbitals at the metal center. $\sigma$-Coordination of a ligand to a metal center will raise the $d_{\sigma}$ orbital energy as shown schematically in Scheme 1.2 using $\mathrm{NH}_{3}$ as an example. One of the two d orbitals shown is oriented to interact with the ammonia lone pair; the other one is orthogonal to it. ${ }^{27 b}$


Scheme 1.2. Interaction between metal d orbitals and ammonia

Where ligands have the ability to participate in both $\sigma$ and $\pi$ interactions, the energy profile of the d orbitals becomes more complicated. This is shown in Scheme 1.3 using CO as an example. On the one hand, the lone pair at carbon can donate to a metal $\mathrm{d}_{\sigma}$ orbital; as a result, it will raise the energy of this orbital. On the other hand, each $\pi^{*}$ orbital of CO is close in energy to one of the other metal $d_{\pi}$ orbitals and will stabilize this orbital through side-to-side overlap.


Scheme 1.3. Interaction of metal d orbitals with carbon monoxide

In this system, overlaps between the metal $\mathrm{d}_{\pi}$ orbital and $\mathrm{CO} \pi^{*}$ orbital are quite large. Thus, the energy gap between HOMO ( $\mathrm{d}_{\pi}$ orbital lowered by $\pi$-interaction) and LUMO ( $\mathrm{d}_{\sigma}$ orbital raised by $\sigma$-interaction) will be larger than for a ligand with only $\sigma$-donor ability. Therefore, carbon monoxide is considered as a ligand with a strong field. The above two interactions are called traditional interactions; they can be expressed well using molecular orbital theory and a fully paired-electron picture. In terms of computational chemistry, a restricted Hartree-Fock (HF) or Kohn-Sham (KS) description (see Section 2.4 in Chapter 2) is appropriate.

A different situation is obtained where the $\pi$-interaction is between orbitals having relatively small overlap, due to the large spread of $\pi^{*}$ orbital with most of its density far away from the coordination center. As a result, this $\pi$-interaction is quite weak. If the original ligand $\pi^{*}$ and metal d orbitals were close in energy, the result can be a situation best pictured as having one electron located mainly in the ligand $\pi^{*}$ orbital antiferromagnetically coupled to an electron located mainly at the metal. Such a singlet biradical cannot be described well by molecular orbital (MO) theory, and is more easily explained in valence bond (VB) terms. VB pairs are formed from two opposite-spin electrons, each in their own orbital. A strong overlap between the two orbitals leads to a traditional electron pair bond. A small overlap (one orbital mainly on the metal, the other mainly on the ligand $\pi^{*}$ ) results in a singlet biradical situation. If the overlap becomes even smaller, the situation with parallel electrons (triplet biradical) typically becomes preferred. Good examples of ligands that can show this type of interaction are the bisimine ligands, ${ }^{13}$ terpyridine ligands, iminoketone, ${ }^{28}$ and diiminepyridine (DIP) ligands. Due to this special property, the "mostly unpaired" electron in the ligand $\pi^{*}$ orbital can be used by the metal center to participate in redox reactions, which will be discussed in detail in the section on non-innocence of the ligand (Section 1.12). Thus, these ligands can also function as electron reservoirs.

### 1.5 Background of DIP ligands

The study of DIP ligands dates back to the synthesis of bis(hydrazone)pyridine and its iron(II), cobalt(II) and nickel(II) complexes reported by Busch and Stoufer in 1956. ${ }^{29}$ Lions and Martin later introduced ligands containing alkylimino arms, ${ }^{30}$ while the now popular bis(arylimino)pyridine (Figure 1.3) was first reported by Alyea and Merrel in $1974 .{ }^{31}$


Figure 1.3. Bis(arylimino)pyridine

After the first publication of DIP type ligands, research focused mainly on simple coordination complexes of transition metals such as the Group VIII metals and copper(II). ${ }^{32}$ Later, the coordination mode (bidentate vs tridentate) in metal carbonyls was further studied by several groups. ${ }^{33}$ However, the prominence of DIP ligands did not emerge until their iron and cobalt dichloride complexes were found by the groups of both Brookhart ${ }^{16}$ and Gibson ${ }^{17}$ to show high efficiency in ethylene polymerization.

### 1.6 Electronic properties of DIP ligands

As DIP ligands contain two imine arms, their conformations are quite flexible. When these two arms are coplanar with the central pyridine ring, a large conjugated $\pi$-system with two low-lying $\pi^{*}$ orbitals ( $\pi^{*}{ }_{\text {asym }}$ and $\pi^{*}$ sym in Figure 1.4) is formed. ${ }^{34}$ These two $\pi^{*}$ orbitals are the combinations of two imine and central pyridine $\pi^{*}$ orbitals.

$\mathrm{d}_{\mathrm{yz}}$

$\mathrm{d}_{\mathrm{xz}}$

$$
\pi_{\mathrm{sym}}^{*}
$$

Figure 1.4. Two lowest $\pi^{*}$ orbitals of diiminepyridine ligands (Picture generated from electron density plot) ${ }^{\text {III }}$ and metal d orbitals.

Thus, DIP ligands cannot only donate electrons to the metal center through lone pairs of electrons at three nitrogen atoms but they also accept electrons from metal centers to their $\pi^{*}$ orbitals. In the situation with ideal symmetry, the $\pi^{*}{ }_{\text {asym }}$ orbital can overlap with the

[^2]metal $d_{y z}$ orbital while the $\pi^{*}$ sym orbital can overlap with the metal $d_{x z}$ orbital. As a result, the ligand has a large electron-accepting ability. However, the extent of electron transfer of this ability depends on the metal to which it coordinates. The bidentate coordination mode has lower electron accepting ability, but the strain induced by the ligand geometric constraints is larger for the tridentate case. Depending on the valence state of the metal centers, the amount of electron transfer from the metal center to DIP ligands varies from small (in high valent metal complexes) to large (in low valent metal complexes).

The special character of the DIP ligand can be illustrated by comparing it with carbon monoxide.

### 1.7 DIP vs CO

DIP ligands can stabilize low valent metal centers in the same way as CO, but they behave quite differently from the carbon monoxide ligand in the following respects:

Firstly, in DIP metal complexes of low valence, DIP oxidizes the metal center to form a ligand-centered radical anion (intramolecular 1-e transfer) while CO complexes are closed-shell: backdonation involves partial delocalization of an electron-pair from metal to CO. This difference in behaviour means that in computational studies, DIP complexes may need special treatment to correctly describe the biradical structure.

Secondly, DIP ligands are easily modified in a chemical sense to accommodate different needs, which is not the case for CO. For example, we can add functional groups to DIP ligands at pyridine, imine arm, and N -aryl positions and so on to change their electronic and steric properties. In contrast, CO cannot be modified very much. One might replace it
by an isocyanide (which is more tuneable), but they are not very pleasant ligands to work with.

Finally, DIP ligands have bidentate and tridentate coordination modes while CO usually has one monodentate coordination mode (the bridging coordination mode is not considered here.

In all, DIP is a both good $\sigma$-donor and good $\pi$-acceptor ligand while CO is a poor $\sigma$-donor but a good $\pi$-acceptor ligand.

### 1.8 Synthesis of DIP ligands

The synthesis of DIP ligands is carried out straightforwardly by condensation of 2,6diacetylpyridine with two equivalents of aniline in toluene catalyzed by $p$-toluene sulfonic acid or in absolute methanol (pure methanol) catalyzed by formic acid at reflux temperature (Scheme 1.4). ${ }^{35 \mathrm{a}} \mathrm{N}$-Alkyl DIP ligands can be made in a similar manner.


Scheme 1.4. Standard method of synthesizing DIP ligands

As for the less reactive 2,6-dibenzoylpyridine, anhydrous nickel dichloride instead of a protic acid was used to facilitate condensation and the free ligand could be obtained after demetalation with aminopropyl silica gel in dichloromethane (Scheme 1.5). ${ }^{35 \mathrm{~b}}$


Scheme 1.5. Use of metal template to synthesize DIP ligand

When the desired 2,6-dicarbonylpyridine is not commercially available, the DIP ligand to be studied can be synthesized through an additional coupling step between a nucleophile and pyridine carbonyl chloride or pyridine imidoyl chloride (Scheme 1.6). ${ }^{36}$


Scheme 1.6. Synthesis of DIP ligand through coupling reactions

For other specific cases, other methods have also been reported. For example, a combination of $\mathrm{AcOH} / \mathrm{EtOH}$ was used to synthesize the aldimine variation of $\mathrm{DIP}^{35 \mathrm{c}}$ and base/MeI was used to modify the imine methyl groups (Scheme 1.7). ${ }^{35 \mathrm{~d}}$



$\mathrm{Ar}=$ 2,4,6-trimethylphenyl or 2,6-diisopropylphenyl

> Scheme 1.7. Alkylation at imine methyl position of DIP ligand

### 1.9 Synthesis of DIP metal dihalide complexes

DIP metal dihalide complexes are good starting materials to make other derivatives of the metal complexes. A standard way to prepare them is to react the free DIP ligand with a metal dihalide in a polar solvent such as THF, $\mathrm{CH}_{3} \mathrm{CN}$ or butanol (Scheme 1.8). The metal salts and the solvents for making DIP transition metal dichlorides are summarized in Table 1.1.


Scheme 1.8. Synthesis of (DIP)MX ${ }_{2}$ complexes

Table 1.1. Metal salts and solvents for making DIP metal chloride complexes

| Entry | Metal-salt/solvent | Entry | Metal-salt/solvent |
| :---: | :---: | :---: | :---: |
| 1 | $\mathrm{ScCl}_{3}(\mathrm{THF})_{3} /$ Toluene ${ }^{37}$ | 11 | $\left(\mathrm{Et}_{4} \mathrm{~N}\right)_{2}\left(\mathrm{Fe}_{2} \mathrm{OCl}_{6}\right) /$ Methanol $^{38}$ |
| 2 | $\mathrm{TiCl}_{4} /$ Toluene ${ }^{39}$ | 12 | $\mathrm{CoCl}_{2} / \mathrm{THF}^{40}$ |
| 3 | $\mathrm{ZrCl}_{4} /$ Toluene or $\mathrm{ZrCl}_{4}(\mathrm{THF})_{2} / \mathrm{CH}_{2} \mathrm{Cl}_{2}{ }^{39}$ | 13 | $\mathrm{RhCl}_{3}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3} /$ Ethanol $^{41}$ |
| 4 | $\mathrm{VCl}_{3}(\mathrm{THF})_{3} / \mathrm{THF}^{42}$ | 14 | $\mathrm{NiCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O} /$ Ethanol $^{43}$ |
| 5 | $\mathrm{CrCl}_{3}(\mathrm{THF})_{3} / \mathrm{CH}_{2} \mathrm{Cl}_{2}$ or acetone ${ }^{44}$ | 15 | $\mathrm{CuCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O} / \mathrm{CH}_{3} \mathrm{CN}^{45}$ |
| 6 | $\left[\mathrm{NH}_{4}\right]_{2}\left[\mathrm{IrCl}_{6}\right] /\left(\mathrm{CH}_{2} \mathrm{OH}\right)_{2}{ }^{46}$ | 16 | $\mathrm{RuCl}_{3} / \mathrm{EtOH}^{47}$ |
| 7 | $\mathrm{Na}_{2}\left[\mathrm{OsCl}_{6}\right] / \mathrm{MeOH}^{48}$ | 17 | $\mathrm{MoCl}_{3}(\mathrm{THF})_{3} / \mathrm{THF}^{49}$ |
| 8 | $\mathrm{MnCl}_{2} \cdot(\mathrm{THF})_{2} /$ Toluene ${ }^{50}$ | 18 | $\mathrm{ZnCl}_{2} / \mathrm{EtOH}^{51}$ |
| 9 | $\mathrm{FeCl}_{2} / n$-butanol ${ }^{52}$ | 19 | $\mathrm{MnCl}_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O} / \mathrm{EtOH}^{51}$ |
| 10 | $\mathrm{CdCl}_{2} \cdot 2.5 \mathrm{H}_{2} \mathrm{O} / \mathrm{CH}_{3} \mathrm{CN}$ or $\mathrm{CH}_{2} \mathrm{Cl}_{2}{ }^{53}$ | 20 | $\mathrm{HgCl}_{2} / \mathrm{MeCN}^{54}$ |

### 1.10 Modification of DIP-type ligands

### 1.10.1 Modification vs Reactivity

After the discovery of the catalytic efficiency of (DIP) $\mathrm{FeCl}_{2}$ and (DIP) $\mathrm{CoCl}_{2}$, a variety of efforts have been put into the modification of the original DIP skeleton, hoping to improve their catalytic efficiency in ethylene polymerization. The positions of these
modifications can be divided mainly into five categories: the 4-position of the central pyridine ring, imine-methyl, N -aryl ring, imine arms and the whole pyridine core (Figure $1.5)^{\text {IV }}{ }^{55}$ The corresponding iron(II) and cobalt(II) dihalides and chromium halide complexes ${ }^{\mathrm{V}}$ have been tested in ethylene polymerization. Among all these changes, modification of the N -aryl ring, replacement of imine arms and the central pyridine core will be illustrated here.


Figure 1.5. Different positions for modification of a diiminepyridine ligand

The substituents at the 2,6-positions of the N -aryl ring play an important role in the catalytic activity of their metal complexes. N-2,6-Diisopropylphenyl works quite well in ethylene polymerization. However, further reducing the steric hindrance down to N -

[^3]phenyl changes the selectivity from ethylene polymerization to ethylene oligomerization. ${ }^{56}$ In addition, although the 4-position of the N -aryl is far away from the metal center, Liu et. al. observed a larger steric than electronic effect in terms of catalytic activity and the mass of polymer produced. ${ }^{57}$

Compared with the above changes at the N -aryl ring, the replacement of the whole imine arms generally leads to disappointing results (Figure 1.6): the replacement by e.g. phosphinimine ${ }^{58}$ or alkyl phosphine ${ }^{59}$ leads to loss of activity; replacement by e.g. thiophenyl ${ }^{60}$ or carbene, ${ }^{61}$ results in catalysts that promote oligomerization; replacement by carbonyl ${ }^{62}$ leads to lower catalytic activity to polymerization or oligomerization (in the case of ester arms, the iron complex catalyzes polymerization while the cobalt complex does oligomerization ${ }^{63}$ ).


Highly active in ethylene polymerization


6-(thiophen-2-yl)-(imino)pyridine oligomerization active


Bis(imino)pyrimidine slightly active in ethylene polymerization


Bisphosphiniminepyridine Inactive

Figure 1.6. Effect of structural changes on catalytic activity of $\mathrm{Fe} / \mathrm{Co}$ complexes in ethylene polymerization.

The replacement of the central pyridine by a relatively electron-poor core such as pyrimidine ${ }^{64}$ (Figure 1.6) reduces the activity of the corresponding complexes to less than half of the original values. However, complexes containing electron-rich cores such as carbazoles ${ }^{65}$ or furans showed no activity at all upon activation with MAO.

Although a variety of DIP ligands have been studied, there has been no significant improvement of the catalytic activity of their metal complexes in ethylene polymerization since compared to the iron complex of the initial $\operatorname{iPrDIP}$. ${ }^{16-17}$ In an attempt to arrive at a better understanding of this, quantification of the electronic properties of DIP type ligands was tried; this will be discussed in detail in Chapter 4. One could also imagine steric properties to be important. Therefore, the work in Chapter 3 analyzes the geometries of Co and Fe dihalide complexes.

### 1.10.2 Steric hindrance

As has been stated in the preceding section, significant steric effects on the properties of DIP ligands have been observed. On the one hand, the preparation of mono-ligand metal complexes was significantly affected by steric hindrance at the 2,6 -positions of the N -aryl ring. ${ }^{66}$ Bristovsek and coworkers ${ }^{66 b}$ systematically explored this steric effect by reacting ligands 1-3 with $\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2} \mathrm{Fe}(\mathrm{OTf})_{2}$ (Table 1.2). For the bulky DIP ligand 1, only (1) $\mathrm{Fe}(\mathrm{OTf})_{2}$ was observed. On reduction of steric bulk to one methyl group per aryl ring, a mixture of mono-ligand and bis-ligand complexes was obtained (entry 2). For the unsubstituted phenyl ligand 3, only a bis-ligand complex was formed. In addition,
whether mono-ligand or bis-ligand complexes are formed depends on the counter anion for the less hindered DIP ligands.

Table 1.2. Steric effects on the formation of mono-ligand or bis-ligand DIP complexes


| Entry | Ligands | Ar | Products |
| :--- | :--- | :--- | :--- |
| 1 | $\mathbf{1}$ | $2,6-{ }^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$ | $(\mathbf{1}) \mathrm{Fe}(\mathrm{OTf})_{2}$ |
| 2 | $\mathbf{2}$ | $2-\mathrm{MeC}_{6} \mathrm{H}_{4}$ | $(\mathbf{2}) \mathrm{Fe}(\mathrm{OTf})_{2}+\left[(\mathbf{2})_{2} \mathrm{Fe}\right]^{2+} 2[\mathrm{OTf}]^{-}$ |
| 3 | $\mathbf{3}$ | $\mathrm{C}_{6} \mathrm{H}_{5}$ | $(\mathbf{3})_{2} \mathrm{Fe}(\mathrm{OTf})_{2}$ |
| 4 | $\mathbf{4}$ | $2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$ | No data |

On the other hand, the catalytic activity of the resulting complexes in ethylene polymerization seems to depend on the steric effect too, as illustrated in the previous section.

Finally, the steric hindrance at the 2,6-positions of the N -aryl ring also determines how easy $\beta-\mathrm{H}$ transfer is in cobalt alkyl complexes: ${ }^{67}$ the rate of hydride transfer in $(\mathbf{1}) \mathrm{Co}(\mathrm{Bu}-$ $n)$ is 16.3 faster than that of $(4) \mathrm{Co}(\mathrm{Bu}-n)$ when reacting with ethylene to give 1-butene (Scheme 1.9).


Scheme 1.9. Reaction of (DIP)Co(Bu-n) complex with ethylene via $\beta-\mathrm{H}$ transfer

### 1.11 Electron-accepting ability of DIP ligands

As DIP ligands have two low-lying $\pi^{*}$ orbitals, their most prominent property is the ability to stabilize the low-valent metals by accepting electron density; examples involving up to three electrons have been reported. For example, the Chirik group ${ }^{67}$ found that (DIP) $\mathrm{CoCl}_{2}$ can be reduced to the cobalt dinitrogen anion $\left.\left[\mathrm{Na}(\text { solvent })_{3}\right]\left[{ }^{\mathrm{iPr}} \mathrm{ADIP}\right) \mathrm{Co}\left(\mathrm{N}_{2}\right)\right] \quad\left({ }^{\mathrm{iPr}} \mathrm{ADIP}: \quad 2,6-\left({ }^{\mathrm{i}} \operatorname{Pr} \mathrm{N}=\mathrm{CMe}\right)_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right) \quad$ by $\quad$ sodium naphthalenide (Scheme 1.10). Although the formal oxidation state of the cobalt center is -1 , patterns of orbital occupation calculated by DFT is consistent with the low-spin cobalt(II), which is explained in terms of three electrons transferring from the cobalt center to two ligand $\pi^{*}$ orbitals to form a singlet biradical situation ${ }^{\text {VI }}$ (singlet biradical character will be illustrated in detail in section 2.4.4 on four coordinate cobalt(I) complex in Chapter 2). The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{Na}(\mathrm{THF})\left[\left({ }^{\mathrm{Pr}} \mathrm{ADIP}\right) \mathrm{CoN}_{2}\right]$ in benzene- $d_{6}$ and THF (1:1) clearly showed that it is diamagnetic.

[^4]

Scheme 1.10. Reduction of ( $\left.{ }^{i \mathrm{Pr}} \mathrm{ADIP}\right) \mathrm{CoCl}_{2}$ by sodium naphthalenide

A direct result of electron-transfer from the metal to the DIP ligand is the elongation of the imine bond and the shortening of the carbon-carbon bond connecting the pyridine ring and the imine carbon. This information can be used to quantify the amount of electron transfer from metal to ligand. ${ }^{68}$

### 1.12 Non-innocence of DIP-type ligands

Normally, the ligand in a catalyst is always considered to stay intact during the catalytic cycles, while the metal center can be oxidized, reduced or undergo chemical reactions. However, this is not necessarily the case for redox-active ligands. The DIP ligand is one of them. Due to its ability to accept electrons, DIP ligands have been found to be noninnocent in redox reactions of the corresponding metal complexes. In other words, it is often the DIP skeleton in the complex that is oxidized or reduced while the oxidation state of the metal center does not change. A good example is the terpyridine nickel(I)
alkyl complex which can perform C-C coupling reactions with alkyl halides (Scheme 1.11). ${ }^{69}$ The terpyridine ligand, not the nickel center, was considered be oxidized. This event is also called ligand-based redox chemistry.


Scheme 1.11. CC coupling of a terpyridine nickel methyl complex with heptyl iodide

Another extensively studied complex which can do ligand-based redox chemistry is the (DIP)Fe( $\left.\mathrm{N}_{2}\right)_{2}$ complex reported by the group of Chirik. ${ }^{70 \mathrm{a}}$ This complex can promote a number of interesting reactions, such as hydrogenation and hydrosilylation of olefins ${ }^{70 b}$ and hydrogenation of ketones, ${ }^{71}$ cyclization of enynes and diynes, ${ }^{72}$ the breaking of C-O bonds of esters ${ }^{73}$ and so on.

Finally, a variety of bidentate redox-active ligands which have similar properties to DIP have also been used in a variety of fields such as material chemistry, to tune the electronic structures of metal centers (e.g. bispyridine) ${ }^{13 \mathrm{~d}}$ or to change the magnetic or optical properties of their metal complexes (e.g. Semiquinone in copper(II) complexes) ${ }^{28 b}$ or optoelectronic properties of organoboron compounds ${ }^{28 c}$ and so on.

### 1.13 Reaction of DIP with organometallic reagents

The reactions of free DIP ligand with simple organometallic reagents have been explored mainly by the groups of Gibson, ${ }^{74}$ Gambarotta and Budzelaar. ${ }^{75}$ Alkylation of the DIP ligand can happen at the pyridine nitrogen, imine carbon and pyridine ring (Figure 1.7), depending on the metal and the alkyl in alkylation reagents used. For example, alkyl lithium reagents normally can alkylate the free DIP ligand at the pyridine nitrogen, while alkylation at the pyridine C 2 position has been observed with alkyl magnesium and alkyl zinc reagents. Alkyl aluminum reagents can alkylate at the imine carbon and at the pyridine C 4 position (although this product is not stable and easily dimerizes). Alkylation at C 3 has been observed recently. ${ }^{76}$


Figure 1.7. Structures of alkylated DIP ligand by main group alkyl reagent

As for DIP in transition metal complexes such as iron, cobalt, manganese and chromium, two types of dimerization reactions have been observed when reacting with main-group organometallic reagents (Scheme 1.12). The first type modifies the ligand by dimerizing through the imine methyl carbons, presumably after they have been deprotonated (Scheme 1.12, top) ${ }^{77}$ while the second type of dimerization happens through the pyridine 3,5-positions probably after the pyridine 4-position was alkylated (Scheme 1.12, bottom). ${ }^{78}$


Scheme 1.12. Dimerization of DIP metal complexes

The reaction with reducing metals such as sodium amalgam ${ }^{79}$ or $\mathrm{NaH}^{80}$ can be more complicated. Depending on the solvent, the DIP metal complexes can be reduced to several possible states (for example, the cobalt complex can be reduced to formally cobalt (0) or cobalt (-1)). ${ }^{79}$

### 1.14 Four coordinate DIP cobalt(I) complexes

Four-coordinate cobalt(I) complexes of DIP ligands are of interest because (DIP)CoR and (DIP)CoX have been shown to be intermediates during the activation of (DIP) $\mathrm{CoCl}_{2}$ by MAO in ethylene polymerization. ${ }^{81}$ The geometries of (DIP)CoR or (DIP)CoX depend on the type of groups that are attached to the imine nitrogen atoms. With aryl groups at N , cobalt(I) complexes are normally square planar (Figure 1.8). When the N -aryl group in the DIP skeleton was replaced by an alkyl group, the cobalt(I) complex distorted significantly from the square planar geometry to have the cobalt-halogen bond bent out of the $\mathrm{N}_{3}$ plane (Figure 1.8). ${ }^{82,83}$ These two types of geometries are associated with different NMR properties. DIP cobalt(I) alkyls are diamagnetic. But DIP cobalt(I) halides bearing alkyl groups at N show spin crossover to a paramagnetic triplet state at around room temperature. ${ }^{82}$ Apparently, the combined effect of the low-field halide ligands and the geometry distortion caused by the N -alkyl substituents is enough to make the triplet state thermally accessible.


Figure 1.8. Structures of (DIP)Co(I) complexes (hydrogen omitted for clarity)

Although DIP cobalt(I) alkyl complexes are diamagnetic, the spectra show some rather abnormal features. The pyridine H 4 peak in the ${ }^{1} \mathrm{H}$ NMR spectrum shifts significantly to low field ( $\delta$ : around 10 ppm ) and the imine methyl group shifts significantly to higher field ( $\delta$ : around -1.0 to -2.0 ppm ). Because of their special positions, these two peaks seldom overlap with other peaks and are easily identified. This information is going to be used a lot in Chapter 7 to identify reaction products.

Although the formal oxidation state of the cobalt centers in (DIP)CoR complex is +1 , a DFT study showed that the actual oxidation state is +2 with one electron located at the cobalt center and antiferromagnetically coupled to another electron located at the DIP ligand (for details of these calculations, see Chapter 2). ${ }^{83}$ Thus, the overall spin state is normally described as a singlet, but the complexes have biradical character as illustrated in Figure 1.9.


Figure 1.9. Electronic structure representation of (DIP)CoR

## Synthesis of (DIP)CoR

The standard procedure to prepare DIP cobalt(I) alkyl complexes is to use organo lithium reagents or Grignard reagents to reduce corresponding cobalt(II) dihalide complexes
(Method I in Scheme 1.13). However, this method does not work where polar functional groups such as ester, keto or nitro groups are present. ${ }^{84}$ Alternatively, one could envisage a procedure similar to that used for the synthesis of the iron analog: reaction of a labile cobalt dialkyl complex with the free ligands (Method II in Scheme 1.13). Prior to the present work, no such conveniently accessible cobalt dialkyl was available. Because of its mildness, method II together with the synthesis of labile cobalt dialkyls were explored in Chapter 5 and Chapter 6 in detail.


Scheme 1.13. Synthesis of (DIP)CoR

### 1.15 Mimicking heavier transition metals by first-row transition metals

As we know, metals in the same column of the Periodic Table can have similar chemical activity. However, for transition metals, in a general sense, there is a big difference between first-row and second-row transition metals. Normally, first-row transition metals prefer high-spin states while second and third-row transition metals prefer low-spin states. The higher cost of heavy metals compared to their light congeners makes the approach to tune light transition metals to mimic heavier congeners of significant interest
for industrial applications. Take CC coupling reactions as an example. Palladium combined with phosphine ligands is the "standard" in this area. However, due to the high cost of palladium, nickel was extensively studied and works quite well in many crosscoupling reactions. The other alternative is to use copper with an appropriate ligand system. Although copper is much less reactive than palladium, it can have high selectivity toward some substrates, lower toxicity and lower cost. Thus by an appropriate choice of the ligand system, the relatively cheap light (3d) transition metals can be used in reactions that are normally catalyzed by heavier ( $4 \mathrm{~d}+5 \mathrm{~d}$ ) metals.

It is the valence electrons that affect the chemical behaviour of the metal center, and firstrow and second-row transition metals have quite different preferences for the electron configuration. The heavier transition metals typically prefer 2-e oxidation state changes during catalytic reactions, while light transition metals often show 1-e steps because of the low splitting energies among the d orbitals of the metal centers. Thus, to mimic heavy metals, the first thing is to mimic the electron configuration. One strategy is to tune the ligand such that they induce preference for a low-spin state of the metal. Based on crystal field theory, one obvious way is to increase the splitting energies of the $d$ orbitals. As a result, the electron-pairing energy will be smaller than the energy gap of $d$ orbitals and a low-spin state will be achieved without removing any electrons from the metal center. A good choice will be carbon monoxide which can stabilize a variety of metals of low oxidation state. Another strategy is to use ligands with orbitals which can act as temporary electron reservoirs. One of the unpaired electrons can transfer to this ligand orbital and then couple antiferromagnetically to another unpaired electron at the metal
center. The DIP ligand, which has a high tendency to support this type of bonding, was chosen as the subject of this thesis research.

A direct advantage of (DIP)Co(I) complexes is that they are diamagnetic. They also show some similarity to rhodium complexes. ${ }^{85}$ For example, they both catalyze the hydrogenation of olefins. The chemistry of (DIP)CoR in hydrogenation and its resulting product in reduction of aryl halides is further discussed in detail in Chapter 7.

## Chapter 2. Methodology

### 2.1 Introduction to NMR and paramagnetic complexes

NMR is widely used in organic chemistry to characterize organic compounds. Peaks in ${ }^{1} \mathrm{H}$ NMR spectra of organic compounds are normally quite sharp (half widths are normally less than 0.5 Hz ) and the total ${ }^{1} \mathrm{H}$ spectrum width is typically less than 15 ppm , with most peaks between 0 and 10 ppm . Based on chemical shifts (indicating types of hydrogen) and the splitting of each peak (providing information about neighbouring atoms), the structure of a molecule can often be built up. For more complicated cases, multidimensional techniques may be applied.

NMR spectra of organometallic complexes can be quite different. For diamagnetic metal complexes, the peaks of the nuclei that are closer to the metal center are often shifted upfield normally by $2-3 \mathrm{ppm}$ relative to that of the uncoordinated ligand, which is attributed to the high electron density and anisotropy at the metal center. ${ }^{86}$ The unusually large ${ }^{1} \mathrm{H}$ shielding for protons that bind directly to a transition metal is, to a large extent, due to the paramagnetic current within the incomplete metal d-shell, which deshields the metal nucleus and shields the bound proton; this effect is similar to the ring current in a benzene ring. ${ }^{87}$ For example, the hydrogen chemical shift in $\left[\mathrm{Rh}(\mathrm{H})_{2}\left(\mathrm{P}^{i} \mathrm{Bu}_{3}\right)_{2}\right]\left[\mathrm{BAr}{ }^{\mathrm{F}}{ }_{4}\right]$ is located at $-21.55 \mathrm{ppm} .{ }^{88}$

On the other hand, the NMR spectra of paramagnetic metal complexes (complexes that have unpaired electrons) are significantly different from those of diamagnetic compounds. First, ${ }^{1}$ H NMR peaks are quite broad: peak half widths are usually more than 10 Hz and can reach more than 1000 Hz . As a result, coupling information cannot be observed, so the spectra provide less information than those of diamagnetic compounds. Second, the spectra will be quite wide: chemical shifts of proton peaks can range from 400 ppm to -400 ppm and the chemical environment of protons usually cannot be determined from their chemical shifts because the unpaired-electron effects on the chemical shifts are much larger than the electron shielding. For example, peaks of aromatic hydrogens in diamagnetic organic molecule can be found at around $\delta=7.2 \mathrm{ppm}$, while in the ${ }^{1} \mathrm{H}$ NMR spectrum of a paramagnetic compound, the chemical shifts of the peaks of aromatic hydrogens can be any value between -200 ppm to +200 ppm . Third, the smaller signal-to-noise in ${ }^{13} \mathrm{C}$ spectra and the broadness of the peaks caused by fast electron spin-relaxation often prevents observation of ${ }^{13} \mathrm{C}$ NMR signals. In addition, due to the wide spread of peaks in ${ }^{1} \mathrm{H}$ NMR spectra, the ${ }^{1} \mathrm{H}$ decoupling technique normally used in ${ }^{13} \mathrm{C}$ NMR to increase peak intensity will be problematic. Finally, chemical exchange is more common in metal complexes than organic compounds due to the weaker coordination bonds between metal centers and the coordinated ligand, which can make paramagnetic spectra even more complicated. Therefore, the NMR spectrum itself often does not provide enough information to fully establish the structure of a paramagnetic compound. Nevertheless, NMR spectra of paramagnetic compounds can be useful to establish their magnetic moments and define spin states. In addition, these NMR
spectra can serve as "fingerprints". In the following sections, the reason why paramagnetic complexes show such special NMR spectra and the terms that contribute to the chemical shifts are explained. Finally, the use of solution NMR to determine the magnetic moment of a paramagnetic complex will be described.

### 2.1.1 NMR spectrum

## Chemical Shifts and their calculations

Differences in chemical shifts in the NMR spectrum are due to differences in shielding of the target nuclei by their surrounding electrons. Thus, the same nucleus can show different resonance frequency (v) in the same external magnetic field depending on its chemical environment. The chemical shift is defined by the following equation: ${ }^{89}$

$$
\delta(\text { in ppm })=10^{6}\left(v-v_{\text {ref }}\right) / v_{\text {ref }}=10^{6}\left(\sigma_{\text {ref }}-\sigma\right) /\left(1-\sigma_{\text {ref }}\right) \approx 10^{6}\left(\sigma_{\text {ref }}-\sigma\right)
$$

- $\quad v$ is the resonance frequency of a target nucleus $(\mathrm{Hz})$
- $v_{\text {ref }}$ is the resonance frequency of the same nucleus in a reference compound (Hz)
- $\sigma$ is the shielding of a target nucleus
- $\sigma_{\text {ref }}$ is the shielding of a reference nucleus (normally TMS or solvent residue)

For closed-shell diamagnetic compounds, the shielding parameter $\sigma$ has been interpreted as the sum of the paramagnetic $\left(\sigma_{\mathrm{p}}\right)$ and diamagnetic $\left(\sigma_{\mathrm{d}}\right)$ contributions (for details about how to calculate these two components, see ref. 86):

$$
\begin{equation*}
\sigma=\sigma_{p}+\sigma_{d} \tag{Eq. 2.1}
\end{equation*}
$$

Where,

- Diamagnetic shielding $\left(\sigma_{\mathrm{d}}\right)$ is considered to be induced by the electron density surrounding the target nuclei. The higher the electron density, the more positive the diamagnetic shielding. The local field induced by diamagnetic shielding is normally anti-parallel to the external field.
- Paramagnetic shielding $\left(\sigma_{\mathrm{p}}\right)$ is considered to be caused by an electron current due to the small energy gap between HOMO and LUMO. Depending on the position of the target nuclei, it can cause shielding or deshielding. Calculation of this contribution using molecular orbital theory involves contributions from excited configurations.

The chemical shift derived from Eq. 2.1 will be named $\delta^{\text {orb }}$ in the remainder of this thesis.

## Chemical shifts of paramagnetic compounds and their calculations

For paramagnetic compounds, the unusual chemical shifts relative to their corresponding diamagnetic analogs are caused by the interaction of the target nuclear spin with the unpaired electron. ${ }^{90}$ The shifting of peaks relative to those in a diamagnetic environment can be divided into two parts: the Fermi contact shift $\left(\delta^{\mathrm{FC}}\right)$ and the pseudo-contact shift
$\left(\delta^{\mathrm{PC}}\right)$. The observed chemical shift ( $\delta^{\mathrm{obs}}$ ) can be interpreted according to following equation: ${ }^{91}$

$$
\begin{equation*}
\delta^{\mathrm{obs}}=\delta^{\mathrm{orb}}+\delta^{\mathrm{FC}}+\delta^{\mathrm{PC}} \tag{Eq. 2.2}
\end{equation*}
$$

The Fermi contact shift $\left(\delta^{\mathrm{FC}}\right)$ is caused by Fermi contact ${ }^{\mathrm{VII}}$ between the electron and the target nucleus, and depends on the magnitude and the sign of the electron spin density at the target nucleus. Because the electron has spin $1 / 2$, it interacts with the target nucleus just as an adjacent hydrogen atom would interact (Scheme 2.1).


Scheme 2.1. Illustration of electron-proton coupling

[^5]However, the expected peak splitting in the ${ }^{1} \mathrm{H}$ NMR spectrum is not observed in practice because the electron normally relaxes rapidly. One might expect such relaxation to lead simply to disappearance of the coupling. However, the relatively large energy difference for electrons between the spin-up $\left(m_{S}=+1 / 2\right)$ and spin-down $\left(m_{S}=-1 / 2\right)$ states affects the chemical shift of the adjacent proton according to the following equation (Eq. 2.3):

$$
\begin{equation*}
\text { Average } v=\mathrm{N}_{+1 / 2} \mathrm{v}_{+1 / 2}+\mathrm{N}_{-1 / 2} \mathrm{v}_{-1 / 2} \tag{Eq. 2.3}
\end{equation*}
$$

- $\mathrm{N}_{+1 / 2}$ and $\mathrm{N}_{-1 / 2}$ correspond to the fraction of each spin population
- $v_{+1 / 2}=v-1 / 2 \mathrm{~J}_{\mathrm{e}-\mathrm{H}}$ and $v_{-1 / 2}=v+1 / 2 \mathrm{~J}_{\mathrm{e}-\mathrm{H}}$
- $\mathrm{J}_{\mathrm{e}-\mathrm{H}}$ is the coupling constant between the electron and the target nucleus

Because the lower-energy level has a larger population, it will contribute with a greater weight $\left(\mathrm{N}_{+1 / 2}>\mathrm{N}_{-1 / 2}\right)$ to the time average of $v$.

Thus the magnitude of the contact shift can be estimated according to the following equation: ${ }^{90}$

$$
\begin{equation*}
\delta^{F C}=A_{i s o} \frac{\overline{\bar{g}} \beta_{e} S(S+1)}{g_{N} \beta_{N} 3 \kappa T} \tag{Eq. 2.4}
\end{equation*}
$$

Where:

- $\bar{g}$ is the rotationally averaged electronic g-value,
- $\mathrm{g}_{\mathrm{N}}$ is the nuclear g-value,
- $\beta_{\mathrm{e}}$ and $\beta_{\mathrm{N}}$ are the Bohr and nuclear magnetons, respectively,
- $\mathrm{A}_{\text {iso }}$ is the isotropic hyperfine coupling constant (the analog of a $J$ coupling) which can be positive or negative,
- $\kappa$ is the Boltzmann constant and T is the absolute temperature,
- $S$ is the total electron spin of the molecule $(1 / 2,1,3 / 2, \ldots)$.

Due to the strong direct interaction between the electron and the nucleus, the Fermi contact shift is often the main contribution to the total chemical shift.

The chemical-shift contribution derived from the pseudocontact interaction is relatively small. It results from the dipolar interaction between the magnetic moment of the nucleus and the electron through space and needs to be considered when the paramagnetic center is strongly anisotropic, which is the case for paramagnetic metal complexes. The chemical shift caused by this effect can be expressed as follows: $:^{90,92 \mathrm{a}}$

$$
\begin{equation*}
\delta^{P C}=\beta_{e}^{2} S(S+1) \frac{3\left(\cos ^{2} \Omega-1\right)}{3 \kappa T R^{3}} F(g) \tag{Eq. 2.5}
\end{equation*}
$$

Where:

- $\Omega$ is the angle between the effective symmetry axis of the paramagnetic moment and the direction to the nucleus of interest.
- R is the distance between the induced magnetic moment and the nucleus under consideration.
- $\mathrm{F}(\mathrm{g})$ is an algebraic function of the g-tensor components, which subsumes the relative magnitudes of various relaxation times.

Depending on the relative positions and orientations of the other atoms to the position of the unpaired electrons, this effect can lead to shielding or de-shielding of the atoms; as a result, the chemical shifts move to higher field or lower field relative to that in the diamagnetic state. Due to the relatively large size of the transition metals ( R is quite large), the amount of pseudo contact shift is normally small.

In all, for the calculation of the chemical shift $\left(\delta^{\mathrm{obs}}\right)$ of a target nucleus in a paramagnetic compound, the orbital contribution ( $\delta^{\text {orb }}$ ) is small but not negligible. For example, in the organic radical 2-methylphenyl-tert-butylnitroxide, the ratio $\left|\delta^{\text {orb }} / \delta^{\mathrm{FC}}\right|$ is calculated to be less than $15 \%$ while pseudocontact shifts $\delta^{\mathrm{PC}}$ contribute less than 0.1 ppm to any of the ${ }^{1} \mathrm{H}$ shifts. ${ }^{92}$ In addition, in the calculation of the acetylacetonate complexes of $\mathrm{Mn}, \mathrm{Fe}$, $\mathrm{Cr},{ }^{91 \mathrm{~b}, 93}$ the pseudocontact shifts were found to be negligible. Thus the contribution of the pseudocontact shift to the chemical shift is normally neglected in the calculation of NMR of paramagnetic complexes, especially for the first row $d^{6}$ and $d^{10}$ transition metals (including cobalt complexes like the ones studied in this thesis). Only $\delta^{\mathrm{orb}}$ and $\delta^{\mathrm{FC}}$ are considered.

The direction of the paramagnetic shift is mainly determined by the sign of the hyperfine coupling constant (see Eq. 2.4), which is in turn determined by the sign of the spin density at the relevant nucleus. ${ }^{92 b}$ One might expect that in e.g. a high-spin Co (II) complex, all spin densities would have the same sign, because there are 3 more $\alpha$ than $\beta$
electrons, but this is not the case. A large spin density in one orbital (due to a single electron of e.g. spin $\alpha$ ) also affects other formally doubly occupied orbitals, which will get an excess of spin $\beta$ density (i.e. the opposite sign spin density) on some atoms (this is called spin polarization). Therefore, signs of hyperfine couplings are hard to predict, and paramagnetic shifts can be in either direction

In practice, chemical shifts of paramagnetic compounds are also concentrationdependent.

A second characteristic property of paramagnetic NMR spectra is that peaks are normally broad (the half width can go up to 1000 Hz ). Although there are many reasons that can lead to peak broadness, such as the chemical exchange, inhomogeneity of the magnetic fields, e.g. due to particles in the sample, inhomogeneity of the molecules such as polymers and so on, the broad peaks in paramagnetic systems are mostly due to fast spin relaxation: according to NMR theory, peak width is inversely proportional to the transverse relaxation rate. ${ }^{94}$ The strong interaction in paramagnetic compounds between the polarized nuclear spin and the dipole moment generated from the unpaired electron at the metal center causes fast nuclear-spin relaxation and a short $\mathrm{T}_{2}$ value.

### 2.1.2 Interpretation of paramagnetic ${ }^{\mathbf{1}} \mathrm{H}$ NMR spectra

Because the peaks of paramagnetic compounds are quite broad, a slight error in the baseline can lead to large errors in peak areas. Thus a good baseline adjustment is
mandatory to obtain reliable integration values for assignments. However, integration data alone are sometimes not enough for complete assignment. In such cases, calculation of $\delta^{\mathrm{orb}}$ and $\delta^{\mathrm{FC}}$ contributions to the chemical shifts using DFT can be useful. ${ }^{92,95}$ This strategy is used in the study of cobalt(II) systems in this thesis and illustrated in Chapter 5 and Chapter 6.

### 2.1.3 The Evans method

The standard methods to measure magnetic susceptibility are the magnetic balance (also called Gouy's balance in the Gouy method or Faraday method) ${ }^{96}$ or the SQUID (Superconducting Quantum Interference Device) magnetometer. ${ }^{97}$ However, it is also possible to use NMR to determine the magnetic moment of a complex; this method was developed by Evans (for theory and the updated equations, see ref. 98). In this method, the chemical-shift change of the reference peak caused by the presence of the paramagnetic compound is used to calculate the effective magnetic moment of the compound according to the following equation: ${ }^{98 b}$

$$
\begin{gather*}
\mu_{e f f}=798 \sqrt{\chi_{M} T}  \tag{Eq. 2.6}\\
\chi_{M}=\left(-\frac{3 \Delta v}{v m}+\chi_{\text {mass }, 0}\right) \bullet M W
\end{gather*}
$$

Where:

- $\mu_{\text {eff: }}$ the effective magnetic moment $\left(\mu_{\mathrm{B}}\right)$
- T : temperature (K)
- MW: molecular weight ( $\mathrm{kg} / \mathrm{mol}$ )
- $\quad v$ : the frequency of the external magnetic field $(\mathrm{Hz})$
- $\Delta v$ : the frequency difference in Hz of a reference substance caused by the presence of the paramagnetic sample.
- $\chi_{\text {mass }, 0}$ is the mass susceptibility of the solvent used $\left(\mathrm{m}^{3} / \mathrm{kg}\right)$
- m: mass concentration $\left(\mathrm{kg} / \mathrm{m}^{3}\right)$
- $\chi_{\mathrm{M}}$ : molar susceptibility of the complex in the magnetic susceptometer $\left(\mathrm{m}^{3} / \mathrm{mol}\right)$ The number of unpaired electrons can be derived by comparing the value of this effective magnetic moment, $\mu_{\text {eff }}$, to the value $\mu_{\mathrm{s}}$ from the ideal "spin-only" formula (where the orbital contribution is neglected):

$$
\begin{equation*}
\mu_{s}=g_{e} \sqrt{S(S+1)} \approx 2 \sqrt{\frac{n}{2}\left(\frac{n}{2}+1\right)} \tag{Eq. 2.7}
\end{equation*}
$$

Where n is the number of unpaired electrons.

Orbital contributions can be significant, but they are similar between same metals with the same spin state. This usually allows unambiguous determination of the spin state of the complex. The Evans method was used for measuring the magnetic moment of cobalt complexes in Chapter 5.

### 2.2 Electron paramagnetic resonance (EPR)

Compared with NMR, EPR is less widely used because it is restricted to paramagnetic compounds. As the electron also has two spin states (like the proton), it can also be polarized, just like the proton in ${ }^{1} \mathrm{H}$ NMR. Thus, the theory in ${ }^{1} \mathrm{H}$ NMR can be applied to EPR except using an electron instead of a proton (for details of EPR theory, see e.g. ref. 99). There are two important parameters which are generated from an EPR spectrum, the g factor (similar to the chemical shift in NMR) and the hyperfine coupling constants (similar to $J$-couplings in ${ }^{1} \mathrm{H} \mathrm{NMR}$ ).

The g-factor observed in solution is different from that in the solid state. In the liquid state, one only observes a single $g$ value, and for each nucleus coupling to the electron, a single hyperfine coupling. Both g and coupling constants are tensors, but rapid tumbling in solution causes them to be time-averaged. In the solid state, the individual components can be observed, leading to individual $g_{x}, g_{y}$ and $g_{z}$ values and corresponding hyperfine coupling constants. EPR usually works quite well for compounds with a single unpaired electron. For metal complexes with more than one unpaired electron, overlapping of the peaks makes interpretation difficult. In addition, peaks in their EPR spectra are often too broad due to fast relaxation; special techniques (e.g. cooling the sample) are required in the EPR measurements, but the application of these techniques are not easy. Most of the paramagnetic complexes we are going to study contain more than one unpaired electron. EPR was not likely to be useful for them and only one cobalt(0) system in Chapter 7 was characterized by EPR.

### 2.3 Single-crystal X-ray diffraction

Single-crystal X-ray diffraction is commonly used to determine three-dimensional structures of complexes and is the most direct method for studying the coordination environments of metal centers. In this thesis, a variety of cobalt and iron complexes will be prepared and knowledge of the metal environments in them is rather important for understanding their chemistry and catalytic activity. Thus, single-crystal X-ray diffraction will be frequently used in determining the structures of new complexes prepared in this thesis. In the following section, the theory of single-crystal X-ray diffraction will be briefly described (for more details of the theory, see ref. 100) and some details of the experiment will be illustrated.

### 2.3.1 Principles

When X-rays hit atoms in a crystal, they will be scattered by the electrons surrounding the nuclei. Whether a beam of X-rays scattered by a periodic arrangement of atoms is in phase or not when reaching the detector can be determined by the Bragg equation as follows (Eq. 2.8, Figure 2.1). ${ }^{100}$


Figure 2.1. Illustration of X-ray diffraction at a single crystal

$$
\begin{equation*}
2 \mathrm{~d} \sin \theta=\mathrm{n} \lambda \tag{Eq. 2.8}
\end{equation*}
$$

Where:

- d is the distance between two atom arrays
- $\theta$ is the angle between the incident X-ray beam and the atom array
- $\lambda$ is the wave length of the X-rays used.

This equation must be obeyed in three dimensions, leading to three reflection conditions for each reflection. As a result, each reflection will actually be observed when the crystal is oriented in a particular manner that leads to all three conditions being fulfilled simultaneously.

When the scattered X-rays reach the detector, spots on the detector representing their intensities (each corresponding to one plane of the crystal) will be collected. The arrangement of spots defines the unit cell and the intensities of the spots contain
information about the electron-density distribution within the unit cell. The electrondensity can be reconstructed from the peak intensity data. From the resulting electron density map, the positions and types of atoms in the cell can be deduced (for details on how direct methods and Patterson methods can be used to solve the important phase problem, please refer to ref. 100).

### 2.3.2 Experimental settings of acquisitions

Most of the samples studied in this thesis are air sensitive and sealing the crystals in thin glass capillaries will be the most appropriate way to protect them. If the crystals are not air sensitive, gluing them directly on top of a thin glass fiber will be appropriate. Our standard settings for data collection will be used: Mo $\mathrm{K} \alpha$ radiation ( $\lambda=0.71073 \AA$ ), one 360 degree $\varphi$ run and then a number of $\omega$ runs (this makes up a hemisphere of data with some redundancy). Full sphere acquisition will be set up when the crystal structure is suspected to be acentric. In addition, the data are processed as follows: data with intensity of higher than $2 \sigma$ are analyzed and indexed using the Bruker smart suite ${ }^{101}$ to refine the cell parameters. All data are integrated using SAINT; ${ }^{101}$ a semi-empirical absorption is done using SADABS; ; ${ }^{102}$ the final hkl data is generated using Xprep. ${ }^{103}$

### 2.3.3 Structure solution

Our standard way to solve single-crystal X-ray structure is as follows: structures are solved with SHELXS97, ${ }^{104}$ using direct methods or Patterson methods. During the structure refinement by SHELXL97, ${ }^{105}$ the command "omit -351 " was used to remove
all reflections with $2 \theta$ value above $51^{\circ}$ and to modify very negative $\mathrm{F}_{\mathrm{o}}{ }^{2}$ (all reflections with $\mathrm{F}_{\mathrm{o}}{ }^{2}<-1.5 \sigma\left(\mathrm{~F}_{\mathrm{o}}{ }^{2}\right)$ are replaced by $\left.1.5 \sigma\left(\mathrm{~F}_{\mathrm{o}}{ }^{2}\right)\right) .{ }^{105}$ The final structures are refined using full-matrix least-squares refinement on $F^{2}$ with SHELXL97. Hydrogen atoms are placed at calculated positions and refined in riding mode. Structures are checked for solventaccessible voids with PLATON; ${ }^{106 a}$ Mercury ${ }^{107}$ is used to view the structure. For cocrystallized solvent molecules, their disorder made locating them exactly sometimes too hard. Thus, they are either modeled as the disorder over two or more positions, or ignored by using the "squeeze" function in the PLATON ${ }^{106 a}$ software to remove the contribution of the solvent molecules from the diffraction data. ${ }^{106 b-c}$

### 2.4 Density Functional Theory (DFT) calculations

DFT has become a good tool in studying transition metal complexes and the results are usually reliable compared with experimental data. DFT methods have proven to be particularly useful for the mechanistic study of reactions which cannot be easily studied by experimental methods. The research in this thesis aims at understanding the properties of DIP metal complexes; DFT will be used as an alternative tool to assist the experimental methodology. In the following sections, the basic theory of DFT will be briefly described (for a thorough description of DFT, see ref. 108), followed by the functionals and basis sets which will be used in this thesis. Most of the complexes in this thesis are paramagnetic; open-shell DFT calculations can be employed and are described later. Finally, the study of electronic structure of (DIP)CoR by DFT will be elaborated.

### 2.4.1 Basic theory of DFT

Quantum mechanics (QM) methods treat a molecular system in terms of nuclei and electrons and the energy is calculated from the total contributions from the interactions among these particles. In QM theory, there are mainly two branches: one branch ("ab initio theory") includes Hartree-Fock and post Hartree-Fock methods; the other one is called Density Functional theory (DFT). In the following section, ab initio theory will be briefly described but DFT will be the main focus.

In QM, the energy of a molecule can be obtained by applying an energy operator to the wave function of the whole system, according to Schrödinger's equation (Eq. 2.9):

$$
\begin{equation*}
\hat{\mathrm{H}} \Psi=\mathrm{E} \Psi \tag{Eq. 2.9}
\end{equation*}
$$

- $\hat{\mathrm{H}}:$ Hamiltonian Operator
- $\Psi:$ the wave function
- E: the energy of the system

As for the Hamiltonian operator, five main contributions to the total energy of the system are normally considered, that is, the kinetic energy of the electrons and nuclei, the attraction of the electrons to the nuclei, and the inter-electronic and inter-nuclear repulsions. Extra terms such as external magnetic or electric fields, relativistic effects, spin-electron couplings and so on are required in more complicated situations. Because electrons move much faster than nuclei, the Born-Oppenheimer Approximation is usually introduced, fixing the nuclei. Thus, the kinetic energy of the nuclei is omitted from the

Hamiltonian operator and the "pure" electronic energy of the molecule will be computed. Because the repulsions between nuclei are constant, for a given structure, attention will be mainly focused on the kinetic energy of the electrons, the attraction energy between electrons and the nuclei, and the interaction between electrons.

In Hartree-Fock (HF) theory, the electrons are treated as moving independently and the exact N -electron wave function ( N : the total number of electrons in a system) is approximated by an antisymmetrized product of N one-electron wave functions (this product is also called a Slater determinant $\Phi_{\mathrm{SD}}$; one-electron wave functions are called spin orbitals). The total Hartree-Fock energy of the system is calculated according to the following equation:

$$
\mathrm{E}_{\mathrm{HF}}=\left\langle\Phi_{S D}\right| \hat{H}\left|\Phi_{S D}\right\rangle=\sum_{i}^{N}\left(\chi_{i}\left|-\frac{1}{2} \nabla^{2}-\sum_{A}^{M} \frac{Z_{A}}{r_{1 A}}\right| \chi_{i}\right)+\frac{1}{2} \sum_{i}^{N} \sum_{j}^{N}\left(\chi_{i} \chi_{i} \mid \chi_{j} \chi_{j}\right)-\left(\chi_{i} \chi_{j} \mid \chi_{j} \chi_{i}\right)
$$

The first two terms are the contributions from the electronic kinetic energy $\left(-\frac{1}{2} \nabla^{2}\right)$ and the electron-nucleus attraction $\left(\frac{Z_{A}}{r_{1 A}}\right)$; the second two terms are the Coulomb $\left(\chi_{\mathrm{i}} \chi_{\mathrm{i}} \mid \chi_{\mathrm{j}} \chi_{\mathrm{j}}\right)$ and exchange ( $\chi_{i} \chi_{j} \mid \chi_{j} \chi_{i}$ ) integrals ( $\chi_{i}$ and $\chi_{j}$ are spin orbitals).

Thus $\mathrm{E}_{\mathrm{HF}}$ is a functional of the spin orbitals $\left(\chi_{\mathrm{i}}\right)$. By applying variational theory (for details of this theory, refer to the book in ref. 109), one-electron Fock operators can be
introduced to solve for the spin orbitals (also called HF molecular orbitals) together with the orbital energies $\left(\varepsilon_{\mathrm{i}}\right)$; this is expressed as follows:

$$
\begin{gather*}
f_{i} \chi_{i}=\varepsilon_{i} \chi_{i}  \tag{Eq. 2.11}\\
f_{i}=-\frac{1}{2} \nabla_{i}^{2}-\sum_{k}^{n u c l e i} \frac{Z_{k}}{r_{i k}}+V_{i}^{H F}\{j\}
\end{gather*}
$$

$V_{i}^{H F}\{j\}$ is the Hartree-Fock potential, which is the average interaction potential of one electron with all of the other electrons occupying orbitals $\{\mathrm{j}\}$. It contains two components: a Coulomb operator and a like-spin electron exchange operator. The HF equations have to be solved iteratively to self-consistence because each $f_{i}$ depends on all the other orbitals.

After spin orbitals have been obtained, the total HF energy is calculated according to Eq. 2.10.

A single Slater determinant is only an approximation to the exact wave function of the real system. In reality, electrons do not move independently of each other. To describe this correlated motion of electrons correctly, one needs a more complicated wavefunction than a single Slater determinant. The electron correlation is defined as the energy difference between the exact non-relativistic energy and the energy in the HF limit (the HF limit is the solution of the Hartree-Fock equations with an infinite basis set). ${ }^{109}$

In order to approach this correlation energy, post HF methods (ab initio theory) try to include configurations from excited states in trial wave functions to approach the exact wave function of the real system without modifying the Hamiltonian operator (for details, see ref. 109). Many theories such as Perturbation theory and Coupled-Cluster theory have been developed for this purpose. This methodology works well for a variety of relatively small systems. However, the near degeneracy of valence orbitals in transition metal complexes forces post HF methods to use more configurations; thus, the cost to calculate them becomes prohibitive. HF scales as $\mathrm{N}^{4}$ (theoretically, due to the four-index integrals; here N stands for the number of basis functions used) or as $\sim \mathrm{N}^{2.7}$ (in practice, due to efficient pre-screening methods). Post-HF methods scale as $\mathrm{N}^{5}(\mathrm{MP} 2), \mathrm{N}^{6}(\mathrm{MP} 3)$, $\mathrm{N}^{7}(\operatorname{CCSD}(\mathrm{~T})) .{ }^{109}$

DFT tries to describe systems in a different way: instead of modifying the wave functions to approach the electron correlation energy, DFT modifies the Hamiltonian operator by introducing an operator specifically to represent the electron exchange and correlation energy. According to the first Hohenberg-Kohn Theorem, the total energy (E) of a system is fully determined by its total electron density $(\rho)$, which can be expressed as follows:

$$
\mathrm{E}=\mathrm{E}_{\mathrm{o}}[\rho]
$$

In order to build the electron density for a real system, the Kohn-Sham approach treats electrons as non-interacting particles moving in an effective potential representing exchange and correlation effects (this system is also called the fictitious system). The electron density of this fictitious system in the ground state exactly equals the density of
the corresponding real, interacting system. Thus the total energy of the real system will be expressed as follows:

$$
\begin{equation*}
\mathrm{E}[\rho]=\mathrm{T}_{\mathrm{ni}}[\rho]+\mathrm{V}_{\mathrm{ne}}[\rho]+\mathrm{V}_{\mathrm{ee}}[\rho]+\mathrm{E}_{\mathrm{XC}}[\rho] \tag{Eq. 2.12}
\end{equation*}
$$

- $T_{n i}[\rho]$ : kinetic energy of the non-interacting electrons
- $\mathrm{V}_{\mathrm{ne}}[\rho]$ : the nuclear-electron interaction
- $\mathrm{V}_{\mathrm{ee}}[\rho]$ : the classical electron-electron repulsion
- $\mathrm{E}_{\mathrm{XC}}[\rho]$ : the energy corrections due to electron exchange and correlation As the second Hohenberg-Kohn Theorem states, this density can be optimized according to the variational principle by minimizing $\mathrm{E}[\rho]$ with respect to independent variations in the orbitals $\left(\chi_{\mathrm{i}}\right)$. Since the fictitious system is non-interacting and a single Slater determinant is normally the exact wave function of a non-interacting system, the electron density in the fictitious system is constructed from a single Slater determinant in DFT. To separate the N -electron problem into N single particle equations, one-electron operators ("Kohn-Sham operators") are introduced, just as the one-electron Fock operator in HF theory. This leads to the Kohn-Sham (KS) equations which can be solved iteratively:

$$
\begin{gathered}
\mathrm{h}_{\mathrm{i}}^{\mathrm{ks}} \chi_{\mathrm{i}}=\varepsilon_{\mathrm{i}} \chi_{\mathrm{i}} \\
h_{i}^{K S}=-\frac{1}{2} \nabla_{i}^{2}-\sum_{k}^{\text {nuclei }} \frac{Z_{k}}{\left|r_{i}-r_{k}\right|}+\int \frac{\rho\left(r^{\prime}\right)}{\left|r_{i}-r^{\prime}\right|} d r^{\prime}+V_{X C}
\end{gathered}
$$

- $\chi_{\mathrm{i}}$ is the Kohn-Sham (KS) orbital
- $\mathrm{h}_{\mathrm{i}}{ }^{\mathrm{ks}}$ is the Kohn-Sham one-electron operator
- $\mathrm{V}_{\mathrm{xc}}$ is the exchange-correlation potential which is unknown
- $\varepsilon_{i}$ is the Kohn-Sham orbital energy

In solving these KS equations, the electron density can be constructed from the KS orbitals. By inserting this electron density into the energy expression in Eq. 2.12, the total energy of the system can be calculated.

Compared with $a b$ initio theory, DFT calculations are much faster for they do not require the calculation of "four-index integrals""VIII, let alone multi-determinant solutions; as a result, DFT is much cheaper for the calculation of transition metal complexes. The calculation time of DFT scales in the order of $\mathrm{N}^{2}-\mathrm{N}^{3}$.

If $\mathrm{V}_{\mathrm{XC}}$ were known explicitly, the energy calculated would be the exact energy. However, it is not. Current theory only states that a $\mathrm{V}_{\mathrm{XC}}$ exists, but not what it would look like. Thus, approximating the $\mathrm{V}_{\mathrm{XC}}$ term is the main issue in DFT research and a wide variety of functionals have been developed. Among them, BP86 with the Becke 88 exchange functional ${ }^{110}$ combined with the Perdew $86^{111}$ correlation functional works quite well for many transition metal systems. ${ }^{112 \mathrm{a}-\mathrm{b}}$ However, BP86 still underestimates the electron repulsion energy and often predicts energies for low-spin states that are too low. By contrast, HF includes electron self-interaction terms, thus generally overestimates the stability of high spin states. Inclusion of a certain amount of HF exchange in DFT ("hybrid" methods) seems to work better in certain cases. For example, the popular B3LYP ${ }^{112 \mathrm{c}}$ functional, which includes around $20 \%$ of HF exchange, was shown to work

[^6]better in certain systems than BP86. However, in other cases, hybrid DFT seems to overestimate the electron repulsion. ${ }^{112 \mathrm{c}}$

One problem with the DFT methods is that there is no systematic way to approach the exact energy of the system. For $a b$ initio theory, the energy can be approached by systematically enlarging the number of configurations and increasing the basis set. For DFT, the basis set can be expanded in the same way, but there is no clear hierarchy of better functionals leading to the exact energy. Although the "Jacob's ladder", IX can be used as a guideline to improve the energy in a general sense, ${ }^{113}$ this is no guaranteed convergence to the exact energy and each rung has particular strengths and weaknesses. The only way to validate a method is to test it to see whether it can predict the right results for a number of related systems.

### 2.4.2 Functional and basis set

A good combination of functional and basis set is important in predicting the right chemistry. In this thesis, the $\mathrm{SV}(\mathrm{P})$ basis set is usually used to optimize the geometry; the larger TZVP basis set is then used to improve the energy (Chapter 4 and Chapter 5) or to

IX "Jacob's ladder" is a ladder with five rungs proposed by J. Perdew as representing the hierarchy of the five generations of DFT functionals with increasing chemical accuracy: the first rung (the local density approximation or LDA), the second rung (the generalized gradient approximation or GGA), the third rung (the meta generalized gradient approximation or M-GGA), the fourth rung (hybrid generalized gradient approximation or H-GGA and the hybrid meta generalized gradient approximation or MH-GGA) and the top rung (the hypothetical description of the exact functional).
improve the geometry (Chapter 6). The Turbomole functionals used in this work ("b3lyp' and "b-p") are similar, but not identical, to the popular "B3LYP" and "BP86" functionals often used with Gaussian or ADF. In Gaussian, BP86 is a combination of the Becke 88 exchange functional and the Perdew 86 correlation functional, ${ }^{110,111}$ while b-p in Turbomole uses Becke 88 as the exchange functional and $\mathrm{VWN}(\mathrm{V})$ and Perdew 86 as correlation functionals. In Turbomole, the correlation functional in b3-lyp ${ }^{114}$ contains VWN(V) (19\%) and LYP(81\%) while B3LYP in Gaussian uses VWN(III) (19\%) and LYP ( $81 \%$ ) for the correlation functional. ${ }^{115}$ The use of VWN(V) in Turbomole instead of VWN(III) is partly because it is easy to implement and recommended in the original paper, ${ }^{116}$ and partly because $\mathrm{VWN}(\mathrm{III})$ is much less well founded than $\mathrm{VWN}(\mathrm{V})$.

The group of Budzelaar has done numerous DFT studies on cobalt systems using the Turbomole program ${ }^{117}$ and the b3-lyp functional combined with $\mathrm{SV}(\mathrm{P})$ or TZVP basis sets and these choices predict the chemistry quite well. ${ }^{68,83}$ In order to keep consistency, these choices were also used in the DFT study in this thesis. For the calculation of certain properties of the complexes, such as NMR and EPR parameters, the Gaussian ${ }^{118}$ and Orca programs ${ }^{119}$ are also used in Chapter 5 and Chapter 6.

### 2.4.3 Open-shell DFT computations

Because the systems studied in this thesis contain unpaired electrons, open-shell DFT has to be used. As the restricted open-shell cannot express the spin polarization situation, unrestricted open-shell DFT formalism will be used. Since only a single determinant
(also called a reference) is used in DFT, contamination from higher spin states is always present, and the $<\hat{S^{2}}>(\hat{S}$ is the spin operator) value can be used as an indicator of such contamination (ideal $<\hat{S^{2}}>$ values: $\frac{n}{2}\left(\frac{n}{2}+1\right)$ ). Although spin projection ${ }^{120 a}$ can be used to remove contamination by the next higher spin state, it has its own drawbacks. If the contribution from even higher spin states can not be neglected, the energy generated after spin projection is still not that of a pure spin state. In addition, the geometry generated from optimization using the spin-contaminated energy does not correspond to the geometry of the pure spin state. However, according to earlier research in related cobalt and iron systems, spin contamination seems not to be a big issue except for the special case of antiferromagnetic coupling between metal-centered and ligand-centered electrons, discussed below. Thus, open-shell DFT will be used in this thesis, with the $<\hat{S^{2}}>$ values always checked for spin contamination.

### 2.4.4 DFT study of (DIP)CoR

## Introduction

The X-ray structures of (DIP)CoR complexes ${ }^{81}$ show that the imine bonds are significantly longer than those in the free DIP ligand; this can be attributed to transfer of a significant amount of electron density from the metal center to the DIP ligand. In these complexes, the DIP ligand is normally described as a radical anion in the literature. ${ }^{83}$ As the ${ }^{1} \mathrm{H}$ NMR spectrum clearly indicates that (DIP)CoR complexes are diamagnetic, a singlet biradical state of the complex is normally considered as the reasonable electronic
structure of the complex. Because of this biradical character, in principle, it can not be described by a single determinant. Therefore, the standard single-determinant restricted Hartree-Fock (HF) and DFT are not sufficient for the calculation of these complexes. Accurate post-HF methods that describe the electron correlation by using more determinants seem to be the right choice. However, the large basis set and the high cost to compute such large systems make these methods unsuitable here. Thus, a brokensymmetry (BS) treatment ${ }^{\mathrm{X}}$ based on the Unrestricted Hartree-Fock (UHF)/Unrestricted Kohn-Sham (UKS) formalism ${ }^{120 b-c}$ is normally used to calculate such systems with biradical character: the geometries predicted by this method are similar to the X-ray structures. ${ }^{81-83}$ Due to the use of the spin-unrestricted formalism, the calculated "singlet state" is always contaminated by the corresponding triplet state. For the (DIP)CoR complexes studied here, $\hat{S^{2}}$ values are normally close to 1 , indicating a close to $1: 1$ mixture of pure singlet $\left(\hat{S^{2}}=0\right)$ and pure triplet $\left(\hat{S^{2}}=2\right)$.

## Singlet-triplet energy gap

The energy gap between singlet and triplet can be important for tuning the properties of the complex. Thus the energies of "pure" singlet and "pure" triplet states are required.

[^7]Because of the spin contamination issues in the unrestricted HF or DFT calculation, several methods have been proposed to arrive at "pure" singlet and triplet energies for singlet biradical compounds: ${ }^{120 \mathrm{~d}}$

1) eliminate or correct spin contamination from electronic energies ${ }^{\mathrm{XI}}$ (for example, spin projection ${ }^{120 a}$ );
2) describe the ground state using the explicit-electron-correlation treatment at the level of post-HF (e.g. MP2, CI, CCSD) with probably multireference methods ${ }^{\text {XII }}$ (e.g. DFT/MRCI ${ }^{120 e-f}$ ) to take care of the non-dynamic correlation. However, these methods are too expensive for large molecules;
3) change the treatment of full-spin occupancy to fractional-spin occupancy (this approach is also called the fractional occupancy approach). ${ }^{121 a-f}$

As the application of the fractional occupancy approach to transition metal complexes has not been validated, ${ }^{\text {XIII }}$ removal of the spin contamination or finding a way to calculate the pure singlet or triplet energy from the broken symmetry solution seems more practical. Removal of the spin contamination can be done using so called spin-projection. ${ }^{120 a}$ Apart

[^8]from problems associated with the method of spin-projection itself (see Section 2.4.3 on Open-shell DFT calculations), the cost to do spin projection is similar to MP2, which makes its application impractical here. In contrast, estimating the singlet and triplet energy gap directly from the broken symmetry solution is relatively easy and several methods have been proposed. ${ }^{1200-\mathrm{c}, 121 \mathrm{~g}}$

By assuming that the singlet state obtained from broken-symmetry solution is a mixture of the singlet ground state and the first excited triplet state and that the spin polarization of the inner electrons can be neglected, Noodleman first proposed Eq. 2.14 to estimate the singlet-triplet energy gap. ${ }^{120 b}$

$$
\begin{equation*}
E_{s}-E_{t}=2\left(E_{u}(B S)-E_{u}(T)\right) \tag{Eq. 2.14}
\end{equation*}
$$

- $\mathrm{E}_{\mathrm{u}}(\mathrm{T})$ is the UHF or UKS energy of the triplet state
- $\mathrm{E}_{\mathrm{u}}(\mathrm{BS})$ is the UHF or UKS energy of the singlet state from the broken symmetry solution

This formula assumes that the BS solution is a $1: 1$ mixture of singlet and triplet states, as would be expected for weak coupling. If the antiferromagnetic coupling is stronger, the contribution of the triplet to the BS solution decreases, and Eq. 2.14 should be probably replaced by Eq. $2.15^{121 \mathrm{~h}-\mathrm{i}}$.

$$
\begin{equation*}
E_{s}-E_{t}=\frac{2\left(E_{u}(B S)-E_{u}(T)\right)}{2-\left\langle S^{2}\right\rangle} \tag{Eq. 2.15}
\end{equation*}
$$

In this expression, the calculated value of $\hat{S^{2}}$ is used to express the contribution of the triplet to BS solution: $\hat{S^{2}}=1$ for weak coupling (1:1 mixing) and 0 for strong coupling \left. (negligible triplet contribution). In the limit of strong coupling ( ${\hat{S^{2}}}^{2} 0\right)$, Eq. 2.15 converts to Eq. 2.16.

$$
\begin{equation*}
E_{s}-E_{t}=E_{u}(B S)-E_{u}(T) \tag{Eq. 2.16}
\end{equation*}
$$

Both Ruiz ${ }^{121 \mathrm{j}}$ and Bachler ${ }^{121 \mathrm{~g}}$ found that even for some not very weakly coupled systems, Eq. 2.16 produces results close to experiment, in particular with use of the B3LYP functional. According to Bachler and coworkwes, ${ }^{121 \mathrm{~g}}$ this is probably due to a fortuitous cancellation of errors.

## Four coordinate DIP cobalt(I) complexes

As an open-shell DFT solution for a singlet biradical system is contaminated mainly by the triplet state, the pure singlet-state energy is expected to have a certain correlation with the energy from the broken-symmetry solution, the corresponding pure triplet-state energy ${ }^{\text {XIV }}$ and their $\hat{S^{2}}$ values. However, to derive the "pure" singlet energy is not trivial for DIP cobalt(I) systems.

[^9]The group of Budzelaar used extrapolation of the presumed linear relation between energy and $\hat{S^{2}}$ to $\hat{S^{2}}=0$ to calculate the approximate energy gap between singlet and triplet for cobalt(I) systems (cobalt(I) hydride, cobalt(I) chloride, cobalt(I) methyl). ${ }^{83}$ The singlet-triplet separation gap was estimated to be between 4.6 and $9.1 \mathrm{kcal} / \mathrm{mol}$ for the complexes examined.

However, for other DIP cobalt(I) complexes with no obvious symmetry, it is not trivial to locate the required corresponding triplet state. Generally, there are two types of triplet states: Type I has two unpaired electrons located at the cobalt center (Triplet I in Figure 2.2); Type II has one electron in a ligand orbital and the other at the metal center (Triplet II in Figure 2.2). The corresponding triplet needed for an energy estimate of the singlet is a Type II triplet. The energy of Triplet II can be higher than that of Triplet I, thus, it may not be possible to converge to a Triplet II solution.


Triplet I


Triplet II

Figure 2.2. Two types of triplet state of (DIP)CoR

The further analysis of the Type II triplet shows that one electron at the metal can come from one of the d orbitals and the other electron at the ligand can come from one of the two $\pi^{*}$ orbitals. Thus there are a lot of possibilities and only one of them is the right triplet for the singlet-energy estimation. However, several DFT calculations failed to converge to the "right" triplet due to its relatively high energy. Therefore, obtaining the "pure" singlet energy for these DIP cobalt(I) systems using equations 2.14-2.16 was often not possible, and we decided to simply use broken-symmetry energy instead.

As the geometry optimized by the broken-symmetry method is very close to the X-ray structure, a broken-symmetry treatment of (DIP)Co(I) complexes is used throughout this thesis.

# Chapter 3. Coordination geometry of pentacoordinate Iron(II) and Cobalt(II) complexes of DIP-type ligands 

### 3.1 Introduction to Five-coordinate complexes

Five-coordinate complexes are less common than four-coordinate or six-coordinate complexes. Whereas geometries of coordination number 4 and 6 are typically welldefined (coordination number 4: tetrahedral or square planar; coordination number 6: octahedral and occasionally trigonal prism), five-coordinate complexes tend to be variable. As five coordinate species exist in environments such as the transition state of $\mathrm{S}_{\mathrm{N} 2}$ reactions at $\mathrm{C}\left(\mathrm{sp}^{3}\right)$ centers ${ }^{122}$ or as intermediates during ligand-displacement reactions of four-coordinate or six-coordinate metal complexes, ${ }^{123}$ the properties of such species are important. To aid the understanding of these properties, it is useful to (a) be able to classify structures in well-defined categories (if possible), and (b) to understand the preference of complexes for specific geometries. A variety of strategies for structure analysis have been published, but most are not universally applicable. For five-coordinate compounds with five identical coordinating atoms, two types of geometries are normally considered (Figure 3.1): trigonal bipyramidal (TBP) and square pyramidal (SP).


Figure 3.1. Structures of $\mathrm{PF}_{5}$ with geometries of trigonal bipyramidal (TBP, left) and square pyramidal (SP, right)

The IR spectrum of $\mathrm{PF}_{5}$ supports a TBP structure. However, the ${ }^{19} \mathrm{~F}$ NMR spectrum at room temperature shows only a single peak, indicating fluxional behaviour. ${ }^{124}$ The current section of this chapter describes general ways to analyze five-coordinate complexes; two specialized methods adapted for DIP metal complexes are then developed and applied.

Up to now, there are mainly two types of methods reported to analyze five-coordinate transition metal complexes: one is to generate an assignment as either TBP or SP without assuming a path between them; ${ }^{125}$ the other one is to scale the similarity to one of them by assuming a specific conversion path. ${ }^{126}$ Of the former methods, the most general one is the full angle analysis (FAA) which analyzes all angle deviations around the metal center (for details, see the following section on FAA). ${ }^{127}$ As for the latter, Berry rearrangement (Turnstile rotation ${ }^{128}$ is in principle the same as Berry pseudorotation ${ }^{\mathrm{XV}}$ ) is

[^10]usually assumed and has been studied a lot for a variety of substrates (for details, see the following section on Berry Pseudorotation). ${ }^{129}$

### 3.2 Berry Pseudorotation

In 1960 , when he analyzed the NMR and IR spectra of $\mathrm{PF}_{5}$, Berry came up with the pseudo-rotation mechanism (this mechanism was later named after him) ${ }^{130,131}$ for changing from one TBP to another TBP without breaking or forming any bond (Scheme 3.1).


Scheme 3.1. Illustration of Berry pseudorotation mechanism

In this mechanism, one of the equatorial atoms (A, Scheme 3.1) in one TBP is chosen as the pivot and the other two equatorial atoms ( $\mathrm{C}, \mathrm{D}$ ) move toward the pivot, while the two apical atoms (B,E) move away from it (Scheme 3.1). After passing through an intermediate SP geometry, a TBP geometry with the new arrangement of atoms is generated. Based on this mechanism, two geometry parameters specifically measuring
progress along this path have been defined ( $\delta$ and $\tau$, see below). Because it will result in the exchange of axial and basal positions, Berry pseudo-rotation mechanism explains quite well the positional exchange in penta-coordinate compounds without large constraints in the skeleton. ${ }^{132}$

### 3.2.1 $\delta$ parameter

In 1974, Muetterties and Guggenburger approached five-coordinate molecules in a quite different way, considering only the dihedral angle $\delta_{\mathrm{ij}}$ that formed between two normals to two adjacent faces (Figure 3.2) without focusing on the central atom. In this methodology, the length of bonds between the metal and coordinated atoms are assumed to be same and the Berry rearrangement is viewed in terms of the coordination polyhedron as shown in Scheme 3.2. ${ }^{132}$


Figure 3.2. Definition of $\delta_{\mathrm{ij}}$ parameter


Scheme 3.2. Illustration of Berry pseudorotation in terms of polyhedron distortion

The conversion of a TBP geometry to a SP geometry will involve the pushing of positions 1 and 5 and the pulling of positions 2 and 4 at the same time. In ideal TBP, there are two types of dihedral angles, the angle formed by two norms to adjacent faces between the upper pyramid and the lower pyramid $\left(53.1^{\circ}\right)$ and the angle formed by two norms to the adjacent faces within one pyramid $\left(116.5^{\circ}\right)$. When changing from TBP to SP, $\delta_{24}$ will change from $53.1^{\circ}$ to $0^{\circ}$. By comparing all $\delta_{i j}$ values (they are also called $\delta$ parameters) in a certain structure with that in ideal TBP or SP, one can check whether Berry pseudorotation pathway is being followed and where the polyhedron lies on the $D_{3 h} \leftrightarrow C_{4 v}$ path. ${ }^{133}$ Later Homes and Deiters reported that, for a certain five-coordinate molecular structure $(\mathrm{C})$, if the quantities $\sum_{i}\left|\delta_{i}(C)-\delta_{i}(T B P)\right|$ and 217.7-$\sum_{i}\left|\delta_{i}(C)-\delta_{i}(S P)\right|$ are same, this structure (C) lies on the TBP-SP Berry pseudorotation
pathway. ${ }^{132 a}$ The percentage of SP can be calculated according to the definition of $\tau$ parameter ${ }^{132 \mathrm{~b}}$ which will be illustrated in the following section. These $\delta$ parameters normally work well for complexes with five identical and non-chelating ligands.

### 3.2.2 $\tau$ parameters

Reedijk and coworkers defined a $\tau$ parameter by following the path from SP to TBP (based on Berry rearrangement mechanism for five-coordinate molecules). ${ }^{134}$ In the definition, the four atoms that define the two largest angles are chosen as the basal atoms and the fifth one is chosen as the apical atom. The larger angle between the two basal angles is chosen as $\beta$ and the other (second-largest) is defined as $\alpha$ (Figure 3.3). The parameter $\tau=\frac{\beta-\alpha}{60}$ then represents the similarity to the ideal SP along the conversion path from ideal SP to ideal TBP. In an ideal TBP conformation, $\tau=1$, while in an ideal SP, $\tau=0$.

Ideal SP, $\alpha=\beta, \tau=0 ; \quad$ Ideal TBP, $\alpha=120^{\circ}, \beta=180^{\circ}, \tau=1$

$$
\tau<0.5: \mathrm{SP} ; \tau>0.5: \mathrm{TBP}
$$

Figure 3.3. Definition of $\tau$ parameter

The $\tau$ parameter works quite well for a variety of five-coordinate copper(II) complexes. For example, the correlation of the $\tau$ parameter with EPR hyperfine coupling constant $\mathrm{A}_{/ /}$ values of five-coordinate $\mathrm{Cu}(\mathrm{II})$ complexes is good. ${ }^{135}$ However, large out-of-plane distortions and ligand strain can make this correlation not feasible any more.

### 3.3 FAA analysis

Bürgi and coworkers ${ }^{125 a}$ reported that the total geometry distortion vector from a reference geometry for a five-coordinate complex can be described using 12 non redundant symmetry coordinates (these coordinates are collected in Table 3.1 for TBP and SP conformations; the ligand numbering and the definitions of each angle and bond length are shown in Figure 3.4) which are linear combinations of angle deviations and
bond-length deviations. The term Full Angle Analysis (FAA) refers to the idea of using the symmetry coordinates composed of bond-angle deviations $\left(\mathrm{S}_{4}, \mathrm{~S}_{6 \mathrm{a}}, \mathrm{S}_{6 \mathrm{~b}}, \mathrm{~S}_{7 \mathrm{a}}, \mathrm{S}_{7 \mathrm{~b}}, \mathrm{~S}_{8 \mathrm{a}}\right.$, and $\mathrm{S}_{8 \mathrm{~b}}$ for TBP; $\mathrm{S}_{3}, \mathrm{~S}_{5}, \mathrm{~S}_{6}, \mathrm{~S}_{8 \mathrm{a}}, \mathrm{S}_{8 \mathrm{~b}}, \mathrm{~S}_{9 \mathrm{a}}$ and $\mathrm{S}_{9 \mathrm{~b}}$ for SP$)$.


TBP


SP

Name of angle: e.g. $\theta_{12}=D^{1}-M-D^{2}$
Name of bond length: e.g. $r_{1}=\Delta\left(\mathrm{D}^{1}-\mathrm{M}\right)$
Figure 3.4. Ligand numbering and angle and bond length naming scheme for TBP (left) and SP (right)

Table 3.1. Twelve non-redundant symmetry coordinates

| Symmetry coordinates of TBP | Symmetry coordinates of SP |
| :--- | :--- |
| $\mathrm{S}_{1}=2^{-1 / 2}\left(\mathrm{r}_{1}+\mathrm{r}_{5}\right)$ | $\mathrm{S}_{1}=\mathrm{r}_{3}$ |
| $\mathrm{~S}_{2}=3^{-1 / 2}\left(\mathrm{r}_{2}+\mathrm{r}_{3}+\mathrm{r}_{4}\right)$ | $\mathrm{S}_{2}=1 / 2\left(\mathrm{r}_{1}+\mathrm{r}_{2}+\mathrm{r}_{4}+\mathrm{r}_{5}\right)$ |
| $\mathrm{S}_{3}=2^{-1 / 2}\left(\mathrm{r}_{1}-\mathrm{r}_{5}\right)$ | $\mathrm{S}_{3}=2^{-1 / 2}\left(\Delta \theta_{15}+\Delta \theta_{24}\right)$ |
| $\mathrm{S}_{4}=6^{-1 / 2}\left(\Delta \theta_{12}+\Delta \theta_{13}+\Delta \theta_{14}-\Delta \theta_{25}-\Delta \theta_{35}-\Delta \theta_{45}\right)$ | $\mathrm{S}_{4}=1 / 2\left(r_{1}+\mathrm{r}_{5}-\mathrm{r}_{2}-\mathrm{r}_{4}\right)$ |
| $\mathrm{S}_{5 \mathrm{a}}=6^{-1 / 2}\left(2 \mathrm{r}_{3}-\mathrm{r}_{2}-\mathrm{r}_{4}\right)$ | $\mathrm{S}_{5}=2^{-1 / 2}\left(\Delta \theta_{15}-\Delta \theta_{24}\right)$ |
| $\mathrm{S}_{5 \mathrm{~b}}=2^{-1 / 2}\left(\mathrm{r}_{2}-\mathrm{r}_{4}\right)$ | $\mathrm{S}_{6}=1 / 2\left(\Delta \theta_{12}+\Delta \theta_{45}-\Delta \theta_{14}-\Delta \theta_{25}\right)$ |
| $\mathrm{S}_{6 \mathrm{a}}=6^{-1 / 2}\left(2 \Delta \theta_{24}-\Delta \theta_{34}-\Delta \theta_{23}\right)$ | $\mathrm{S}_{7 \mathrm{a}}=2^{-1 / 2}\left(\mathrm{r}_{1}-\mathrm{r}_{5}\right)$ |


| Symmetry coordinates of TBP | Symmetry coordinates of SP |
| :--- | :--- |
| $\mathrm{S}_{6 \mathrm{~b}}=2^{-1 / 2}\left(\Delta \theta_{34}-\Delta \theta_{23}\right)$ | $\mathrm{S}_{7 \mathrm{~b}}=2^{-1 / 2}\left(\mathrm{r}_{4}-\mathrm{r}_{2}\right)$ |
| $\mathrm{S}_{7 \mathrm{a}}=12^{-1 / 2}\left(2 \Delta \theta_{13}-\Delta \theta_{12}-\Delta \theta_{14}+2 \Delta \theta_{35}-\Delta \theta_{25}-\Delta \theta_{45}\right)$ | $\mathrm{S}_{8 \mathrm{a}}=2^{-1 / 2}\left(\Delta \theta_{13}-\Delta \theta_{35}\right)$ |
| $\mathrm{S}_{7 \mathrm{~b}}=1 / 2\left(\Delta \theta_{12}-\Delta \theta_{14}+\Delta \theta_{25}-\Delta \theta_{45}\right)$ | $\mathrm{S}_{8 \mathrm{~b}}=2^{-1 / 2}\left(\Delta \theta_{34}-\Delta \theta_{23}\right)$ |
| $\mathrm{S}_{8 \mathrm{a}}=12^{-1 / 2}\left(2 \Delta \theta_{13}-\Delta \theta_{12}-\Delta \theta_{14}-2 \Delta \theta_{35}+\Delta \theta_{25}+\Delta \theta_{45}\right)$ | $\mathrm{S}_{9 \mathrm{a}}=2^{-1 / 2}\left(\Delta \theta_{12}-\Delta \theta_{45}\right)$ |
| $\mathrm{S}_{8 \mathrm{~b}}=1 / 2\left(\Delta \theta_{12}-\Delta \theta_{14}-\Delta \theta_{25}+\Delta \theta_{45}\right)$ | $\mathrm{S}_{9 \mathrm{~b}}=2^{-1 / 2}\left(\Delta \theta_{14}-\Delta \theta_{25}\right)$ |

In FAA, all angles at the metal center will be evaluated and deviations from the corresponding angles in the reference structure will be combined to generate sevendimensional vectors in seven non-redundant coordinates. As a result, the total distortion vector (Dist) will be the sum of these seven vectors:

$$
\begin{array}{r}
|\operatorname{Dist}(\mathrm{TBP})|=\sqrt{S_{4}^{2}+S_{6 a}^{2}+S_{6 b}^{2}+S_{7 a}^{2}+S_{7 b}^{2}+S_{8 a}^{2}+S_{8 b}^{2}} \\
|\operatorname{Dist}(\mathrm{SP})|=\sqrt{S_{3}^{2}+S_{5}^{2}+S_{6}^{2}+S_{8 a}^{2}+S_{8 b}^{2}+S_{9 a}^{2}+S_{9 b}^{2}}
\end{array}
$$

In order to calculate the distortion vector, the reference geometry (ideal structure) and the way of matching angles between the complexes studied and the reference structure need to be chosen carefully. For penta-coordinate complexes in general, there are two ideal geometries: ideal TBP and ideal SP. The assignment of the structure for a certain complex will be "distorted TBP" if the total distortion vector from ideal TBP is smaller than that from SP and vice versa. Although the definition of an ideal TBP is simple, with $180^{\circ}$ for two apical positions, $120^{\circ}$ among three basal positions and $90^{\circ}$ between apical and basal positions, there is no unique choice for the ideal SP (Figure 3.5). Any structure having four equal apical-equatorial $\left(\theta_{13}, \theta_{23}, \theta_{34}\right.$ and $\left.\theta_{35}\right)$ and four equal equatorial-
equatorial angles $\left(\theta_{12}, \theta_{25}, \theta_{45}\right.$ and $\left.\theta_{14}\right)$ should probably be classified as SP regardless of the value of this apical-equatorial angle.


TBP reference


SP reference

Figure 3.5. TBP and SP reference structures

Without the choice of one specific $\theta_{24}$ value for ideal SP , the $\mathrm{S}_{3}$ coordinate can not be evaluated for the calculation of SP distortion vector; thus Bürgi and coworkers used 7dimensional vectors to measure the distortion from ideal TBP and 6-dimensional vectors to measure the distortion from SP where trans-basal angles are same. However, 7dimensional vectors can be used in the calculation of distortion from SP by defining one value for the trans-basal angle $\left(\theta_{24}\right)$ for ideal SP. The matching of angles between two structures was solved by permuting over all possible atom labellings of the complex. The labelling that gives the lowest distortion vector will be kept as the assignment to one specific complex. Because FAA considers all angle deviations from ideal geometry, it works quite well for complexes without significant constraint among coordinating atoms. However, the total distortion vectors from ideal geometries cannot be used as the reaction
coordinate for the conversion between TBP and SP because they contain distortions that are perpendicular to the path connecting TBP and SP. ${ }^{\mathrm{XVI}}$

### 3.4 Introduction to five-coordinate DIP metal complexes

Diiminepyridine (DIP) ligands have attracted a lot of attention due to the high efficiency of their iron and cobalt complexes in ethylene polymerization; ${ }^{16,17}$ however, any further modification of the ligand skeleton has so far not led to significant improvement in catalysis. ${ }^{55}$ A lot of studies have been done to understand the reasons behind this. ${ }^{81 a, 136}$ The variety of X-ray structures of cobalt and iron dihalide complexes of DIP type ligands has attracted our attention. Some show distorted TBP geometries (one example is at the top in Figure 3.6) and some show distorted SP (one example is at the bottom in Figure 3.6). They also show quite different catalytic activity in ethylene polymerization: the former showed no activity at all while the latter is highly active. ${ }^{55}$ Thus, one might suspect a correlation of geometry preference with catalytic activity. The work in this chapter aims at establishing whether such a correlation is to be expected.
${ }^{\mathrm{XVI}}$ When the total distortion vector contains distortions that are perpendicular to the connecting path, the absolute value of the vector cannot describe the percentage of the similarity to ideal TBP or SP.


Figure 3.6. Skeletons of (A) TBP-like (1) $\mathrm{CoCl}_{2}{ }^{137}$ and (B) SP-like (5) $\mathrm{FeCl}_{2}{ }^{16}$

Structure analysis of all (DIP)MX ${ }_{2}$ complexes (M: $\mathrm{Fe}, \mathrm{Co} ; \mathrm{X}: \mathrm{F}, \mathrm{Cl}, \mathrm{Br}, \mathrm{I}$ ) in the Cambridge Structural Database (CSD) ${ }^{140}$ (for references, see Table A. 1 in Appendix A) is not simple due to the strong ligand-induced geometry distortions. ${ }^{138}$ However, I believe the structures shown in Figure 3.6 represent two cases where the correct classification is easy and unambiguous. Several methods for structure analysis reported in the literature were first tried in this system. The $\tau$ parameter values for these complexes are all low, leading to a classification of every system as $\mathrm{SP}^{\mathrm{XVIII}}$; thus it appears not to be suitable for our systems. For example, for (1) $\mathrm{CoCl}_{2}$ (Figure 3.6) which is "clearly TBP", $\tau$ was calculated to be 0.45 , indicating SP. FAA similarly leads to the non-discriminating results
${ }^{\text {XVII }}$ For (DIP)CoX ${ }_{2}, \tau \leq 0.48$; for (DIP)FeX ${ }_{2}$, with two exceptions, $\tau$ is less than 0.44 . One of these exceptions is the somewhat atypical (11) $\mathrm{FeCl}_{2}$, see Figure 3.11
which will be illustrated in detail in the Results and Discussion section. Thus, an alternative or modified strategy is desirable for these DIP complexes.

As Figure 3.6 shows, the major distortion of the whole structure comes from the large constraint among the three coordinated nitrogen atoms and this constraint is more or less constant among all (DIP)MX $2_{2}$ complexes. For example, all cis-NMN angles in these complexes are close to $74^{\circ}$ which deviate significantly from the ideal $90^{\circ}$ or $120^{\circ}$ of SP and TBP structures. Because FAA analysis, which considers all possible angle distortions, seems to be a good basis for analyzing the metal environment in DIP complexes, we decided to apply it in the current system but with a modification aimed at making it more discriminating. Furthermore, since FAA itself does not define a reaction coordinate for the inter-conversion between TBP and SP, a new two-angle criterion was devised to describe the reaction coordinate of our system. This criterion was then used to study the flexibility of the geometry along the interconversion coordinate, hoping to find the relation between geometry and reactivity.

### 3.5 Results and Discussion

### 3.5.1 Modified FAA analysis

## Choice of ideal TBP and SP geometries

In order to apply the FAA methodology to our system, reference geometries for ideal TBP and SP must be defined. For the ideal TBP, this is straightforward (Figure 3.7(a)).

However, there is some freedom in the choice of an ideal SP. There are two types of ideal SP: ${ }^{125,139}$ Carugo ${ }^{139}$ used a flat SP in which the trans basal L-M-L angle is $180^{\circ}$ and the angle between apical and basal positions is $90^{\circ}$ (Figure 3.7(b)); Bürgi used a so-called bent SP with $150^{\circ}$ for the trans basal L-M-L angle and $105^{\circ}$ between the apical and basal positions ${ }^{125 a}$ (Figure 3.7(c)). Both were tested for the systems in which we are interested.


Figure 3.7. Reference geometries for FAA analysis

My colleague Andrew Chalaturnyk and I wrote a program named "calcGeom" (written in Python; the code is listed in the section "Program" in the Appendix A) to assist with the analysis; 7-dimensional vectors were used for both TBP and SP. ${ }^{125 a}$ After screening through all available X-ray structures of $\mathrm{FeX}_{2}$ and $\mathrm{CoX}_{2}$ complexes of DIP type ligands, the results showed that all complexes were classified as distorted TBP if a flat SP was used as the reference geometry; if a bent SP was chosen as reference, all screened complexes were identified as distorted SP. The reason why this happens is that the large deviation from $180^{\circ}$ of the imine-metal-imine angle, enforced by ligand-backbone constraints, is the main contribution to the total distortion for all DIP complexes. In order
to make the FAA analysis meaningful and applicable to our system, a better choice of the reference geometries is to incorporate the constrained angles from the three coordinated nitrogen atoms in the reference geometries of both ideal TBP and flat SP, leaving the rest unchanged as shown in Figure 3.8. Thus, the geometries of reference TBP and SP are distorted, but the choice of them can be used to describe the main distortion difference among all DIP metal complexes I am interested in. The angle between the two constrained arms was chosen by averaging the corresponding cis-NMN angle (the angle formed by adjacent coordinating nitrogen atoms) over a total of 106 molecules of DIP iron and cobalt dihalide complexes which were either exported from the Cambridge Structural Database (CSD) ${ }^{140}$ or prepared by me for this work: $\mathrm{N}^{1} \mathrm{MN}^{2}=74.0^{\circ}, \mathrm{N}^{1} \mathrm{MN}^{5}=$ $148.0^{\circ}$.


Figure 3.8. Ideal TBP (left) and ideal SP (right) for DIP complexe

## Analysis

Using these modified reference geometries, all (DIP) $\mathrm{MX}_{2}$ (M: Fe, Co; X: F, Cl, Br, I) in the $\mathrm{CSD}^{140}$ or prepared by us were re-screened using our "calcGeom" program (for details, see Table A.1, Table A.2, and Table A. 3 in the Appendix). The statistical analysis
results are shown in Figure 3.9. They are consistent with a somewhat subjective identification based on visual inspection. For cobalt, $69 \%$ of 36 X-ray structures are classified as distorted TBP, while for iron, $77 \%$ of 70 X-ray structures are assigned as TBP. As many complexes analyzed contain 2,6-diisopropyl phenyl groups at imine nitrogen (which might lead to a steric bias in the distribution of these complexes), the geometry preference for iron or cobalt cannot be deduced based only on Figure 3.9.


Figure 3.9. Analysis of cobalt(II) halides and iron(II) halides by modified FAA analysis

### 3.5.2 Definition of a reaction coordinate

FAA does not specify any inter-conversion coordinate between TBP and SP. This is unfortunate because the ease of deformation of a certain metal complex from its local minima to other geometries (which may include the actual geometry in the active state) is important for understanding the relation between the structures of pre-catalysts and the resulting reactivities. After going through all X-ray structures of (DIP) $\mathrm{MX}_{2}(\mathrm{M}: \mathrm{Fe}, \mathrm{Co})$, visual inspection shows that the main variation is in the two chlorine positions relative to
the $\mathrm{N}_{3}$ plane, and in the movement of the metal center out of the $\mathrm{N}_{3}$ plane (see Figure 3.6). One possible description would be the net difference between the distances of the two chlorine atoms relative to the $\mathrm{N}_{3}$ plane (the plane defined by central pyridine ring and the two imine arms). However, this does not seem to work well because the two chlorine atoms are far away from the metal center. Even if distances of two chlorine atoms from the N 3 plane were same, the position of the metal center would not be uniquely defined, let alone angles around the metal center. Thus, we decided that analyzing the differences between angles around the metal center was a more reasonable way to quantify the distortion of the metal environment relative to the ideal situation. Therefore, this analysis strategy is independent of the metal ligand bond lengths. As the constraints of the two imine arms are similar among all complexes in which we are interested, the NMN angles are not considered and the focus will be on the changes of $\mathrm{N}(\mathrm{Py})-\mathrm{M}-\mathrm{X}$ angles (Scheme 3.3). The change from TBP to SP geometries for DIP metal dihalide complexes can be simply illustrated in Scheme 3.3: $\mathrm{MCl}_{2}$ unit tilts (A in Scheme 3.3), and at the same time, the metal moves up from $\mathrm{N}_{3}$ plane (B in Scheme 3.3). The repulsion between the N -aryl ring and the $\mathrm{MCl}_{2}$ unit is the main cause for the $\mathrm{MCl}_{2}$ unit to move out of the $\mathrm{N}_{3}$ plane (see top view in Scheme 3.3).


Scheme 3.3. Schematic changes of the geometry in: (A) TBP $\rightarrow$ SP deformation, (B) metal out-of-plane movement

The tilting of the $\mathrm{MCl}_{2}$ unit and the metal movement out of the $\mathrm{N}_{3}$ plane cannot be clearly separated, but they seem to follow each other well (see Figure A. 1 in the Appendix A). In order to describe the metal environment and concentrate on the main reaction coordinate for the conversion of TBP to SP, a two-angle criterion is introduced here; the angle difference between $N^{2}-\mathrm{M}-\mathrm{X}^{3}$ and $\mathrm{N}^{2}-\mathrm{M}-\mathrm{X}^{4}$ in Figure 3.8 is used to define a reaction path between TBP and SP for this specific system. Metal distortion out of the $\mathrm{N}_{3}$ plane as a function of $\omega$ is summarized in Figure A. 2 in the Appendix A; it shows that the tilting of the $\mathrm{MCl}_{2}$ is much more significant than the metal deviation from the $\mathrm{N}_{3}$ plane in terms of energy ${ }^{\text {XVIII }}$.

[^11]
### 3.5.3 Two-angle criterion

The larger of the two $\mathrm{N}(\mathrm{Py})-\mathrm{M}-\mathrm{X}$ angles is defined as $\alpha$ and the smaller one is defined as $\beta$ (Scheme 3.4). We propose to use $\omega=(\alpha-\beta) / 90$ as a parameter describing the interconversion. If $\omega$ is zero, we have "perfect" TBP; when $\omega$ is 1 , the structure is "perfect" SP (within the limitations imposed by the ligand framework). Using the $\omega$ criterion, the structures is assigned as TBP $(\omega<0.5)$ or $\mathrm{SP}(\omega>0.5)$. In contrast to the FAA classification, this $\omega$ criterion provides a reaction coordinate connecting TBP and SP structures.



Scheme 3.4. Illustration of two-angle criterion

This criterion was then applied to all structures previously analyzed by our modified FAA. For all structures except one, the $\omega$-based assignment corresponds to that using the modified FAA. The distributions of structures over $\omega$ values are plotted in Figure 3.10. (DIP)FeX ${ }_{2}$ structures are seen to cluster around $\omega$ values near 0.1 (preference for TBP
geometries) while the geometries of (DIP) $\mathrm{CoX}_{2}$ tend to spread over the whole $\omega$ space. Values close to $\omega=1$ ("flat SP") are rare.


Figure 3.10. Distribution of observed structures over $\omega$ values

### 3.5.4 Substituent effects

With a suitable reaction coordinate defined, how steric hindrance and electronic properties affect the preference for TBP or SP geometries was subsequently studied in
detail by analysis of representative X-ray structures (ligands $\mathbf{3}$ and 5-12, in Figure 3.11) and DFT computations (ligands 1-6, in Figure 3.11).



3





10



Figure 3.11. Structures of ligands explored for steric and electronic effects

## Analysis of X-ray structures

Structures of (3) $\mathrm{FeCl}_{2},{ }^{141} \quad$ (5) $\mathrm{CoCl}_{2},{ }^{16} \quad$ (5) $\mathrm{FeCl}_{2},{ }^{16} \quad$ (6) $\mathrm{FeCl}_{2},{ }^{52} \quad$ (11) $\mathrm{FeCl}_{2}{ }^{142}$ and (12) $\mathrm{FeCl}_{2}{ }^{143}$ were obtained from the CSD database, ${ }^{140}$ while ligands $\mathbf{7 , ~ 8 , ~ 9 , ~} \mathbf{1 0}$ and their corresponding metal dihalides and (3) $\mathrm{CoCl}_{2}$ complexes were prepared by me to obtain their X-ray structures.

## Synthesis of cobalt and iron dichloride complexes

The complex (3) $\mathrm{CoCl}_{2}$ can be easily obtained by reaction of $\mathrm{CoCl}_{2}$ with the free ligand in THF solvent or butanol (for more details about the preparation of $\mathrm{CoCl}_{2}$ complexes, see Section 1.9 in Chapter 1). A single crystal suitable for X-ray diffraction was obtained by slow evaporation of a dichloromethane solution, although the quality was poor (for the Xray structure, see Figure 9.1 in Chapter 9). However, the same recipe did not work for cobalt and iron complexes of ligand 7. As illustrated in Chapter $4,{ }^{144}$ ligand 7 with electron withdrawing $\mathrm{CF}_{3}$ groups at the imine carbons is a very weak $\sigma$-donor ligand. Thus the coordinating solvents used might compete with this ligand to coordinate to the metal center. Unfortunately, the reaction of the anhydrous metal chloride with 7 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was also unsuccessful. However, the reaction of 7 with $\mathrm{CoCl}_{2}(\mathrm{THF})_{1.5}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ generated the desired complex; the iron(II) chloride complex could be prepared in a similar manner. The success of this procedure is probably due to the fact that when THF is not the solvent, the coordinated $\mathrm{CoCl}_{2}(\mathrm{THF})_{1.5}$ will dissociate THF to generate the "naked" $\mathrm{CoCl}_{2}$ which can be captured by the free ligand. However, washing (7) $\mathrm{CoCl}_{2}$ with toluene seemed to release part of the ligand and produce some off-white powder, tentatively identified as $\mathrm{CoCl}_{2}$. Thus the complex is not very stable to dissociation into 2
and bulk $\mathrm{CoCl}_{2}$. X-ray structures of the corresponding iron and cobalt complex are shown in Figure 3.12 and Figure 3.13. The complex (7) $\mathrm{CoCl}_{2}$ co-crystallized with one molecule of dichloromethane, while (7) $\mathrm{FeCl}_{2}$ co-crystallized with toluene. The metal centers in both complexes have a distorted TBP environment with a small metal distortion from the $\mathrm{N}_{3}$ plane, similar to the corresponding complex of ligand 3.


Figure 3.12. X-ray structure of (7) $\mathrm{FeCl}_{2}$ (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms and co-crystallized toluene are omitted for clarity). Selected bond distances $(\AA)$ and angles (deg): $\mathrm{Fe}(1)-\mathrm{N}(1): 2.248(5) ; \mathrm{Fe}(1)-\mathrm{N}(2): 2.124(4) ; \mathrm{Fe}(1)-\mathrm{N}(3)$ : 2.267(5); $\mathrm{Fe}(1)-\mathrm{Cl}(1): 2.255(2) ; \mathrm{Fe}(1)-\mathrm{Cl}(2): 2.279(2) ; \mathrm{C}(2)-\mathrm{N}(1): 1.264(7) ; \mathrm{C}(2)-\mathrm{C}(3)$ : $1.478(8) ; \mathrm{C}(3)-\mathrm{N}(2): 1.335(7) ; \mathrm{C}(7)-\mathrm{N}(2): 1.345(7) ; \mathrm{C}(7)-\mathrm{C}(8): 1.493(8) ; \mathrm{C}(8)-\mathrm{N}(3):$ 1.284(7); $\mathrm{N}(1)-\mathrm{Fe}(1)-\mathrm{N}(2): 72.9(2) ; \mathrm{N}(2)-\mathrm{Fe}(1)-\mathrm{N}(3): 72.9(2) ; \mathrm{N}(1)-\mathrm{Fe}(1)-\mathrm{N}(3): 145.3(2)$; $\mathrm{N}(2)-\mathrm{Fe}(1)-\mathrm{Cl}(1): 136.01(14) ; \mathrm{N}(2)-\mathrm{Fe}(1)-\mathrm{Cl}(2): 116.35(14)$.


Figure 3.13. X-ray structure of (7) $\mathrm{CoCl}_{2}$ (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms and co-crystallized $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ have been omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): ): $\mathrm{Co}(1)-\mathrm{N}(1): 2.274(5) ; \mathrm{Co}(1)-\mathrm{N}(2): 2.047(4) ; \operatorname{Co}(1)-$ $\mathrm{N}(3): 2.249(5) ; \mathrm{Co}(1)-\mathrm{Cl}(1): 2.216(2) ; \mathrm{Co}(1)-\mathrm{Cl}(2): 2.245(2) ; \mathrm{C}(2)-\mathrm{N}(1): 1.278(7) ; \mathrm{C}(2)-$ $\mathrm{C}(3): 1.491(9) ; \mathrm{C}(3)-\mathrm{N}(2): 1.339(7) ; \mathrm{C}(7)-\mathrm{N}(2): 1.338(7) ; \mathrm{C}(7)-\mathrm{C}(8): 1.493(8) ; \mathrm{C}(8)-$ $\mathrm{N}(3): 1.272(7) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2): 74.9(2) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(3): 75.3(2) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(3):$ 149.3(2); $\mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{Cl}(1): 136.6(2) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{Cl}(2): 109.42(14)$.

Ligands (8-10) were prepared from 2,6-dibromopyridine through several steps (acylation, ${ }^{145}$ condensation, ${ }^{146} \mathrm{C}$-P coupling reaction and the oxidation by azide ${ }^{142}$ ); the representative synthesis of ligand $\mathbf{8}$ is shown in Scheme 3.5 (for the X-ray structure of ligand 8, see Figure 9.2 in Chapter 9).




Scheme 3.5. Synthesis of ligand 8

The corresponding complexes of $\mathrm{CoCl}_{2}$ and $\mathrm{FeCl}_{2}$ can be prepared according to the standard procedure for the DIP ligand. ${ }^{16} \mathrm{CoCl}_{2}$ complexes of ligands $\mathbf{8 - 1 0}$ have been prepared; however, only (10) $\mathrm{CoCl}_{2}$ formed X-ray quality crystals (Figure 3.14). X-ray structures of $\mathrm{FeCl}_{2}$ complexes for all three ligands $\mathbf{8 - 1 0}$ (see Section 9.1, experimental section for Chapter 3) could be obtained. Although the quality of the crystals of (8) $\mathrm{FeCl}_{2}$ (X-ray structure, see Figure 9.4) and (10)FeCl ${ }_{2}$ (X-ray structure, see Figure 9.3) was not high, it was sufficient to establish the connectivity of the atoms and allow FAA and $\omega$ analysis.


Figure 3.14. X-ray structure of (10) $\mathrm{CoCl}_{2}$ (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms omitted for clarity). Selected bond distances $(\AA)$ and angles (deg): $\mathrm{Co}(1)-\mathrm{N}(1): 2.311(2) ; \mathrm{Co}(1)-\mathrm{N}(2): 2.060(2) ; \mathrm{Co}(1)-\mathrm{N}(3): 2.109(2) ; \mathrm{Co}(1)-\mathrm{Cl}(1):$ 2.2550(6); $\mathrm{Co}(1)-\mathrm{Cl}(2): 2.2940(6) ; \mathrm{N}(1)-\mathrm{C}(68): 1.276(3) ; \mathrm{C}(11)-\mathrm{C}(68): 1.485(3) ; \mathrm{N}(2)-$ $\mathrm{C}(11): 1.339(3) ; \mathrm{N}(2)-\mathrm{C}(15): 1.337(3) ; \mathrm{C}(15)-\mathrm{P}(2): 1.824(2) ; \mathrm{N}(3)-\mathrm{P}(2): 1.598(2) ; \mathrm{N}(1)-$ $\operatorname{Co}(1)-\mathrm{N}(2): 73.39(6) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(3): 84.94(6) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(3): 157.10(6) ; \mathrm{N}(2)-$ $\mathrm{Co}(1)-\mathrm{Cl}(1): 135.03(5) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{Cl}(2): 100.96(5)$.

Analysis of selected $X$-ray structures
FAA and $\omega$ analysis results for the X-ray structures of selected iron dichloride and cobalt dichloride complexes are shown in Table 3.2.

Table 3.2. Analysis results for selected complexes

| Entry | Metal complex | FAA analysis <br> results | $\omega$ | Metal deviation <br> $(\AA)$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathbf{( 3 )}) \mathrm{CoCl}_{2}$ | TBP | 0.04 | 0.01 |
| 2 | $(\mathbf{3}) \mathrm{FeCl}_{2}$ | TBP | 0.14 | 0.09 |
| 3 | $(7) \mathrm{CoCl}_{2}$ | TBP | 0.30 | 0.20 |
| 4 | $(7) \mathrm{FeCl}_{2}$ | TBP | 0.22 | 0.16 |
| 5 | $(\mathbf{5}) \mathrm{CoCl}_{2}$ | SP | 0.64 | 0.56 |
| 6 | $(\mathbf{5}) \mathrm{FeCl}_{2}$ | SP | 0.59 | 0.56 |
| 7 | $\mathbf{( 1 0 )} \mathrm{CoCl}_{2}$ | TBP | 0.38 | 0.18 |
| 8 | $\mathbf{( 1 0 )} \mathrm{FeCl}_{2}$ | TBP | 0.44 | 0.17 |
| 9 | $(\mathbf{8}) \mathrm{FeCl}_{2}$ | SP | $0.67(0.76)^{\mathrm{a}}$ | $0.41(0.42)^{\mathrm{a}}$ |
| 10 | $\mathbf{( 9 )} \mathrm{FeCl}_{2}$ | SP | 0.66 | 0.44 |
| 11 | $\mathbf{( 1 1 )} \mathrm{FeCl}_{2}$ | TBP | $0.00(0.05)^{\mathrm{a}}$ | $0.05(0.11)^{\mathrm{a}}$ |
| 12 | $(\mathbf{6}) \mathrm{FeCl}_{2}$ | TBP | $0.35(0.14)^{\mathrm{a}}$ | $0.35(0.09)^{\mathrm{a}}$ |
| 13 | $\mathbf{( 1 2 )} \mathrm{FeCl}_{2}$ | TBP | 0.44 | 0.40 |

${ }^{\mathrm{a}}$ The data in parentheses correspond to the second molecule in the asymmetric unit of the crystal.

Increasing steric hindrance (entries 1-2, 5-10 and 12) or electron-withdrawing ability (entries 3-4 and 13) of substituents at the 2,6-positions of the N -aryl ring or the imine methyl position seems to stabilize the SP over the TBP geometry. Replacement of one imine arm by phosphinimine also seems to favour this geometry (entries 6 and 9), but induces smaller metal deviations from the $\mathrm{N}_{3}$ plane $(0.56 \AA$ in entry 6 vs $0.44 \AA$ in entry 9), probably due to the reduced constraint imposed by the phosphinimine arm. Replacement of both imine arms by less hindered phosphinimine favors the TBP geometry (entry 11). The question arises whether the geometries of the complexes are flexible, in other words, how significant is any particular geometry observed in a crystal structure? In the following section, this will be addressed by DFT calculations.

## DFT study of the TBP-SP inter-conversion

In order to study the structural rigidity of DIP complexes, we first used the two-angle coordinate to study the conversion of TBP to SP by fixing $\omega$ at 0.11 intervals and fully optimizing all other structural parameters. ${ }^{147}$ Ligands 1-6 in Figure 3.11 and their $\mathrm{CoCl}_{2}$ and $\mathrm{FeCl}_{2}$ complexes were used to analyze the electronic and steric effects on this reaction path, and results are shown in Figure 3.15..


Figure 3.15. Deformation curves for (A) $\mathrm{FeCl}_{2}$ and (B) $\mathrm{CoCl}_{2}$ complexes of DIP ligands(electronic energy, $\mathrm{kcal} / \mathrm{mol}$, calculated at $\mathrm{b} 3-\mathrm{lyp} / \mathrm{TZVP} / / \mathrm{b} 3-\mathrm{lyp} / \mathrm{SV}(\mathrm{P})$ ).

For $\mathrm{CoCl}_{2}$, the energy ranges for geometry changes from ideal TBP to SP are within 5.5 $\mathrm{kcal} / \mathrm{mol}$ for ligands $\mathbf{1 - 5}$. For $\mathrm{FeCl}_{2}$, the range of energies is slightly higher ( $\sim 6.5$ $\mathrm{kcal} / \mathrm{mol})$. For complexes with unsubstituted DIP (1: $\mathrm{Ar}=\mathrm{Ph}$ ), TBP is preferred for both metals with a very flat PES (the changing of $\omega$ from 0 up to 0.75 only requires 3 $\mathrm{kcal} / \mathrm{mol}$ ). Substituents at the 2,6 -positions of the N -aryl rings will make TBP less favourable due to repulsion between these substituents and the halides at the metal. One interesting thing is the effect of fluorine atoms at the 2,6-positions of the N -aryl group. As the fluorine atom is not much larger than the hydrogen atom, we would not expect large steric effects, and the electronic effect should dominate. Comparing the plots for complexes of ligand $\mathbf{1}$ in Figure 3.15 with those for difluorinated 4 complexes reveals that replacing the 2,6-hydrogen atoms by fluorine stabilizes the SP geometry relative to the TBP geometry by a few $\mathrm{kcal} / \mathrm{mol}$. One possible interpretation of this "fluorine effect" is electrostatic repulsion between the fluorine atoms and the metal-bonded chlorine atoms.

Comparison of the deformation curves in Figure 3.15 with the $\omega$ distributions in Figure 3.10 and the X-ray analysis results in Table 3.2 suggests that experimentally, (DIP) $\mathrm{MCl}_{2}$ structures are on average more TBP-like than predicted by our calculations (calculated local minima fall mostly around $\omega=0.6$ ). Because of the small energy cost for the whole distortion, individual variations might be due to crystal-packing effects, ${ }^{\text {XIX }}$ but a
${ }^{\text {XIX }}$ A possible way to assess the crystal packing effect is to compare the structures in solution with that in the solid state. Although it seems simple, the main difficulty is to
systematic difference would not be expected. A closer look at the X-ray structures reveals that many complexes show short contacts of halides with e.g. pyridine H 4 atoms or cocrystallized solvent molecules (water, dichloromethane, ether) and such interactions might be systematically more difficult to achieve for the axial halide in SP geometries, biasing solid-state structures toward TBP geometries.

However, it is also possible that the b3-lyp hybrid functional we have used exaggerates the non-bonded repulsions between aryl substituents and halides, hence biasing the calculations toward the SP geometry. ${ }^{148}$ Nevertheless, the predicted trends toward SP geometries for increased substituent size seems to be reflected in the solid-state structures, and the spread in $\omega$ values for observed structures confirms the small energy difference between TBP and SP geometries.

### 3.5.5 Metal effects

The small energy difference caused by substituents prompted us to explore the influence of the number of 3d electrons at the metal center, since preferred coordination geometries are often found to depend strongly on the valence electron count. For example, for 4coordinate complexes, low-spin $\mathrm{d}^{8}$ electronic configurations lead to square planar geometries while $\mathrm{d}^{10}$ configurations favor tetrahedral coordination. ${ }^{125 b, 149}$ Figure 3.16
obtain a 3-dimensional structure of the complex in solution. As far as I know, there is no such method that can provide angle information accurate enough to be useful.
shows the calculated deformation curves of complexes (3) $\mathrm{MCl}_{2}$ (M: first row transition metal) in their high-spin states.


Figure 3.16. Deformation curves for (3) $\mathrm{MCl}_{2}$ complexes. (M: first row transition metal, electronic energy, $\mathrm{kcal} / \mathrm{mol}$, calculated at b3-lyp/TZVP//b3-lyp/SV(P))

As the PES in Figure 3.16 indicate, all metals except $\mathrm{CuCl}_{2}$ prefer TBP or intermediate geometries. It is best to start with zinc, for its 3 d shell is fully filled and electron transfer from metal to ligand is not expected. The curve is quite flat on the TBP side with a minimum at $\omega$ of 0.4 , and it costs only $1 \mathrm{kcal} / \mathrm{mol}$ for $\omega$ to reach either 0 or 0.6 . This can be considered as the intrinsic geometry preference for transion metals without unpaired d electrons or unfilled d orbitals. $\mathrm{Mn}^{2+}$, with a half-filled 3d shell, shows a similar trend. The $\mathrm{Cr}^{2+}, \mathrm{Fe}^{2+}, \mathrm{Co}^{2+}$ and $\mathrm{Ni}^{2+}$ curves are close to each other, with SP around $1 \mathrm{kcal} / \mathrm{mol}$
higher than TBP. However, $\mathrm{Cu}^{2+}$ shows a completely opposite trend, ${ }^{\mathrm{XX}}$ with the minimum located at $\omega \approx 0.8$, which is also consistent with X-ray structure analysis (12 out of 19 Cu complexes prefer the SP geometry). A closer look at the geometry shows a significant difference between the apical and equatorial copper-chlorine bonds (in the DFT structure: apical $\mathrm{Cu}-\mathrm{Cl}=2.326 \AA$, equatorial $\mathrm{Cu}-\mathrm{Cl}=2.206 \AA$ ), which is expected for $\mathrm{d}^{9}$ metal centers due to the distortion ${ }^{\mathrm{XXI}}$ that is similar to the idea behind Jahn-Teller distortion.

### 3.6 Extension to (DIP)FeR $\mathbf{R}_{2}$ complexes

As we know, DIP metal alkyl complexes are possible intermediates in the activation of (DIP) $\mathrm{FeCl}_{2}$ and (DIP) $\mathrm{CoCl}_{2}$ complexes in ethylene polymerization reactions. ${ }^{150} \mathrm{We}$ therefore also wanted to analyze the corresponding five-coordinate DIP metal dialkyl complexes by modified FAA and our two-angle criterion.

Unfortunately, there are not a lot of relevant data in the CSD; only four pentacoordinate (DIP) $\mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ complexes (DIP: ligands $\mathbf{3}, \mathbf{5}, \mathbf{1 3}, 14$ in Figure 3.17) can be found and were extracted from CSD. One additional complex (Pybox)Fe( $\left.\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ (Pybox: ligand 15 in Figure 3.17), was prepared by me according to a procedure for the

[^12]preparation of (3) $\mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ reported by Cámpora. ${ }^{151}$ Both modified FAA and the two-angle criterion indicate them to be distorted TBP (see Table A. 1 and Table A. 2 in the Appendix A and Table 3.3).


3


13


5




15

Figure 3.17. Structures of DIP ligands in $\mathrm{FeR}_{2}$ complexes

Table 3.3. Analysis results of two-angle criterion and values of the metal deviation

| Name $^{\mathrm{a}}$ | $\omega$ | Metal dev $(\AA)$ | Catalytic activity $^{\mathrm{b}}$ |
| :---: | :---: | :---: | :---: |
| $\mathbf{( 5 )} \mathrm{FeR}_{2}$ | 0.36 | 0.54 | Highly active |
| $(\mathbf{1 4}) \mathrm{FeR}_{2}$ | 0.34 | 0.43 | active |
| $(\mathbf{3}) \mathrm{FeR}_{2}$ | 0.32 | 0.50 | active |
| $(\mathbf{1 3}) \mathrm{FeR}_{2}$ | 0.00 | 0.01 | No data ${ }^{\mathrm{c}}$ |
| $(\mathbf{1 5}) \mathrm{FeR}_{2}$ | $0.02(0.05)$ | $0.00(0.05)$ | Not active |
| a: $\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}$. b: ethylene polymerization. c: active in acrylate polymerization. ${ }^{\text {. }}$. |  |  |  |

Compared with the $\mathrm{FeCl}_{2}$ complexes, $\mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ complexes have a higher tendency to adopt TBP geometries while the metal deviation from the $\mathrm{N}_{3}$ plane is same as that in the dichlorides. As the $\mathrm{Fe}-\mathrm{C}$ bond is shorter than the $\mathrm{Fe}-\mathrm{Cl}$ bond, the alkyl is closer to the $\mathrm{N}_{3}$ plane. The shift from SP to TBP by changing ligands from chlorine to alkyl groups is probably due to the larger size of the metal-bound alkyl ligands and the stronger repulsion with the N -aryl rings.

The Fe complexes of ligands in Figure 3.17 show different catalytic activity in polymerizations. Fe complexes of ligands 3, 5, $\mathbf{1 4}{ }^{152}$ are active in ethylene polymerization, while there is no activity for ligand 15 complex, although (13) $\mathrm{FeCl}_{2}{ }^{153}$ showed some activity in acrylate polymerization. Table 3.3 shows that the most active ethylene polymerization catalyst (5) $\mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ has the largest metal deviation from $\mathrm{N}_{3}$ plane, but whether there is a direct correlation can not be interpreted from our results.

### 3.7 Relation between geometries and catalytic activity

The DFT study on the conversion between TBP and SP and the structure analysis on representative X-ray structures clearly showed that sterically bulky ligands seem to induce deformation to the SP geometry and increase metal displacement out of the $\mathrm{N}_{3}$ plane. Although metal complexes with higher steric hindrance show higher catalytic activity, the geometries of these complexes do not seem to be very important to their reactivity because deformation over a wide range of geometries was calculated to be quite easy. The observed higher reactivity in ethylene polymerization by sterically bulky
ligands is probably due to the fact that steric bulk can protect the metal center against side reactions (e.g. disproportionation to $L_{2} \mathrm{M}$ complexes) ${ }^{66}$ and prevent $\beta$-hydrogen transfer $(\mathrm{BHT})^{67}$.

### 3.8 Conclusions

Structures of five-coordinate cobalt dichloride and iron dichloride with DIP type ligands were analyzed by modified FAA analysis and a new two-angle criterion $\omega$ was devised based on the path for conversion of TBP to SP. Overall energy costs for the conversion from TBP to SP are small for $\mathrm{FeCl}_{2}$ and $\mathrm{CoCl}_{2}$. The number of d electrons at the metal center does not significantly affect the geometric preference of first-row transition-metals in their high spin states, except for $\mathrm{CuCl}_{2}$. Extension to metal dialkyl complexes shows that precursors to the catalysts active in ethylene polymerization tend to have a larger metal deviation from $\mathrm{N}_{3}$ plane.

# Chapter 4. DFT study on properties of Diiminepyridine (DIP) type ligands 

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In homogeneous catalysis, the catalyst plays a key role in the whole catalytic process and the selectivity of products formed. A change of the ligand skeleton will sometimes result in complete loss of catalytic activity or in the formation of completely different products. It seems logical to assume that there might be a correlation between ligand properties and properties of the resulting metal complexes, and this has led to the generation of parameters to quantify ligand properties. Conversely, the ligand parameters obtained can be further used to study the properties of the complexes and their catalytic reactions:

1) to probe the reaction mechanisms of organometallic reactions. ${ }^{154}$ By correlation of the reaction rate with the ligand parameters, mechanisms can in favourable cases be discriminated based on the theory that ligand effects on different mechanisms are different.
2) to predict the properties of the resulting complexes such as stability or the redox potential.
3) as a guideline to design new catalysts and predict their properties.

Among all possible applications of ligand parameters, the most important use of ligand parameters is in their predictive ability, when a catalyst needs to be optimized or a new ligand needs to be made. On the one hand, if a certain variation has been predicted to decrease the catalytic activity, there is little need to make the ligand or spend more time on it. On the other hand, based on the correlation of ligand parameters with the properties of the reaction, one parameter might be the main contributor to catalyst performance and optimization of the catalyst can use this as a guideline.

The most significant achievement in quantifying ligand properties was the development of the Tolman parameters, ${ }^{155}$ which apply mainly to monophosphine ligands, although they can be extended to bisphosphine ligands. ${ }^{156}$ After this, a variety of strategies to further decompose Tolman electronic parameter into several contributors or to describe the steric hindrance effects of bisphosphine or other ligands were developed. Among them, the most accurate method is QALE (quantitative analysis of ligand effects) developed by Giering and coworkers, ${ }^{157}$ which is based mainly on the assumption that various properties of a complex (thermodynamic properties and catalytic performance) can be expressed as a linear combination of stereoelectronic parameters of the ligands involved. The main theory behind these strategies is similar to the linear free energy relation (LFER) explained below.

### 4.1 Tolman Parameters

Quantification of ligand properties can be traced back to Tolman, who used two parameters to characterize monophosphine ligands: ${ }^{155}$ one electronic parameter $(\chi)^{158}$ and one steric parameter ( $\theta$, cone angle). For the electronic parameter $\chi$, Tolman and coworkers took the difference between the $\mathrm{A}_{1}$ carbonyl stretching frequency of $\mathrm{LNi}(\mathrm{CO})_{3}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and $2056.1 \mathrm{~cm}^{-1}$ (the frequency when $\mathrm{L}=$ tri- $t$-butylphosphine). The steric parameter $\theta$ was measured mechanically from space-filling (or CPK) molecular models using a protractor (Figure 4.1, left). For ligands with some flexibility, substituents are folded back to minimize the subtending cone while three-fold symmetry at the phosphorous atom is maintained.

(a)

(b)
(reproduced with permission from the paper (Tolman, C.A. J. Am. Chem. Soc. 1970, 92, 2956). Copyright (1970), American Chemical Society)

Figure 4.1. (a) Ligand angle measuring device, (b) the ligand cone

The advantage of the Tolman method is that it is rapid and convenient. The disadvantage is that there is only one electronic parameter, which is not always enough to completely describe the interaction between the metal and the coordinating ligands. In addition, some types of ligands simply do not form stable $\mathrm{LNi}(\mathrm{CO})_{3}$ complexes.

### 4.2 Linear free energy relation

A linear free energy relation is intended to quantitatively correlate equilibrium or reactivity with structure. ${ }^{159 \mathrm{a}}$ Quantification of substituent effects is very useful in terms of understanding reaction mechanisms, improving current catalysts or devising new ones. A good example of the application of LFER is the use of Hammett parameters. in organic chemistry. ${ }^{159 b-c}$ Parameters $\sigma_{p}$ (to describe para substituent effects) and $\sigma_{m}$ (to describe meta substituent effects) were defined using the ionization of benzoic acid as the model reaction (Scheme 4.1).


Scheme 4.1. Definitions of Hammett parameters. $\left(\mathrm{K}_{\mathrm{H}}\right.$ is the ionization constant for benzoic acid and $\mathrm{K}_{\mathrm{X}}$ is the ionization constant for substituted benzoic acid).

### 4.3 QALE

As an extension of Tolman parameters (electronic $(\chi)$ and steric $(\theta)$ effects), quantitative analysis of ligand effects (QALE) ${ }^{157}$ developed by Giering ${ }^{160}$ and coworkers works surprisingly well in a variety of reactions and has been successfully applied in the generation of ligand parameters for monophosphines and extension to other central atoms.

During the development of QALE, the electronic parameter $\chi$ of Tolman was decomposed into three main components:

1) $\chi_{d}$ is used to describe the $\sigma$-donor ability of phosphine ligands (a small value means a good $\sigma$-donor);
2) $\pi_{p}$ is a measure of the $\pi$-acceptor property (a large value means a strong $\pi$ acceptor);
3) $E_{a r}$ is used to evaluate the " $E_{a r}$ effect", ${ }^{160}$ which originally denoted the aryl effect due to the big difference in behaviour between aryl and alkyl substituents, but was later extended to phosphite and $\mathrm{PCl}_{3}$ ligands.

Apart from these, they found that steric effects did not change beyond a certain cone angle, and introduced a steric threshold and a $\lambda$ variable to trigger the steric effect. With these modifications, the final equation for describing the properties as a function of ligand parameters becomes:

$$
\begin{equation*}
\text { Property }=\mathrm{a}\left(\chi_{\mathrm{d}}\right)+\mathrm{b}\left(\theta-\theta_{\mathrm{st}}\right) \lambda+\mathrm{c}\left(\mathrm{E}_{\mathrm{ar}}\right)+\mathrm{d}\left(\pi_{\mathrm{p}}\right)+\mathrm{f} \tag{Eq. 4.1}
\end{equation*}
$$

Where,

$$
\lambda\left\{\begin{array}{l}
=1 \text { when } \theta>\theta \text { st. Property }=a\left(\chi_{d}\right)+b\left(\theta-\theta_{s t}\right)+c\left(E_{a r}\right)+d\left(\pi_{p}\right)+f \\
=0 \text { when } \theta<\theta \text { st. Property }=a\left(\chi_{d}\right)+c\left(E_{a r}\right)+d\left(\pi_{p}\right)+f^{161}
\end{array}\right.
$$

However, when $\mathrm{PZ}_{3-\mathrm{i}} \mathrm{H}_{\mathrm{i}}$ type ligands were used, fits for phosphines with different numbers of hydrogens were unsatisfactory. In order to accommodate this situation, another variable i was introduced to denote the number of hydrogen substituents; the modified equation is:

$$
\begin{equation*}
\text { Property }=\mathrm{a}\left(\chi_{\mathrm{d}}\right)+\mathrm{b}\left(\theta-\theta_{\mathrm{st}}\right) \lambda+\mathrm{c}\left(\mathrm{E}_{\mathrm{ar}}\right)+\mathrm{d}\left(\pi_{\mathrm{p}}\right)+\mathrm{ei}+\mathrm{f} \tag{Eq. 4.2}
\end{equation*}
$$

All parameters in the above equations can be obtained by graphical analysis and linear regression on the known properties. The coefficients (a, b, c, d, e, f) for each equation (or
property) indicate how sensitive the property is to the substituent parameter, and are generated at the same time. As a result, they are further used to obtain ligand parameters for new ligands or predict their properties. There are several things which need to be addressed about the generation of these parameters.

Firstly, the definition of $\chi_{\mathrm{d}}$ used in Eq. 4.1 is different from the original definition of Tolman for $\chi$ :

1) for common trialkyl phosphines and triaryl phosphines, it is same as the Tolman $\chi$ parameter using the following equation reported by Bartik: ${ }^{162}$

$$
\chi_{\mathrm{PX} 3}=v(\mathrm{CO})\left(\mathrm{A}_{1}\right)-2056.1 \mathrm{~cm}^{-1}
$$

where, $v(\mathrm{CO})\left(\mathrm{A}_{1}\right)$ is the A 1 carbonyl stretching frequency for $\mathrm{LNi}(\mathrm{CO})_{3}$
2) for mixed alkyl-aryl phosphine ligands, $\chi_{d}$ is obtained by studying $E^{0} / T$ of the following reaction:

$$
\mathrm{Cp}(\mathrm{CO})(\mathrm{L}) \mathrm{Fe}(\mathrm{COMe})^{+}+\mathrm{e} \rightleftharpoons \mathrm{Cp}(\mathrm{CO})(\mathrm{L}) \mathrm{Fe}(\mathrm{COMe})
$$

From the plot of $\mathrm{E}^{\circ} / T$ versus $1 / \mathrm{T}, \Delta \mathrm{H}^{0}$ (the slope) and $\Delta \mathrm{S}^{\circ}$ (the intercept) can be obtained.
With all these data, $\chi_{\mathrm{d}}$ can be generated by projecting $\Delta \mathrm{H}^{\circ}$ onto the calibration curve of $\Delta \mathrm{H}^{0}$ versus $\mathrm{Z}_{3}$ (a linear combination of $\chi$ and $\theta$ ) calibrated by two ligands $\left(\mathrm{PMe}_{3}\right.$ and $\left.\mathrm{PPh}_{3}\right) .{ }^{163}$

For both above two types of phosphines, $\chi_{\mathrm{d}}$ can also be obtained by linear regression from the $\mathrm{pK}_{\mathrm{a}}$ value: ${ }^{161}$

$$
\chi_{\mathrm{d}}=1.47 \mathrm{pK}-0.069 \theta+27.8
$$

3) for phosphite ligands, $\chi_{d}$ was generated by linear regression on five properties: pKa values, ionization potentials (IP) for $\mathrm{PZ}_{3}, v_{c o}$ for $\eta-\mathrm{Cp}(\mathrm{CO})\left(\mathrm{PZ}_{3}\right) \mathrm{Fe}(\mathrm{COMe})^{0}$ and $\mathrm{E}^{0}$ $(229 \mathrm{~K})$ and $\Delta \mathrm{H}^{0}$ for the $\eta-\mathrm{Cp}(\mathrm{CO})\left(\mathrm{PZ}_{3}\right) \mathrm{Fe}(\mathrm{COMe})^{+/ 0}$ couple. Together with the generation of the $\chi_{d}$ value, this also generates $\mathrm{E}_{\mathrm{ar}}$ and $\pi_{\mathrm{p}}$ parameters for this type of ligand.

Secondly, the steric parameter $\theta$ was taken as the Tolman cone angle but with a threshold $\theta_{\text {st }}$. The threshold $\theta_{\text {st }}$ for each specific property can be obtained by plotting the property against $\theta$ values: the cone angle corresponding to the break in the curve will be the threshold value. ${ }^{161}$

Thirdly, $\pi_{\mathrm{p}}$ was introduced to describe phosphite ligands since there is a significant $\pi$ effect in phosphites compared to that in trialkylphosphine ligands. ${ }^{164}$

Finally, the parameter $\mathrm{E}_{\mathrm{ar}}{ }^{165}$ was introduced as an ad-hoc correction for aryl phosphines: it depends only on the number of aryl groups attached to the central phosphorous atoms. Values of $0,1.0,2.0,2.7$ are assigned to $\mathrm{E}_{\text {ar }}$ of phosphines containing zero, one, two and three aryl groups, respectively. Later on, it was found that better fits for $\mathrm{PCl}_{3}$ and phosphites were obtained by assigning their ligands non-zero $\mathrm{E}_{\text {ar }}$ values. $\mathrm{E}_{\mathrm{ar}}$ can be generated as the co-products of regression for generating the $\chi_{\mathrm{d}}$ for phosphite ligands. Normally, it is included in situations where $\chi$ and $\theta$ are not sufficient to describe the electronic effects of ligands.

In all, the central principle of QALE is to use ligand parameters to fit properties. These properties can be metal-phosphine bond length, vibration of carbon monoxide in metal
complexes, the enthalpy of the ligand-displacement reaction, ${ }^{13} \mathrm{C}$ NMR shifts etc. When the property can not be expressed well by existing parameters, a new parameter can be introduced ${ }^{\mathrm{XXII}}$. These parameters, especially $\chi$ and $\pi$, can be scaled to apply to donor groups in such as sulphides, ${ }^{166}$ silyls, ${ }^{167}$ nitriles, ${ }^{168}$ amines, arsines, carbenes ${ }^{168}$ and so on. ${ }^{160,169}$ However, it seems that QALE can not be used to compare the properties of a phosphine ligand and a ligand with a significantly different skeleton such as a monocarbene, as there is no well-defined way to determine the cone angle of a monocarbene. In addition, to generate the ligand parameters, a variety of experimental data are required. This is a problem if we want to apply QALE to other types of ligands because, for ligands other than monophosphines, there are usually not enough experimental data available.

### 4.4 Introduction to Diiminepyridine ligands

Diiminepyridine ligands are unique in ethylene polymerization and have attracted a variety of researchers. ${ }^{170}$ Although the original ligands work well, modifications of the original structure have not led to significant improvement of the catalyst (see also Chapter 1 for more details). On the contrary, nearly all non-trivial modifications virtually kill catalyst activity. We believe that quantifying the $\sigma$-donor ability and $\pi$-acceptor ability of the DIP type ligand can be a good starting point for explaining this observation.

XXII The choice of this new parameter is not random. After analysis of the possible effects in the new system, the new parameter is introduced, to describe a reasonable effect that exists in the new system.

On the one hand, although QALE is a good method for the separation of $\sigma$-donor, $\pi$ acceptor and steric properties of monophosphines, ${ }^{171}$ the application of QALE to diiminepyridine ligands is problematic. First, in order to generate the $\sigma$-donor parameter as in QALE, the ligand pKa is required. However, there are three nitrogen centers in DIP ligands: it is not even clear which pKa should be used. Similar arguments apply to the other parameters required by QALE: $\theta, \mathrm{E}_{\mathrm{ar}}, \pi_{\mathrm{p}}$. Additionally, there is a big difference between the conformation of the free DIP ligand and that in a coordinated state. Thus the protonation might lead to a conformation that is not relevant to the coordination chemistry. On the other hand, use of the original Tolman $\chi$ parameter ( $v_{\mathrm{CO}}$ of a ligand nickel carbonyl complex) for DIP ligands can also be problematic because the DIP ligand is tridentate and flat, while monophosphine ligands in the Tolman approach are monodentate. As four-coordinate nickel(0) complexes prefer tetrahedral geometry, (DIP)Ni(CO) will be quite unstable. Even if (DIP)Ni(CO) complexes could be prepared, the nickel center will adopt square planar geometry instead of tetrahedral geometry in Tolman's (phosphine) $\mathrm{Ni}(\mathrm{CO})_{3}$ reference complexes anyway. ${ }^{\text {XXIII }}$ Finally, similarly to the Tolman approach, a stretching frequency of a square planar (DIP)M(CO) complex (M: transition metals) can be used to measure the properties of these tridentate ligands, but this approach produces only a single parameter. As we are interested in separating $\sigma$ donor and $\pi$-acceptor properties, this approach will not be very useful.
xxIII The IR frequency from the square planar (DIP)Ni(CO) will be hard to compare with those in tetrahedral $\mathrm{LNi}(\mathrm{CO})_{3}$ complexes.

The alternative method of separating metal-ligand interaction energies for each complex into $\sigma$ - and $\pi$-components by identifying the corresponding interacting orbitals can also be problematic in our system, although this method works well in monophosphine and carbon monoxide complexes. ${ }^{172}$ The key reason is that many of the DIP complexes that we want to study have only $C_{1}$ symmetry and hence show no clean separation between orbitals involved in donation and back-donation interactions.

Due to the reasons cited above, we here try to design a new strategy, conceptually close to LFER, to quantify the ability of DIP-type ligands to stabilize metal fragments.

### 4.5 Principle of ligand-parameter determination

### 4.5.1 Definitions

## Binding energy

The binding energy of a ligand L (to a metal-containing fragment F ) in its lowest energy state relative to the reference ligand $L^{\prime}$ in its lowest energy state can be defined as the overall change in electronic energy of the following Eq. 4.3.

$$
\mathrm{L}+\mathrm{L}^{\prime} \mathrm{F} \rightarrow \mathrm{LF}+\mathrm{L}^{\prime} \quad \Delta \mathrm{E}_{\text {bind }}(\mathrm{F}, \mathrm{~L})
$$

## Reorganization energy

Although conformations of DIP metal complexes are not flexible, free DIP ligands have a variety of conformations. Among them, three typical local minima with different
arrangements of the two arms are highly relevant to the coordination of DIP ligands to the metal centers, as shown in Figure 4.2.


Figure 4.2. Structures of three local minima of the reference DIP ligand

The closed geometry ( NCCN torsion angles close to $0^{\circ}$ ) is the pre-organized conformation for coordination to metal centers, while the extended geometry (NCCN torsion angles close to $180^{\circ}$ ) is the lowest in energy. Thus the energy cost for the conversion from the extended to the closed conformation should probably not be counted as a contribution to the stabilization of the metal center. Therefore, this energy difference is assigned as the reorganization energy ${ }^{173}$ of the ligand, denoted as $\Delta \mathrm{E}_{\text {reorg }}(\mathrm{L})$ relative to that of reference ligand $L^{\prime}$ (the more negative, the easier for a ligand to reorganize) and the net binding energy of ligands in their lowest energy state of equation Eq. 4.3 can be written as Eq. 4.4.

$$
\begin{equation*}
\Delta \mathrm{E}_{\text {bind }}(\mathrm{F}, \mathrm{~L})=\Delta \mathrm{E}_{\text {reorg }}(\mathrm{L})+\Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{~L}) \tag{Eq. 4.4}
\end{equation*}
$$

Here, $\Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{L})$ is the relative "stabilization energy" of F by L , which will be the main concern of this chapter.

## Stabilization energy

We assume that the above stabilization energy can be written or approximated as a linear energy expression in Eq. 4.5:

$$
\begin{equation*}
\Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{~L})=\alpha_{\mathrm{F}} \sigma_{\mathrm{L}}+\beta_{\mathrm{F}} \pi_{\mathrm{L}} \tag{Eq. 4.5}
\end{equation*}
$$

- $\alpha_{\mathrm{F}}$ depends on the metal fragment F , measuring its Lewis acidity (the ability to accept electrons from a ligand through $\sigma$-interactions)
- $\quad \beta_{\mathrm{F}}$ depends on the metal fragment F , measuring its $\pi$-basicity (the ability to donate electrons to a ligand through $\pi$-interactions)
- $\sigma_{L}$ depends on the ligand $L$, representing its $\sigma$-donation ability
- $\pi_{\mathrm{L}}$ depends on the ligand L , representing its $\pi$-acceptor ability

With this definition, the more negative $\Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{L})$, the more stable the corresponding complex of the ligand relative to the reference ligand $\mathrm{L}^{\prime}$.

### 4.5.2 Generation of parameters

As Eq. 4.5 shows, there is only one $\Delta \mathrm{E}_{\text {stab }}$ for any combination of F and L but four parameters $\left(\alpha_{\mathrm{F}}, \beta_{\mathrm{F}}, \sigma_{\mathrm{L}}, \pi_{\mathrm{L}}\right)$. In order to obtain these four variables, one simple approach is to use two reference metal fragments to define a scale for metal parameters and one reference ligand to set the reference point for other ligand parameters. After two reference fragments $\mathrm{F}\left(\mathrm{F}_{1}\right.$ and $\left.\mathrm{F}_{2}\right)$ and their $\alpha_{\mathrm{F}}$ and $\beta_{\mathrm{F}}$ values were chosen, $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ for all other ligands referenced to the standard ligand ( $\mathrm{L}^{\prime}$ ) will be completely determined by calculating their $\Delta \mathrm{E}_{\text {stab }}$ with $\mathrm{F}_{1}$ and $\mathrm{F}_{2}$ and fitting to Eq. 4.5. Thus, parameters for any new ligand can be generated simply by calculating its $\Delta \mathrm{E}_{\text {stab }}$ for two reference metals.

### 4.6 Results and Discussion

### 4.6.1 Choice of metal fragments

The choice of reference fragments and their $\alpha_{\mathrm{F}}$ and $\beta_{\mathrm{F}}$ values is, in a sense, arbitrary. However, we wish to choose them such that the resulting $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ parameters represent $\sigma$-donation and $\pi$-back donation. Ideally we want one "pure $\sigma$-acid" fragment F , for which we set $\alpha(\mathrm{F})=1, \beta(\mathrm{~F})=0$, and one "pure $\pi$-base" fragment F , which has $\alpha(\mathrm{F})=0$ and $\beta(\mathrm{F})=1$. In practice, it does not quite work like that.

As for probing the $\sigma$-donation interaction, the fragment $\mathrm{ZnCl}_{2}$ is a good choice due to the $\mathrm{d}^{10}$ character of $\mathrm{Zn}^{2+}$ (which means donation of d electrons from $\mathrm{Zn}^{2+}$ to the ligand will not be significant). For selected ligands (the same set of ligands also used to generate metal parameters for first-row transition metals; see Section 4.6.6), comparison with the $\mathrm{MgCl}_{2}$ fragment (where one could never have back-donation) is shown in Figure 4.3. The high correlation further supports the eligibility of the $\mathrm{ZnCl}_{2}$ fragment as the probe for $\sigma$ donation interactions.


Figure 4.3. $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{MgCl}_{2}\right)$ vs $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZndCl}_{2}\right)$ with 10 selected ligands. (for structures of ligands, see Figure 4.7; linear correlation coefficient: $\rho=0.989$ )

However, as for probing the $\pi$-acceptor interaction, it is hard to find suitable metal fragments which show only $\pi$-basicity without Lewis acidity. Thus, we are forced to select a fragment with strong $\pi$-basicity but non-negligible Lewis acidity. In (DIP)CoMe systems, there is strong back donation from the cobalt(I) center to the DIP ligand skeleton. ${ }^{83,174}$ Thus we decided to first explore how the stabilization energies of $\mathrm{ZnCl}_{2}$ and CoMe change as a function of the substituents to see whether these two metal fragments can probe $\sigma$-donation and $\pi$-acceptor interactions differently.

Figure 4.4 shows the substituent effects at the 4 -position of the pyridine ring (ligands 2-7 in Figure 4.7) plotted against Taft $\sigma_{\mathrm{p}}$ and $\sigma_{\mathrm{p}}{ }^{-}$parameters. ${ }^{175}$ As the Figure shows, the substituent effects on the stability of $\mathrm{ZnCl}_{2}$ and CoMe are quite different. For $\mathrm{ZnCl}_{2}$, the presence of electron-donating groups increases the complex stability while electronwithdrawing groups result in destabilization. In contrast, for the CoMe fragment, electron-withdrawing groups stabilize the complex while electron-donating groups have the opposite effect. Therefore, $\sigma$-donation is more important for $\mathrm{ZnCl}_{2}$ fragments, and $\pi$ back-donation provides the dominant contribution to the metal-ligand binding for the CoMe fragment. ${ }^{\text {XXIV }}$

[^13]

Figure 4.4. Effect of pyridine 4-substituent on stabilization energies of the complexes of $\mathrm{ZnCl}_{2}(■, \rho=0.988$, $)$ and $\operatorname{CoMe}(\uparrow, \rho=-0.983)$ fragment, plotted against Taft $\sigma_{\mathrm{p}}$ and $\sigma_{\mathrm{p}}{ }^{-}$ parameters ${ }^{175}$

Secondly, Figure 4.5 (ligands $\mathbf{8 - 1 3}$ in Figure 4.7) shows the substituent effects at the 4position of the N -aryl rings. The range of energies covered in Figure 4.5 is much smaller than that in Figure 4.4 (range of energy change is $13 \mathrm{kcal} / \mathrm{mol}$ in Figure 4.4 and 6 $\mathrm{kcal} / \mathrm{mol}$ in Figure 4.5) and electron-withdrawing groups induce destabilization for both $\mathrm{ZnCl}_{2}$ and CoMe fragments (Figure 4.4). Although $\pi$-back donation plays the major role in the stabilization of CoMe fragments, it is not much affected by substituent changes, because the N -aryl ring is nearly orthogonal to the large conjugated $\pi$-system (pyridine + imine arms). In addition, the coefficients of the ligand $\pi^{*}$ orbitals at the imine nitrogen atoms predicted by DFT are relatively small. ${ }^{75}$ Thus we can conclude that substituents at
the 4-position of the N -aryl group mainly affect interactions through $\sigma$-donation to the metal center.


Figure 4.5. Effect of N -aryl 4-substituent on $\mathrm{ZnCl}_{2}(■, \rho=0.971)$ and $\mathrm{CoMe}(\star, \rho=$ 0.981 ) fragment stabilization energies, plotted against Taft $\sigma_{p}$ parameters ${ }^{175}$

Finally, for all of the above variations, the substituents are located far away from the metal center, and thus the steric effects will not be significant. When it comes to the substituents closer to the metal center such as the variation at the imine carbon atom (ligands 14-19) (Figure 4.6), the total substituent effects are quite large and there is no clear correlation with, for example, $\sigma_{p}$ parameters. Here a combination of electronic and steric effects may be responsible for these substituent effects.


Figure 4.6. Effect of substituents at the imine carbon atom on $\mathrm{ZnCl}_{2}(\boldsymbol{\square})$ and $\mathrm{CoMe}(\mathbf{\Delta})$ fragment stabilization energies, plotted against Taft $\sigma_{p}$ parameters ${ }^{175}$

Therefore, it seems that $\mathrm{ZnCl}_{2}$ ( $\mathrm{d}^{10}$, Lewis acid with negligible $\pi$-basicity) and CoMe (good $\pi$-basicity, but Lewis acidity cannot be ignored) are reasonable choices for our two reference metal fragments to probe $\sigma$-donor and $\pi$-acceptor properties of the DIP-type ligands. Now two equations (Eq. 4.6 and Eq. 4.7) can be generated from Eq.4.5.

$$
\begin{array}{ll}
\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZnCl}_{2}, \mathrm{~L}\right)=\alpha\left(\mathrm{ZnCl}_{2}\right) \sigma_{\mathrm{L}}+\beta\left(\mathrm{ZnCl}_{2}\right) \pi_{\mathrm{L}} & \text { Eq. } 4.6 \\
\Delta \mathrm{E}_{\text {stab }}(\mathrm{CoMe}, \mathrm{~L})=\alpha(\mathrm{CoMe}) \sigma_{\mathrm{L}}+\beta(\mathrm{CoMe}) \pi_{\mathrm{L}} & \text { Eq. } 4.7
\end{array}
$$

### 4.6.2 Solving ligand parameters

Based on the properties of the two metal fragments above, it is reasonable to set $\beta\left(\mathrm{ZnCl}_{2}\right)$ $=0$ and $\beta(\mathrm{CoMe})=1$ to define the $\pi$-basicity scale and $\alpha\left(\mathrm{ZnCl}_{2}\right)=1, \alpha(\mathrm{CoMe}) \neq 0$ to define the Lewis acidity scale. Unfortunately, there is no unique way to assign a value to $\alpha(\mathrm{CoMe})$. Thus we derive a "reasonable" value by requiring orthogonality of variations in $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ parameters over our test set of ligands (33 ligands, for structures, see Figure 4.7):

$$
\begin{align*}
& \sum_{\mathrm{L}}\left(\sigma_{\mathrm{L}}-\bar{\sigma}\right)\left(\pi_{\mathrm{L}}-\bar{\pi}\right)=0 \\
& \bar{\sigma}=\frac{1}{n(\mathrm{~L})} \sum_{\mathrm{L}} \sigma_{\mathrm{L}} \quad \bar{\pi}=\frac{1}{n(\mathrm{~L})} \sum_{\mathrm{L}} \pi_{\mathrm{L}} \tag{Eq. 4.8}
\end{align*}
$$

By satisfying the above equation $4.8,{ }^{176} \alpha(\mathrm{CoMe})$ was calculated to be 0.25 , which seems reasonable as long as there is no systematic correlation between $\sigma$-donation and $\pi$ acceptor properties of the ligands studied. By combining all settings together, Eq. 4.6 and Eq. 4.7 can be rewritten as Eq. 4.9 and Eq. 4.10 to generate the $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ parameters. As $\alpha_{F}$ and $\beta_{F}$ are dimensionless, $\sigma_{L}$ and $\pi_{L}$ will have units of energy.

$$
\begin{align*}
& \sigma_{\mathrm{L}}=\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZnCl}_{2}, \mathrm{~L}\right)  \tag{Eq. 4.9}\\
& \pi_{\mathrm{L}}=\Delta \mathrm{E}_{\text {stab }}(\mathrm{CoMe}, \mathrm{~L})-0.25 \Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZnCl}_{2}, \mathrm{~L}\right) \tag{Eq. 4.10}
\end{align*}
$$

With Eq. 4.9 and Eq. 4.10 in hand, the overall electronic energy of Eq. 4.3 will be calculated by DFT for a number of ligands and the corresponding ligand parameters can be solved. Similarly, by knowing the ligand parameters, the parameters of the other metal fragments are easily solved by fitting to Eq. 4.5.

With this model established, parameters for a variety of DIP type ligands have been developed.

### 4.6.3 Ligands and complexes to be explored

We have explored the DIP type ligands shown in Figure 4.7, with ligand 1 chosen as a reference.

$1 \mathrm{X}=\mathrm{H}$
$2 \mathrm{X}=\mathrm{NO}_{2}$
$3 \mathrm{X}=\mathrm{CN}$
$4 \mathrm{X}=\mathrm{CF}_{3}$
$5 \mathrm{X}=\mathrm{COOMe}$
$6 \mathrm{X}=\mathrm{OMe}$
$7 \mathrm{X}=\mathrm{NMe}_{2}$
$8 \mathrm{X}=\mathrm{CN}$
$9 \mathrm{X}=\mathrm{CF}_{3}$
$10 X={ }^{i} \operatorname{Pr}$
$11 X={ }^{t} \mathrm{Bu}$
$12 X=O M e$
$13 \mathrm{X}=\mathrm{NMe}_{2}$

$14 X=C N$
$15 \mathrm{X}=\mathrm{CF}_{3}$
$16 \mathrm{X}=\mathrm{Ph}$
$17 X={ }^{t} \mathrm{Bu}$
$18 \mathrm{X}=\mathrm{OMe}$
$19 \mathrm{X}=\mathrm{NMe}_{2}$

$20 X=C_{6} F_{5}$
$21 X=2,6-{ }^{-} \mathrm{PrC}_{6} \mathrm{H}_{5}$
$22 X=M e$


26
27


23


24


28


25




Figure 4.7. Structures of DIP type ligands studied

These ligands can be classified into four types:

Type I: change the central pyridine core, by putting a substituent at the 4-position of pyridine (ligands 1-7), or by replacing the whole pyridine ring by a pyrazine, pyrimidine, or triazine ring (ligands 31-33).

Type II: change the substituent at the N -aryl ring (ligands 8-13 and 20-22).

Type III: change the substituent at the imine carbon (ligands 14-19) .
Type IV: replacing the whole imine arms by phosphinimine, carbene, amine or pyridine groups (ligands 23-30).

Representative DFT-optimized structures of the corresponding $\mathrm{ZnCl}_{2}$ and CoMe complexes are shown in Figure 4.8.

(1) $\mathrm{ZnCl}_{2}$

(1) CoMe

Figure 4.8. Calculated structures of (1) $\mathrm{ZnCl}_{2}$ and (1)CoMe

As expected, the $\mathrm{ZnCl}_{2}$ complex has a strongly distorted square-pyramidal (SP) geometry with two inequivalent chlorine atoms. The geometries of CoMe complexes of DIP-type
ligands are typically square-planar, which is also the expected geometry for a fourcoordinate DIP cobalt(I) methyl complex. ${ }^{81}$ The DFT calculations showed that these CoMe complexes have singlet biradical character containing a low-spin cobalt(II) antiferromagnetically coupled to a ligand radical anion (for details, see Section 2.4.4 in Chapter 2). ${ }^{83}$ Thus, unrestricted DFT calculations were done for CoMe complexes and the broken-symmetry solutions produced mixtures of singlet and triplet states with $\hat{S}^{2}$ values in the range of 0.8 to 1.2 (expected: 1.0 for a "pure" $1: 1$ mixture of singlet and triplet). Only unrestricted DFT energies directly from this broken-symmetry solution were used here.

### 4.6.4 Generation of $\sigma_{L}$ and $\pi_{L}$ parameters

By using the above models and optimizing structures of the DIP ligands and the corresponding $\mathrm{ZnCl}_{2}$ and CoMe complexes, parameters for ligands in Figure 4.7 have been generated according to Eq. 4.9 and Eq. 4.10 (shown in Table 4.1).

Table 4.1. Fragment stabilization energies, $\sigma_{\mathrm{L}} / \pi_{\mathrm{L}}$ parameters, and ligand reorganization energies ( $\mathrm{kcal} / \mathrm{mol}$ )

| Ligand | $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZnCl}_{2}\right), \sigma_{\mathrm{L}}$ | $\Delta \mathrm{E}_{\text {stab }}(\mathrm{CoMe})$ | $\pi_{\mathrm{L}}$ | $\Delta \mathrm{E}_{\text {reorg }}$ |
| :---: | ---: | ---: | ---: | ---: |
| Type I |  |  |  |  |
| $\mathbf{1}$ | $(0)$ | $(0)$ | $(0)$ | $(0)$ |
| $\mathbf{2}$ | 3.46 | -7.33 | -8.19 | -0.84 |
| $\mathbf{3}$ | 3.05 | -4.17 | -4.93 | -0.23 |
| $\mathbf{4}$ | 2.40 | -2.27 | -2.87 | -0.28 |
| $\mathbf{5}$ | 1.02 | -3.76 | -4.01 | -0.96 |


| Ligand | $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZnCl}_{2}\right), \sigma_{\mathrm{L}}$ | $\Delta \mathrm{E}_{\text {stab }}(\mathrm{CoMe})$ | $\pi_{\mathrm{L}}$ | $\Delta \mathrm{E}_{\text {reorg }}$ |
| :---: | ---: | ---: | ---: | ---: |
| $\mathbf{6}$ | -1.26 | 2.73 | 3.05 | 0.46 |
| $\mathbf{7}$ | -3.49 | 4.09 | 4.96 | 0.91 |
| Type II |  |  |  |  |
| $\mathbf{8}$ | 3.50 | 2.76 | 1.88 | -1.12 |
| $\mathbf{9}$ | 2.77 | 2.15 | 1.45 | -0.77 |
| $\mathbf{1 0}$ | 0.09 | 0.23 | 0.21 | -0.06 |
| $\mathbf{1 1}$ | 1.09 | 0.10 | -0.17 | -0.02 |
| $\mathbf{1 2}$ | -0.40 | -0.42 | -0.32 | -0.31 |
| $\mathbf{1 3}$ | -1.55 | -1.26 | -0.87 | 0.26 |
| Type III |  |  |  |  |
| $\mathbf{1 4}$ | 9.92 | -5.37 | -7.85 | -7.43 |
| $\mathbf{1 5}$ | 10.67 | 1.60 | -1.07 | -7.03 |
| $\mathbf{1 6}$ | 2.13 | -0.09 | -0.63 | -5.30 |
| $\mathbf{1 7}$ | 6.76 | 6.09 | 4.40 | -1.94 |
| $\mathbf{1 8}$ | 3.45 | 13.78 | 12.91 | -9.95 |
| $\mathbf{1 9}$ | 7.95 | 15.08 | 13.09 | -4.80 |
| Type II |  |  |  |  |
| $\mathbf{2 0}$ | 8.46 | -0.09 | -2.21 | 0.49 |
| $\mathbf{2 1}$ | 1.41 | 0.96 | 0.61 | -0.26 |
| $\mathbf{2 2}$ | -10.16 | -6.84 | -4.30 | 1.79 |
| $\mathbf{2 3}$ | 11.39 | -2.36 | -5.21 | -11.33 |
| Type IV |  |  |  |  |
| $\mathbf{2 4}$ | 4.31 | 18.80 | 17.73 | -3.70 |
| $\mathbf{2 5}$ | -15.16 | 2.16 | 5.95 | -0.08 |
| $\mathbf{2 6}$ | 1.93 | 7.28 | 6.80 | -2.41 |
| $\mathbf{2 7}$ | 3.10 | 8.45 | 7.67 | 0.67 |
| $\mathbf{2 8}$ | -6.01 | -1.65 | -0.15 | 2.36 |
| $\mathbf{2 9}$ | -6.48 | 26.43 | 28.05 | -6.09 |
| $\mathbf{3 0}$ | -17.54 | -17.42 | -13.03 | 5.40 |
| Type I |  |  |  |  |
| $\mathbf{3 1}$ | 3.06 | -1.10 | -1.87 | -1.51 |
| $\mathbf{3 2}$ | 0.50 | -0.15 | -5.80 |  |
| $\mathbf{3 3}$ |  |  |  | -12.23 |
|  |  |  |  |  |

As we go through all parameters in Table 4.1, the replacement of one or two whole imine arms in Type IV ligands has the most significant effect on both $\sigma$-donor (from -17.54 $\mathrm{kcal} / \mathrm{mol}$ to $3.10 \mathrm{kcal} / \mathrm{mol}$ ) and $\pi$-acceptor properties (from $28.05 \mathrm{kcal} / \mathrm{mol}$ to -13.03 $\mathrm{kcal} / \mathrm{mol}$ ). Type III ligands, where substituents are much closer to the metal center, have larger effects than Type I ligands. Although modifications in Type I and Type II ligands have similar effects on the $\sigma$-donor parameters, substituents at the N -aryl ring have relatively smaller effects on $\pi$-acceptor properties of DIP ligands. Taking the cyano group as an example, at the imine carbon position (ligand 14), $\sigma$-donor ability decreases significantly with the $\sigma$ parameter changing from 0 (for ligand 1) to $9.92 \mathrm{kcal} / \mathrm{mol}$ (for ligand 14); at the same time, the $\pi$-acceptor ability increases with $\pi$-parameter changing to -7.85 (for ligand 14) $\mathrm{kcal} / \mathrm{mol}$. Introduction of CN at the 4-position of the N -aryl ring results in a much smaller reduction of $\pi$-acceptor ability as indicated by the change of $\pi$ parameter from 0 (for ligand $\mathbf{1}$ ) to 1.88 (for ligand $\mathbf{8}$ ) $\mathrm{kcal} / \mathrm{mol}$.

### 4.6.5 Transferability of $\sigma_{\mathrm{L}}$ and $\boldsymbol{\pi}_{\mathrm{L}}$ parameters

Ligand parameters will be useful only if they can also be applied to other metal fragments using Eq. 4.5. Thus the transferability of these ligand parameters was subsequently studied using the small metal fragments $\mathrm{Fe}(\mathrm{I}) \mathrm{Me}$ and $\mathrm{FeN}_{2}$ together with a representative set of 10 ligands (1, 3, 7, 8, 13, 15, 24, 28-30 in Figure 4.7) with different combinations of $\sigma$ and $\pi$ properties. For each fragment $\mathrm{F}, \alpha_{\mathrm{F}}$ and $\beta_{\mathrm{F}}$ parameters were obtained by fitting to Eq. 4.5 using ligand $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ parameters in Table 4.1; therefore, $\alpha_{\mathrm{F}}$ obtained will be the value relative to $\mathrm{ZnCl}_{2}\left(\alpha\left(\mathrm{ZnCl}_{2}\right)=1\right)$ and $\beta_{\mathrm{F}}$ will be the value relative to CoMe $(\beta(\mathrm{CoMe})=1)$. As the fitting is performed on two variables, the quality of the fitting is
graphically shown in Figure 4.9 (for $\mathrm{Fe}(\mathrm{I}) \mathrm{Me}$ ) and Figure 4.10 (for $\mathrm{FeN}_{2}$ ) by plotting calculated $\Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{L})$ against predicted $\Delta \mathrm{E}_{\text {stab }}^{\prime}(\mathrm{F}, \mathrm{L})$ (using the best fit to Eq. 4.5). ${ }^{\mathrm{XXV}}$

As we can see from Figure 4.9 and Figure 4.10, the fits for both FeMe and $\mathrm{FeN}_{2}$ are very good, with linear correlation coefficients $\rho$ of 0.975 for FeMe and 0.994 for $\mathrm{FeN}_{2}$. For both metal fragments, Lewis acidity parameters are close to zero while the $\pi$-basicity parameter for $\mathrm{FeN}_{2}\left(\beta_{\mathrm{FeN} 2}=1.23\right)$ is larger than that of $\mathrm{FeMe}\left(\beta_{\mathrm{FeMe}}=0.99\right)$, indicating that $\mathrm{FeN}_{2}$ is more $\pi$-basic than both CoMe and FeMe .
${ }^{\mathrm{XXV}}$ If it can be expressed as a linear combination (e.g. in the form of Eq. 4.5) of the two ligand parameters ( $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ ), the calculated $\Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{L})$ will have a high correlation with any value $\left(\Delta \mathrm{E}^{\prime}\right.$ stab $\left.(\mathrm{F}, \mathrm{L})\right)$ that comes from this linear combination. If the correlation coefficient equals $1, \Delta \mathrm{E}_{\text {stab }}(\mathrm{F}, \mathrm{L})$ will equal $\Delta \mathrm{E}_{\text {stab }}^{\prime}(\mathrm{F}, \mathrm{L})$.


Figure 4.9. Comparison of calculated $\Delta \mathrm{E}_{\text {stab }}(\mathrm{FeMe})$ values with those predicted $\Delta \mathrm{E}^{\prime}{ }_{\text {stab }}(\mathrm{FeMe})$ using the best fit to Eq. $4.5\left(\alpha_{\mathrm{FeMe}}=0.02 \pm 0.12, \beta_{\mathrm{FeMe}}=0.99 \pm 0.08 ; \rho=\right.$ 0.975 ; The solid line represents the ideal $\Delta \mathrm{E}_{\text {stab }}(\mathrm{FeMe})=\Delta \mathrm{E}_{\text {stab }}^{\prime}(\mathrm{FeMe})$ relation $)$.


Figure 4.10. Comparison of calculated $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{FeN}_{2}\right)$ values with those predicted $\Delta \mathrm{E}_{\text {stab }}^{\prime}\left(\mathrm{FeN}_{2}\right)$ using the best fit to Eq. $4.5\left(\alpha_{\mathrm{FeN} 2}=-0.07 \pm 0.07, \beta_{\mathrm{FeN} 2}=1.23 \pm 0.05 ; \rho=\right.$ 0.994; The solid line represents the ideal $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{FeN}_{2}\right)=\Delta \mathrm{E}_{\text {stab }}^{\prime}\left(\mathrm{FeN}_{2}\right)$ relation $)$.

### 4.6.6 Generation of metal-fragment parameters

Encouraged by the above results, the same representative ligands were subsequently used to generate the parameters for first-row transition metal $\mathrm{MCl}_{2}$ fragments $(\mathrm{M}=\mathrm{Sc}-\mathrm{Zn})$ in
their high spin states in the same manner. The fitted data and the corresponding $\alpha_{\mathrm{F}}$ and $\pi_{\mathrm{F}}$ values are summarized in Table 4.2 and plotted in Figure 4.11.

Table 4.2. $\alpha_{\mathrm{F}}$ and $\beta_{\mathrm{F}}$ parameters of $\mathrm{MCl}_{2}$ fragments for first-row transition metals and the linear-correlation coefficients $\rho$ between calculated $\Delta \mathrm{E}_{\text {stab }}(\mathrm{F})$ and predicted $\Delta \mathrm{E}_{\text {stab }}^{\prime}(\mathrm{F})$ by fitting to Eq. 4.5

| $\mathrm{MCl}_{2}$ | $\alpha_{\mathrm{F}}$ | $\beta_{\mathrm{F}}$ | $\rho$ |
| ---: | ---: | ---: | ---: |
| $\mathrm{ScCl}_{2}$ | $0.11 \pm 0.16$ | $0.65 \pm 0.10$ | 0.911 |
| $\mathrm{TiCl}_{2}$ | $0.35 \pm 0.09$ | $0.59 \pm 0.06$ | 0.972 |
| $\mathrm{VCl}_{2}$ | $0.81 \pm 0.05$ | $0.41 \pm 0.03$ | 0.993 |
| $\mathrm{CrCl}_{2}$ | $1.00 \pm 0.06$ | $0.23 \pm 0.04$ | 0.990 |
| $\mathrm{MnCl}_{2}$ | $1.00 \pm 0.04$ | $0.02 \pm 0.03$ | 0.992 |
| $\mathrm{FeCl}_{2}$ | $0.98 \pm 0.06$ | $0.16 \pm 0.04$ | 0.987 |
| $\mathrm{CoCl}_{2}$ | $1.11 \pm 0.05$ | $-0.01 \pm 0.03$ | 0.993 |
| $\mathrm{NiCl}_{2}$ | $1.27 \pm 0.06$ | $0.03 \pm 0.04$ | 0.995 |
| $\mathrm{CuCl}_{2}$ | $1.33 \pm 0.13$ | $0.03 \pm 0.08$ | 0.972 |
| $\mathrm{ZnCl}_{2}$ | $(1)$ | $(0)$ | $(1)$ |

The $\mathrm{ScCl}_{2}$ fragment gives a poor fit and larger errors in the parameters, but the other metals generally produce good fits $(\rho=0.970-1.0)^{\mathrm{XXVI}}$.
xxvi $\mathrm{ScCl}_{2}$ differs from the other $\mathrm{MCl}_{2}$ fragments (M: firs-row transition metals) in several respects, and any of these could be responsible for giving a poorer fit. The most obvious difference is that Sc is much more electropositive, leading to much more ionic bonding between $\mathrm{ScCl}_{2}{ }^{+}$and DIP ${ }^{-}$fragments. Secondly, Sc , is significantly larger than the other first-row transition metals. Finally, for $\mathrm{ScCl}_{2}$ there will always be transfer of nearly exactly one electron to the ligand, whereas for the other metals the amount of electron transfer may vary depending on details of the ligand structure.


Figure 4.11. $\alpha_{\mathrm{F}}(\boldsymbol{\square})$ and $\beta_{\mathrm{F}}(\star)$ values fitted for fragments $\mathrm{ScCl}_{2}-\mathrm{ZnCl}_{2}$ and a set of 10 test ligands using Eq 4.5.Error bars indicate $\pm 1 \sigma$

As Figure 4.11 shows, Lewis acidity $\left(\alpha_{F}\right)$ increases monotonically from $d^{1}$ to $d^{9}$. In contrast, $\pi$-basicity $\left(\beta_{\mathrm{F}}\right)$ decreases to zero as the number of d electrons increases from 1 to 5 (from $\mathrm{ScCl}_{2}$ to $\mathrm{MnCl}_{2}$ ). After the number of d electrons was further increased to 6 $\left(\mathrm{FeCl}_{2}\right), \beta_{\mathrm{F}}$ becomes significant again. For the remaining metal fragments, $\beta_{\mathrm{F}}$ is not important. This trend of $\pi$-basicity $\left(\beta_{\mathrm{F}}\right)$ for first-row transition metals in their high-spin states is consistent with the bond elongation of the imine which is attributed to the back donation of electrons from metal to ligand as shown in Figure 4.12. A good correlation between $\pi$-basicity $(\beta)$ and the amount of imine bond elongation was obtained.


Figure 4.12. Correlation between $\beta_{\mathrm{F}}$ parameter and calculated $\mathrm{C}=\mathrm{N}$ bond length in (DIP) $\mathrm{MCl}_{2}$ complexes (correlation coefficient $\rho=0.964$ )

### 4.6.7 Issues addressed

The choice of $\alpha_{\text {CoMe }}$
As we reconsider our model to generate $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ for DIP type ligands and $\alpha_{\mathrm{F}}$ and $\beta_{\mathrm{F}}$ values for metal fragments, the absolute values of these parameters depend on the choices of the $\alpha$ and $\beta$ values for the two reference fragments $\mathrm{ZnCl}_{2}$ and CoMe . As for the $\beta$ -
scale, the choice of the setting $\left(\beta_{\mathrm{ZnCl} 2}=0, \beta_{\mathrm{CoMe}}=1\right)$ is OK due to the safe assumption that back-donation from $\mathrm{ZnCl}_{2}$ is negligible. However, for the $\alpha$-scale, while the assignment of 1 to $\alpha_{\mathrm{ZnCl} 2}$ is acceptable, the choice of $\alpha_{\mathrm{CoMe}}$ is still somewhat arbitrary, and it is useful to analyze how this choice can affect the results.

On the one hand, according to Eq. 4.10 , the choice of $\alpha_{\mathrm{CoMe}}$ affects only the $\pi_{\mathrm{L}}$ values. For ligands where $\Delta \mathrm{E}_{\text {stab }}\left(\mathrm{ZnCl}_{2}\right)$ is large relative to $\Delta \mathrm{E}_{\text {stab }}(\mathrm{CoMe})$, the $\pi_{\mathrm{L}}$ value will change significantly if $\alpha_{\mathrm{CoMe}}$ is changed. Among the reasonable range of values for $\alpha_{\mathrm{CoMe}}$ (estimated as $0.15-0.50)^{\mathrm{XXVII}}, \boldsymbol{\pi}_{\mathrm{L}}$ values would be significantly affected for ligands $\mathbf{1 5}, \mathbf{1 7}$, 20, 22, 29 and 30. Taking ligand 30 as an example, it was predicted to be a strong $\sigma$ donor and a strong $\pi$-acceptor when $\alpha_{\text {CoMe }}$ equals 0.25 . However, whether it is a good $\pi$ acceptor is still a matter of debate. If it were a weak $\pi$-acceptor, then a more positive $\pi_{\mathrm{L}}$ would be preferred. Thus, in order to reduce $\pi_{30}$ value to zero (making it only as strong a $\pi$-acceptor as ligand $\mathbf{1}$ ), $\alpha_{\text {CoMe }}$ needs to be set to around 1.0 , which means that the Lewis acidity of CoMe would be as large as that of $\mathrm{ZnCl}_{2}$. This clearly does not make chemical sense because $\mathrm{CoCl}_{2}$ has similar Lewis acidity to $\mathrm{ZnCl}_{2}$ and the Lewis acidity of CoMe is expected to be much smaller than that of $\mathrm{CoCl}_{2}$.

On the other hand, the choice of the $\alpha_{\mathrm{CoMe}}$ value can also affect the parameters of the other metal fragments. Values for the $\pi$-basicity $\left(\beta_{\mathrm{F}}\right)$ remain unchanged, but the $\alpha_{\mathrm{F}}$

[^14]parameters vary roughly in parallel with $\alpha_{\text {CoMe }}$. For example, for the fragment $\operatorname{Fe}\left(\mathrm{N}_{2}\right), \alpha_{\mathrm{F}}$ is calculated to be close to zero; however, it would be negative when $\alpha_{\text {CoMe }}<0.25$, which indicates repulsive $\sigma$-interactions compensated by stronger attractive $\pi$-interactions. Although possible, this still does not seem very reasonable. Therefore, the margins for choosing different $\alpha_{\text {CoMe }}$ values (and hence obtaining significantly different ligand parameters) are quite limited.

In summary, any choice of $\alpha_{F} / \beta_{F}$ for the reference fragments will produce scales for $\sigma_{\mathrm{L}} / \pi_{\mathrm{L}}$ for ligands and $\alpha_{F} / \beta_{F}$ for other metal fragments. As long as linear dependencies are avoided, any choice will produce the same predicted $\Delta \mathrm{E}_{\text {stab }}$ (Eq. 4.5) and $\Delta \mathrm{E}_{\text {bind }}$ (Eq. 4.4) values and would lead to the same predictions regarding, for example, catalytic activity. When the interpretations of these parameters in terms of separating $\sigma$-effects and $\pi$ effects are concerned, the choice of $\alpha_{\mathrm{CoMe}}$ will matter a lot.

## Steric effects

Our procedure does not produce a separate steric parameter. Thus $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ represent the interactions that include the contributions by steric effects of the ligand. In addition, steric effects can also affect the reorganization energy $\Delta \mathrm{E}_{\text {reorg }}$. Thus, the parameters developed here also contain a steric contribution.

### 4.7 Conclusions

Ligand parameters $\sigma_{L}$ and $\pi_{\mathrm{L}}$ for DIP-type ligands have been devised through DFT calculations and represent the overall $\sigma$-donation and $\pi$-accepting ability of the ligands. Although there is some uncertainty about the choice of $\alpha_{\mathrm{CoMe}}$, the results make chemical sense. DIP was shown to be a strong $\pi$-acceptor, although bis(carbene)pyridine (ligand $\mathbf{3 0}$ in Figure 4.7) is even better. Bis(phosphinimine)pyridine ligands are acceptable $\sigma$-donors but very poor $\pi$-acceptors. These results can explain why so far only DIP and bis(carbene)pyridine ligands generate stable cobalt(I) alkyl complexes. ${ }^{177}$

The other advantage of our strategy is that it generates not only ligand parameters, but also scales for metal fragments, $\alpha_{\mathrm{F}}$ (representing Lewis acidity relative to $\mathrm{ZnCl}_{2}$ ) and $\beta_{\mathrm{F}}$ (representing $\pi$-basicity relative to CoMe). Our study of $\mathrm{MCl}_{2}$ fragments $(\mathrm{M}=\mathrm{Sc}-\mathrm{Zn})$ showed that Lewis acidity increases monotonically from $\mathrm{ScCl}_{2}$ to $\mathrm{CuCl}_{2}$ while $\pi$-basicity first goes to zero from $\mathrm{ScCl}_{2}$ to $\mathrm{MnCl}_{2}$, then increases again for $\mathrm{FeCl}_{2}$, finally becoming insignificant for the remaining metal fragments.

### 4.8 Future outlook

As we mentioned earlier, the ligand parameters developed here do not contain a separate steric description, although $\sigma_{\mathrm{L}}$ and $\pi_{\mathrm{L}}$ will contain some contributions from steric effects. However, steric effects are important in the chemistry of DIP-type ligands. Taking the common DIP ligand for an example, sterically hindered ligand 21 in Figure 4.7 is good in
ethylene polymerization ${ }^{16,17}$ and forms (DIP) $\mathrm{FeCl}_{2}$ when reacted with $\mathrm{FeCl}_{2}$. By contrast, the less hindered phDIP-ligand (2,6-(phenylimino)ethylpyridine) is good at oligomerization ${ }^{137}$ and prefers to form the bis-ligand coordinated complex $\left[\mathrm{L}_{2} \mathrm{Fe}\right]^{2+}$ $\left[\mathrm{FeCl}_{4}\right]^{2-}$ when reacted with $\mathrm{FeCl}_{2} .{ }^{178}$ Development of reasonable parameters for measuring the steric effects of DIP-type ligands can be useful in terms of controlling the selectivity for oligomerization vs polymerization and the type of polymer produced. Steric effects can indirectly affect the electronic properties of ligands by changing the structures and conformations of ligands, so they cannot be completely separated from electronic effects. However, a reasonable description of this steric hindrance (mainly from N -aryl groups) is still desirable.

## Chapter 5. Synthesis of labile-ligand cobalt (II) dialkyls

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### 5.1 Introduction

Labile-ligand metal complexes can be useful as precursors to make metal complexes of other ligands. Pyridine, TMEDA and bipyridine are commonly used labile ligands in the organometallic area. The replacement reaction of a labile ligand in the complex by other useful ligands is popular as an alternative to alkylating the corresponding metal halide with an organo-lithium or Grignard reagent as shown in the following Scheme 5.1.


Scheme 5.1. Two methods for the synthesis of metal alkyl complexes of neutral ligand

Among the first-row late-transition metals, only cobalt does not have such a convenient labile metal alkyl source. For example, $(\mathrm{Py})_{2} \mathrm{FeR}_{2},{ }^{179}(\mathrm{TMEDA}) \mathrm{NiMe}_{2},{ }^{180}(\mathrm{Py})_{2} \mathrm{MnR}_{2}{ }^{181}$
( R represents alkyl here) are widely used in the synthesis of metal alkyl complexes, while there is no report, to the best of my knowledge, of a similar approach for cobalt. During our research on cobalt(I) alkyl complexes with DIP-type ligands, the simple alkylation of cobalt dichloride complexes of bisphosphiniminepyridine ligands ${ }^{142}$ by organo-lithium or Grignard reagents was not successful; a similar problem has been encountered with a less-hindered biscarbene pyridine ligand. ${ }^{177}$ Several cobalt aryl complexes have been reported, but application of them to the synthesis of other ligand complexes is not likely to work. For example, the ligand-free $\left[\mathrm{Co}\left(2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}\right)_{2}\right]$ was made by the Theopold group according to the following equation, ${ }^{182}$ but the synthesis is quite demanding.


Although the synthesis of the more hindered $\mathrm{Co}\left[2,6-\left(2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}\right)_{2}-\mathrm{C}_{6} \mathrm{H}_{3}\right]_{2}$ from $\mathrm{CoCl}_{2}$ and the corresponding aryl lithium is much simpler, ${ }^{183}$ further coordination to other ligands like the DIP ligand is unlikely. In addition, cobalt alkyl complexes are more useful than aryl complexes at the moment. All the above stimulated us to explore the synthesis of possible labile-ligand cobalt dialkyl complexes.

Fifty years ago, Matsuzaki and coworkers ${ }^{184}$ used MeMgBr to alkylate $(\mathrm{Py})_{2} \mathrm{CoCl}_{2}$ to generate a very unstable product formulated as $(\mathrm{Py})_{2} \mathrm{CoMe}_{2}$. The only characterization of this product was by EPR, which is not enough to unambiguously prove its identity. Around thirty years later, Hay-Motherwell and coworkers ${ }^{185}$ found that
(TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ can be made by reducing anhydrous $\mathrm{CoCl}_{2}$ with 4.0 eq. $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ in the presence of 2.0 eq TMEDA, but the reaction procedure is quite demanding and the yield is only $11 \%$. In addition, I found that it was hard to repeat the procedure. Therefore, although these labile cobalt dialkyl complexes have indeed been reported, there have been no applications, up to now, in the synthesis of other cobalt alkyl complexes. As cobalt is next to iron in the Periodic Table and belongs to the Group VIII metals, very similar physical properties and probably comparable chemical reactivity to iron could be expected. The group of Cámpora ${ }^{151}$ has been successful in the synthesis and use of iron and nickel labile-ligand alkyl precursors. ${ }^{186}$ I decided to try their strategy for cobalt.

### 5.2 Exploration of the synthesis of $(\mathbf{P y})_{2} \mathrm{CoR}_{2}\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$

Anhydrous (Py) $)_{4} \mathrm{CoCl}_{2}$ was treated with 2.0 eq. of $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ in hexane at $-70{ }^{\circ} \mathrm{C}$, followed by slow warming to room temperature. Simple filtration to remove LiCl and evaporation to remove all the volatile compounds cleanly generated the green oily $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. The ${ }^{1} \mathrm{H}$ NMR spectrum of this green oil is shown in Figure 5.1A.


Figure 5.1. ${ }^{1} \mathrm{H} \quad \mathrm{NMR}$ spectra of (A) $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and (B) (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ (* denotes solvent peaks and a,b,c, and d are the labelings of the protons in cobalt dialkyl complexes)

As there is no similar cobalt dialkyl complex which can be used as a reference, its neighbour $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ was also prepared ${ }^{151}$ and the comparison of their ${ }^{1} \mathrm{H}$ NMR data are summarized in Table 5.1.

Table 5.1. Comparison of ${ }^{1} \mathrm{H}$ NMR shifts ( ppm ) for $(\mathrm{Py})_{2} \mathrm{M}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ complexes $(\mathrm{M}=$ $\mathrm{Co}, \mathrm{Fe}$ )

|  | $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ |  | $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}{ }^{151}$ |  |
| :--- | :---: | ---: | :---: | ---: |
|  | $\delta(\mathrm{ppm})$ | $\Delta \mathrm{v}_{1 / 2}(\mathrm{~Hz})$ | $\delta(\mathrm{ppm})$ | $\Delta v_{1 / 2}(\mathrm{~Hz})$ |
| SiMe $_{3}$ | 10.3 | 80 | 11.2 | 318 |
| Py H2 | 114 | 1600 | $129^{\mathrm{a}}$ | $1614^{\mathrm{a}}$ |
| Py H3 | 38.4 | 500 | 35.5 | 657 |
| Py H4 | -8.5 | 190 | 17.4 | 348 |

${ }^{\text {a }}$ This chemical shift was not reported by Cámpora. ${ }^{151} \mathrm{CoCH}_{2}$ and $\mathrm{FeCH}_{2}$ were not observed probably due to the broadness of the peaks and the large chemical shift induced directly by iron or cobalt.

All proton chemical shifts of $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ are similar to those of the iron analog except Py H4: for iron, it is around 17.4 ppm while for cobalt, it shifts to high field to 8.5 $\mathrm{ppm} .{ }^{\mathrm{XXVIII}}$ The broadness of the peaks in Figure 5.1 A is due to the paramagnetic nature of
xxviII Normally, the observed chemical shift of a paramagnetic compound can be interpreted as the following equation (for details, see Section 2.1.1):

$$
\delta^{\text {obs }}=\delta^{\text {orb }}+\delta^{\mathrm{FC}}+\delta^{\mathrm{PC}}
$$

The $\delta^{\text {orb }}$ for high-spin iron(II) and cobalt(II) complexes of the same ligand should be very similar. As the $\delta^{\mathrm{PC}}$ contributions to the chemical shifts of both cobalt(II) and iron(II) are usually negligible, $\delta^{\mathrm{FC}}$ will play the major role in the difference between these two metals, which result from the Fermi contact interaction between unpaired electrons and the target nuclei. As the number of unpaired electrons is different in these two metal systems, an orbital occupation analysis will be useful to understand the similarity between the spectra of iron and cobalt complexes.
To illustrate the idea, we will assume an ideal tetrahedral environment for both metals. For $\mathrm{Co}(\mathrm{II})$, three unpaired electrons will be located in the $\mathrm{d}_{\mathrm{xy}}, \mathrm{d}_{\mathrm{xz}}$, and $\mathrm{d}_{\mathrm{yz}}$ orbitals, while for iron(II), four unpaired electrons are in $d_{x y}, d_{x z}, d_{y z}$ and $d_{x 2-y 2}$ orbitals. The contributions of the $d_{x y}, d_{x z}$, and $d_{y z}$ electrons will be very similar for the two metals, and
the compound; integration of the peaks strongly supports the formulation as $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. In addition, this compound is stable at $-35{ }^{\circ} \mathrm{C}$ for at least one month, and survives at room temperature for weeks. However, it is very air sensitive and moisture sensitive.

Although the whole procedure is simple, care is needed to reproduce the reaction successfully:

1) The quality of the $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ used plays a key role in obtaining high yield and high purity. Different batches of the $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ directly purchased from commercial companies gave different results and the accompanying unknown black oil generated can hinder purification and result in a poor yield. In order to avoid these problems, $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ was crystallized from the freshly received solution by cooling it to $-35^{\circ} \mathrm{C}$ and the crystalline solid obtained was stored in a glove box at low temperature to maintain its quality.
2) Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$ used was prepared from anhydrous $\mathrm{CoCl}_{2}$ and dry pyridine, rather than from the commonly used hydrated cobalt dichloride, to avoid potential problems in the reaction with $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$. When this complex is dried in vacuum, it easily loses coordinated pyridine, changing from pink to purple-blue. This loss of pyridine also occurred when the pink solid was
the additional unpaired electron in the $d_{x 2-y 2}$ orbital of iron will account for the main difference between high-spin iron(II) and high-spin cobalt(II) NMR spectra. Only the nuclei that have significant Fermi contact interaction with the electron in this $\mathrm{d}_{\mathrm{x} 2 \mathrm{y} 2}$ orbital will be affected significantly. This is might be the case for the pyridine H 4 proton of $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$.
suspended in pentane or hexane in the synthesis of $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$, but this dissociation did not affect the outcome of the reaction.
3) Chirik and coworkers ${ }^{187}$ reported that the mono alkyl complex $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Cl}$ can be prepared from the reaction of $(\mathrm{Py})_{4} \mathrm{FeCl}_{2}$ with only 1.0 equivalent of $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$. However, for the Co case studied here, we found that $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right) \mathrm{Cl}$ could not be detected when 1.0 equivalent of RLi was used. Instead, only $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ was generated together with a blue solid suspected to be unreacted $(\mathrm{Py})_{n} \mathrm{CoCl}_{2}{ }^{\mathrm{XXIX}}$.

The main characterization of this compound is by ${ }^{1} \mathrm{H}$ NMR as reported above. The oily nature of the product prevented the determination of a crystal structure. In order to further characterize $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$, an internal standard (hexamethylbenzene) was used to quantify the amount of $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and its hydrolysis products. The purity of the product was estimated to be $91 \%$ from the ${ }^{1} \mathrm{H}$ NMR spectrum; hydrolysis results indicate that the ratio of pyridine and trimethylsilane is approximately $1: 1$ within experimental error. Furthermore, the magnetic moment was measured by the Evans method $^{98}$ to be $4.8(3) \mu_{\mathrm{B}}$ which falls in the commonly observed range of high spin cobalt(II) (4.3-5.2 $\mu_{\mathrm{B}}$ ). ${ }^{188}$ In addition, the presence of the cobalt dialkyl fragment was proved indirectly by transferring it to another labile ligand (TMEDA).
xxIX The further addition of another equivalent of $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ converted this blue solid
into $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. into $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$.

### 5.3 Synthesis of (TMEDA)CoR $\mathbf{2}_{2}\left(\mathrm{R}=\mathbf{C H}_{2} \mathrm{SiMe}_{3}\right)$

By adding 10 eq. of dry TMEDA to freshly prepared green $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in hexane or diethyl ether at $-20{ }^{\circ} \mathrm{C}$, a brown solution was obtained. As (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ is violet, this suggested that the reaction was not complete (a DFT calculation showed that the exchange reaction of pyridine with TMEDA in this complex is close to thermoneutral, see Table B. 1 in the Appendix B). After warming to room temperature and evaporating all solvent from the filtrate, pure bluish purple crystalline (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ was obtained by crystallization from a hexane solution containing one drop of TMEDA at $-35^{\circ} \mathrm{C}$. The total yield over two steps from the starting material $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$ was $57 \%$. The simplicity of the whole procedure and the high yield will make this method preferable to the procedure reported by HayMotherwell ${ }^{185}$ and wide application can be expected in the future. The ${ }^{1} \mathrm{H}$ NMR spectrum of (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ showed three characteristic peaks with two of them overlapping. However, this spectrum (Figure 5.1B) can be interpreted using deconvolution as implemented in SpinWorks. ${ }^{189}$ The comparison of this spectrum with that of (TMEDA)Fe $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ is shown in Table 5.2.

Table 5.2. Comparison of ${ }^{1} \mathrm{H}$ NMR shifts (ppm) for (TMEDA) $\mathrm{M}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ complexes $(\mathrm{M}=\mathrm{Co}, \mathrm{Fe})^{\mathrm{a}}$

|  | $(\mathrm{TMEDA}) \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ |  | (TMEDA)Fe$\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}{ }^{179 \mathrm{c}}$ |  |
| :--- | :---: | ---: | ---: | ---: |
|  | $\delta(\mathrm{ppm})$ | $\Delta v_{1 / 2}(\mathrm{~Hz})$ | $\delta(\mathrm{ppm})$ | $\Delta v_{1 / 2}(\mathrm{~Hz})$ |
| $\mathrm{SiMe}_{3}$ | 9.6 | 70 | 12.14 | 180 |
| $\mathrm{NCH}_{3}$ | 78 | 350 | 86.8 | 1100 |
| $\mathrm{CH}_{2} \mathrm{~N}$ | 80 | 600 | 72.6 | 890 |

$\overline{{ }^{\mathrm{a}} \mathrm{CoCH}_{2} \text { and } \mathrm{FeCH}} 2_{2}$ were not observed possibly due to the broadness of the peaks and the large chemical shift induced directly by iron or cobalt.

In the original report by Hay-Motherwell and coworkers, ${ }^{185}$ the only characterization method used was X-ray diffraction. In order to see whether we made the same complex, we also determined the crystal structure of our (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ (Figure 5.2).


Figure 5.2. Thermal ellipsoid plot for (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. ( $30 \%$ probability, hydrogens omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): $\mathrm{Co}(1)-\mathrm{N}(1)$ : 2.186(2); $\mathrm{Co}(1)-\mathrm{N}(2): 2.179(2) ; \mathrm{Co}(1)-\mathrm{C}(7): 2.035(2) ; \mathrm{Co}(1)-\mathrm{C}(8): 2.035(2) ; \mathrm{C}(7)-\mathrm{Co}(1)-$ $\mathrm{N}(1): 115.55(10) ; \mathrm{C}(8)-\mathrm{Co}(1)-\mathrm{N}(2): 113.40(11) ; \mathrm{C}(7)-\mathrm{Co}(1)-\mathrm{N}(2): 106.80(9) ; \mathrm{C}(7)-$ $\mathrm{Co}(1)-\mathrm{C}(8): 122.91(11)$.
(TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ prepared according to our method has the same unit cell and the same structure that previously reported ${ }^{185}$ with the cobalt center having tetrahedral coordination geometry. This clearly confirms the identity of (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. Although it is highly air and moisture sensitive, this complex is very stable in the solid state at room temperature under an inert atmosphere.

### 5.4 Synthesis of $\left(\mathrm{Py}_{2}\right)_{2} \mathrm{CoR}_{2}{ }_{2}\left(\mathrm{R}^{\prime}=\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)$

Because the X-ray structure of $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ could not be obtained and knowledge of the geometry of a cobalt dialkyl with pyridine as the labile ligand is still desirable, variation of the R group was investigated. ${ }^{\mathrm{XXX}}$ For iron, Cámpora ${ }^{151}$ found that $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ did not form a crystal, but $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}$ crystallized well. Thus, we decided to prepare $\left.(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}\left(\mathrm{R}^{\prime}=\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}\right)$, hoping it would generate X-ray quality crystals. However, the reaction turned out to be not as simple as for $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. As $\mathrm{R}^{\prime} \mathrm{Li}$ is not commercially available, $\mathrm{R}^{\prime} \mathrm{MgCl}$ was used to react with $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$ in diethyl ether at $-50{ }^{\circ} \mathrm{C}$, followed by warming to room temperature. After addition of pyridine to stabilize the expected product, filtration and crystallization from pentane together with one drop of pyridine at $-35{ }^{\circ} \mathrm{C}$ furnished dark-green crystals. The X-ray structure of this complex is shown in Figure 5.3 and a comparison with the iron analog is summarized in Table 5.3.

[^15]

Figure 5.3. X-ray structure of $(\mathrm{Py})_{2} \mathrm{CoR}^{2}$. (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): $\mathrm{Co}(1)-\mathrm{C}(1): \quad 2.066(3) ; \quad \mathrm{Co}(1)-\mathrm{C}(31): 2.075(4) ; \quad \mathrm{Co}(1)-\mathrm{N}(1): 2.117(3) ; \quad \mathrm{Co}(1)-\mathrm{N}(2):$ 2.108(3); $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2): 127.32(15) ; \mathrm{C}(11)-\mathrm{Co}(1)-\mathrm{C}(31): 96.20(11)$.

Table 5.3. X-ray structures: comparison of $\left(\mathrm{Py}_{2}\right)_{2} \mathrm{CoR}^{\prime}{ }_{2}$ and $(\mathrm{Py})_{2} \mathrm{FeR}^{\prime}{ }_{2}$

|  | $\left(\mathrm{Py}_{2} \mathrm{CoR}_{2}^{\prime}\right.$ | $\left(\mathrm{Py}_{2} \mathrm{FeR}_{2}^{\prime}{ }^{151}\right.$ |
| ---: | ---: | ---: |
| $\mathrm{a}(\AA)$ | $11.8183(11)$ | $11.6538(12)$ |
| $\mathrm{b}(\AA)$ | $11.8294(12)$ | $11.8197(12)$ |
| $\mathrm{c}(\AA)$ | $12.1892(12)$ | $12.0936(13)$ |
| $\alpha(\mathrm{deg})$ | $105.652(2)$ | $108.971(2)$ |
| $\beta(\mathrm{deg})$ | $109.119(2)$ | $105.834(2)$ |
| $\gamma(\mathrm{deg})$ | $108.825(2)$ | $108.571(2)$ |
| Average M-C $(\AA)$ | 2.071 | 2.091 |
| Average M-N $(\AA)$ | 2.112 | 2.149 |
| Average N-M-C(deg) | 104.76 and 109.74 | 104.08 and 109.31 |
| $\mathrm{~N}-\mathrm{M}-\mathrm{N}(\mathrm{deg})$ | $96.20(11)$ | 91.70 |
| $\mathrm{C}-\mathrm{M}-\mathrm{C}(\mathrm{deg})$ | $127.32(15)$ | 131.31 |

As Table 5.3 shows, the two structures are very similar except that the angle NMN is around $5^{\circ}$ larger and the angle CMC is around $5^{\circ}$ smaller for Co. Unfortunately, $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ was found to be unstable. During measurement of the X-ray diffraction experiment, after around 20 h at room temperature, there is no X-ray diffraction any more. In addition, its benzene- $d_{6}$ solution decomposed completely within 2 h at room temperature. The stability difference between $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ is probably due to the fact that the trimethysilylmethyl groups stabilizes the negative charge on carbon better and make the corresponding cobalt(II) dialkyl complex more stable. Furthermore,
the ability of the alkyl fragment to stabilize the metal center was studied by DFT (Table 5.4) and the $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ group clearly has a stronger tendency to form a more stable metal alkyl compound.

Table 5.4. Comparison of the radical stability through an assumed reaction.
$\cdot \mathrm{CH}_{2} \mathrm{SiMe}_{3}+\mathrm{R"Li} \longrightarrow \mathrm{LiCH}_{2} \mathrm{SiMe}_{3}+\cdot \mathrm{R"}$

| DFT | $\cdot \mathrm{CH}_{2} \mathrm{SiMe}_{3}$ | $\cdot \mathrm{CH}_{2} \mathrm{CMe}_{3}$ | $\cdot \mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}$ |
| ---: | ---: | ---: | ---: |
| $\mathrm{b} 3-\operatorname{lyp}(\mathrm{SVP})$ | $\Delta \mathrm{E}(\Delta \mathrm{G})^{\mathrm{a}}, \mathrm{kcal} / \mathrm{mol}$ | $\Delta \mathrm{E}(\Delta \mathrm{G})^{\mathrm{a}}, \mathrm{kcal} / \mathrm{mol}$ | $\Delta \mathrm{E}(\Delta \mathrm{G})^{\mathrm{a}}, \mathrm{kcal} / \mathrm{mol}$ |
| $\mathrm{b} 3-\operatorname{lyp}(\mathrm{TZVP})$ | $0.0(0)$ | $-7.3(-7.1)$ | $-2.9(-2.9)$ |

${ }^{\text {a }}$ The overall electronic energies are calculated using Turbomole package and the energy in the parenthesis is the free energy. All energy units are $\mathrm{kcal} / \mathrm{mol}$.

During the preparation of $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$, the use of the magnesium reagent is problematic due to the formation of $(\mathrm{Py})_{2} \mathrm{MgR}^{\prime}{ }_{2}$. The similar solubility of the Mg and Co analogs makes purification difficult. In order to verify the identity of the impurity $(\mathrm{Py})_{2} \mathrm{MgR}^{\prime}{ }_{2}$, it was prepared separately by adding pure pyridine to an ether solution of $\mathrm{ClMgCH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}$ followed by crystallization from a pentane solution at $-35{ }^{\circ} \mathrm{C}$; its identity was confirmed by ${ }^{1} \mathrm{H}$ NMR, ${ }^{13} \mathrm{C}$ NMR and 2D Gradient HSQC. Later, we found that the change from $\mathrm{Et}_{2} \mathrm{O}$ to THF solvent affords a highly pure product (there are still trace amounts of toluene solvent left and some possibly decomposed side products in it) based on ${ }^{1} \mathrm{H}$ NMR (Figure 5.4), although the yield was only $20 \%$. The chemical shifts of pyridine in $(\mathrm{Py})_{2} \mathrm{CoR}_{2}^{\prime}$ are similar to those in $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and the comparison with the iron analog is shown in Table 5.5.


Figure 5.4. ${ }^{1} \mathrm{H}$ NMR spectrum of $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$

Table 5.5. Comparison of ${ }^{1} \mathrm{H}$ NMR shifts (ppm) for $(\mathrm{Py})_{2} \mathrm{MR}^{\prime}{ }_{2}$ complexes $(\mathrm{M}=\mathrm{Co}, \mathrm{Fe})^{\mathrm{a}}$

|  |  | $\left(\mathrm{Py}_{2} \mathrm{CoR}_{2}\right.$ | $\left(\mathrm{Py}_{2} \mathrm{FeR}_{2}^{\prime 151}\right.$ |  |
| :---: | ---: | ---: | ---: | ---: |
|  | $\delta(\mathrm{ppm})$ | $\Delta \mathrm{v}_{1 / 2}(\mathrm{~Hz})$ | $\delta(\mathrm{ppm})$ | $\Delta v_{1 / 2}(\mathrm{~Hz})$ |
| Py H2 | 108 | 5300 | No data. | No data. |
| Py H3 | 32.7 | 1700 | 35.27 | 174 |
| Py H4 | -8.1 | 590 | 12.92 | 117 |
| CMe $_{2}$ | 21.6 | 270 | 25.23 | 462 |
| Ph Ho | 10.2 | 160 | $119.99^{\mathrm{b}}$ | $1350^{\mathrm{b}}$ |
| Ph Hm | 7.4 | 27 | 5.42 | 48 |
| Ph Hp | 3.9 | 17 | 11.77 | 330 |

${ }^{\text {a }} \mathrm{CoCH}_{2}$ and $\mathrm{FeCH}_{2}$ were not observed, probably due to the broadness of the peaks and the large chemical shift induced directly by iron or cobalt. ${ }^{b}$ I think this assignment is not right in the original report ${ }^{151}$ and it is more reasonable to assign it as pyridine $H 2$ position. Because the phenyl group is far from the iron center compared with the pyridine, according to their X-ray structures, it should not show a line width larger than the $\mathrm{CMe}_{2}$ group. Also, one would expect for $(\mathrm{Py})_{2} \mathrm{FeR}^{\prime}{ }_{2}$ chemical shifts of coordinate pyridines similar to those observed for $(\mathrm{Py})_{2} \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$.

### 5.5 DFT study of labile cobalt(II) dialkyl complexes

All the cobalt(II) dialkyl complexes prepared here are paramagnetic and have a strong similarity to the corresponding iron analogs. Due to the broadness of the ${ }^{1} \mathrm{H}$ NMR
signals, simple integration is not always enough for unambiguous assignment. Therefore, a computational method, which has the capacity of predicting the paramagnetically shifted signals, can be a good tool to help the assignments. The application of this method to cobalt(II) dialkyl complexes will be illustrated here.

### 5.5.1 Principles of calculation of paramagnetic ${ }^{1} \mathrm{H}$ NMR

The theory of the paramagnetic chemical shifts has been discussed in detail in Chapter 2. Here, the details on how we ${ }^{\mathrm{XxXI}}$ do the calculation will be described briefly.

The observed paramagnetic chemical shift can be derived from three components and written as Eq. 5.1 (same as Eq. 2.2). ${ }^{92,190}$

$$
\begin{equation*}
\delta^{\mathrm{obs}}=\delta^{\mathrm{orb}}+\delta^{\mathrm{FC}}+\delta^{\mathrm{PC}} \tag{Eq. 5.1}
\end{equation*}
$$

In this equation, $\delta^{\text {orb }}$ is the reference chemical shift, which would be observed in a similar but diamagnetic environment. This contribution is not particularly sensitive to the temperature. We calculated $\delta^{\text {orb }}$ using Gaussian $03^{118}$ at the B3LYP/TZVP level after the geometry was optimized using Turbomole at b3-lyp/TZVP.

The Fermi contact term $\delta^{\mathrm{FC}}$ comes from the interaction between the nuclear magnetic moment and the average spin density at the position of the nucleus. It can be calculated according to Eq. 5.2 (similar to Eq. 2.4). ${ }^{191}$
${ }^{\text {xxxI }}$ The calculation of DFT was done by Peter H.M. Budzelaar and me.

$$
\begin{equation*}
\delta^{F C}=A_{i s o} \frac{g_{e} \beta_{e} S(S+1)}{g_{N} \beta_{N} 3 k T} \tag{Eq. 5.2}
\end{equation*}
$$

where,

- $A_{\text {iso }}$ is the isotropic hyperfine coupling constant, calculated using ORCA (B3LYP/TZVP). ${ }^{119}$
- $g_{e}$ is the rotationally averaged electronic $g$-value.
- $g_{\mathrm{N}}$ is the nuclear g-value.
- $\beta_{\mathrm{e}}$ and $\beta_{\mathrm{N}}$ are the Bohr and nuclear magnetons, respectively.
- $S$ is the total spin quantum number (multiplicity $=2 S+1$ )
- KT is the thermal energy.
$\delta^{\mathrm{PC}}$ is the pseudo-contact term which arises from the long-range dipolar interaction between the induced magnetic moment at the radical site and the nuclear magnetic moment. Its contribution to the total chemical shift is usually small, so it is normally neglected in the total calculation. ${ }^{93}$

The DFT calculations for high-spin (TMEDA) $\mathrm{CoR}_{2}\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$ (Table B. 2 in the Appendix B) and (Py) ${ }_{2} \mathrm{CoR}^{\prime}{ }_{2}$ (Table B. 3 in the Appendix B) with the b3-lyp functional predict tetrahedral structures similar to the corresponding X-ray structures, with the Co-N bond a little longer; the structures optimized with the b-p functional have somewhat larger deviations. In order to find which functional predicts more accurate ${ }^{1} \mathrm{H}$ NMR
shifts, both b3-lyp and b-p were used. Structures were optimized using the Turbomole package with both b3-lyp and b-p functionals and the ${ }^{1} \mathrm{H}$ NMR chemical shifts of $(\mathrm{Py})_{2} \mathrm{CoR}_{2},(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ and (TMEDA)CoR ${ }_{2}$ were calculated using B3LYP and BP86 with the Gaussian and Orca programs. Results for the B3LYP functional are shown in Table 5.6 (BP86 results are shown in Table B. 4 in the Appendix B).

Table 5.6. B3LYP calculation of paramagnetic ${ }^{1} \mathrm{H}$ shifts for Co complexes ${ }^{\mathrm{a}}$

| System | H | $\mathrm{A}_{\text {iso }}(\mathrm{MHz})$ | $\delta_{\text {orb }}(\mathrm{ppm})^{\text {a,b }}$ | $\delta_{\text {pred }}(\mathrm{ppm})^{\text {b }}$ | $\begin{array}{r} \delta_{\text {obs }} \\ (\mathrm{ppm}) \end{array}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ | Py H2 | 0.867 | 8.954 | 123.1 | 114 |
|  | Py H3 | 0.240 | 7.339 | 39.0 | 38.4 |
|  | Py H4 | -0.078 | 7.733 | -2.6 | -8.5 |
|  | $\mathrm{CoCH}_{2}$ | 2.756 | 1.360 | 364.3 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.063 | -0.492 | 7.8 | 10.3 |
| (TMEDA) $\mathrm{CoR}_{2}$ | $\mathrm{NCH}_{2}$ | 0.543 | 2.545 | 74.1 | 80 |
|  | $\mathrm{NMe}_{2}$ | 0.580 | 2.067 | 78.4 | 78 |
|  | $\mathrm{CoCH}_{2}$ | 2.797 | 1.203 | 369.5 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.079 | -0.209 | 10.1 | 9.6 |
| $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ | Py H2 | 0.865 | 8.630 | 122.5 | 108 |
|  | Py H3 | 0.227 | 7.054 | 36.9 | 32.7 |
|  | Py H4 | -0.068 | 7.521 | -1.5 | -8.3 |
|  | $\mathrm{CoCH}_{2}$ | 3.339 | 3.812 | 443.4 | n.o. |
|  | $\mathrm{CMe}_{2}$ | 0.147 | 0.905 | 20.3 | 21.6 |
|  | Ph Ho | -0.024 | 7.619 | 4.5 | 10.2 |
|  | Ph Hm | 0.022 | 7.227 | 10.1 | 7.4 |
|  | Ph Hp | -0.043 | 7.075 | 1.4 | 3.9 |

[^16]The correlation between calculated and experimentally observed chemical shifts is very high (correlation coefficient is 0.993 ) as indicated in Figure 5.5. In contrast, the
prediction by BP86 is consistently off (see Figure B. 1 in the Appendix B). Thus B3LYP predictions seem to be more reliable for cobalt(II) systems and will be used in the later calculation of paramagnetic ${ }^{1} \mathrm{H}$ NMR chemical shifts for cobalt(II) complexes in Chapter 6.


Figure 5.5. Comparison of calculated (B3LYP: $\delta^{\mathrm{orb}}+\delta^{\mathrm{FC}}$ only) and observed ${ }^{1} \mathrm{H}$ chemical shifts. (The solid line represents the ideal $\delta_{\text {obs }}=\delta_{\text {calc }}$ relation).

### 5.6 Conclusions

A new complex $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ was easily prepared from $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$ in high yield and high purity. Although its oily nature prevented full characterization, ${ }^{1} \mathrm{H}$ NMR, magnetic moment measurements (Evans method) and hydrolysis experiments clearly support the
constitution of the complex. In addition, the " $\mathrm{CoR}_{2}$ " fragment of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ can be transferred to TMEDA to form (TMEDA)CoR ${ }_{2}$ in high yield. The identification of (TMEDA)CoR ${ }_{2}$ was confirmed by single-crystal X-ray diffraction; the structure is the same as that reported by Hay-Motherwell and coworkers. ${ }^{185}$ Both complexes are stable at room temperature for at least one week. The new synthesis method will make their application more convenient. The structure of the related complex (Py) ${ }_{2} \mathrm{CoR}^{\prime}{ }_{2}$ was determined by single-crystal X-ray diffraction; it is similar to the iron analog. However, it is much less stable than $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and will not be as useful as a source of $\mathrm{CoR}^{\prime}{ }_{2}$. The ${ }^{1} \mathrm{H}$ NMR chemical shifts predicted for paramagnetic cobalt(II) dialkyl complexes have high correlation with experimentally observed chemical shifts. Thus the DFT computation of NMR chemical shifts was useful in the assignment of our paramagnetic ${ }^{1} \mathrm{H}$ NMR spectrum.

# Chapter 6. Experimental and computational study on the generation of $\mathbf{C o}(\mathrm{I})$ monoalkyl complexes 

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### 6.1 Introduction

A (DIP)Co(I) monoalkyl complex was found to be an intermediate on the path of conversion of (DIP) $\mathrm{CoCl}_{2}$ into the active species in ethylene polymerization. ${ }^{81}$ The standard method to make (DIP)cobalt(I) alkyl complex is to use a Grignard or organolithium reagent to reduce and alkylate the corresponding (DIP)cobalt(II) dihalides. However, for less hindered DIP ligands, reaction of RLi compounds with (DIP) $\mathrm{CoCl}_{2}$ complexes always produces significant impurities caused by R attack at the ligand skeleton, which makes purification problematic. ${ }^{192}$ What is worse is that this synthesis does not tolerate a wide variety of DIP-type ligands. How the final cobalt(I) alkyl is formed is not completely clear because the reaction involves both alkylation and reduction. The general opinion seems to be that the RLi reagent first does a singleelectron transfer to reduce the dihalide complex into a monohalide complex, which then reacts with another equivalent of organo-lithium reagent to generate the final product. ${ }^{81 b}$

[^17] experimental part in Chapter 9 are copied directly from the published paper.

However, whether (DIP) $\mathrm{CoR}_{2}$ or (DIP) CoRCl is an intermediate or not during the reduction procedure (alkylation could happen before reduction) is not clear at this point.

An alternative mild way to generate the cobalt alkyl complexes is to use labile-ligand cobalt alkyl precursors. To the best of our knowledge, there is no report on the synthesis using this strategy, probably because there was no easily accessible cobalt alkyl source. In Chapter 5, we succeeded in synthesizing $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$, (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}$ in a convenient way. The further application of these labile cobalt alkyl precursors will be explored in this chapter. Because $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}$ is not stable at room temperature, only stable $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ were applied to ligand-exchange reaction with DIP-type ligands to generate (DIP) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ or (DIP) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in the following content of this chapter, $\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ ).

### 6.2 Synthesis of (DIP)Co(I)R complexes

### 6.2.1 Choice of DIP-type ligands

In order to explore the potential for exchanging the labile ligand in these two cobalt dialkyl precursors by other ligands, DIP-type ligands in Figure 6.1 with different steric properties and combinations of $\sigma$-donor and $\pi$-acceptor abilities (see also Chapter 4 ) were explored.

1: $R=2,6-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$

5: $\mathrm{R}=2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$

6
2: $R=2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$
3: $R=\mathrm{C}_{6} \mathrm{H}_{5}$
4: $\mathrm{R}=\mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}$
7: $\mathrm{R}=2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$


9: $\mathrm{R}=2,6 \mathrm{-}^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$
$R^{\prime}=2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$


10: $\mathrm{Ar}=2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$
8: $R=2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}$


Figure 6.1. Structures of DIP type ligands examined

Of the ligands in Figure 6.1, only cobalt (I) alkyl complexes of ligands 1, 2, and 7 have been reported in the literature; they were generated by reaction of the (DIP) $\mathrm{CoCl}_{2}$ precursor with the organo-lithium reagent. ${ }^{81}$ Although iron dihalide complexes of ligands 3, 4, and $\mathbf{8}$ have been tested in ethylene polymerization, ${ }^{193}$ the cobalt alkyl complexes of these ligands have not been reported. In addition, the chromium trichloride complex of the bulky variation of ligand $\mathbf{1 0}$ was reported to be highly active in ethylene oligomerization, but showed no activity in ethylene polymerization. ${ }^{61 b}$

According to the DIP ligand-property study (see Chapter 4), ligands 1-4 are electronically similar to the commonly used DIP ligand 7 but have less steric-shielding ability; thus they were chosen to explore steric effects. The fluorinated ligand $\mathbf{5}$ is a stronger $\pi$ acceptor, but weaker $\sigma$-donor while ligand $\mathbf{6}$ is a much weaker $\pi$-acceptor than ligand 7
but a comparable $\sigma$-donor. Among the remaining two variations, ligand $\mathbf{8}$ is a weaker $\sigma$ donor and weaker $\pi$-acceptor than ligand 7 , while ligand 9 is a combination of imine and phosphinimine characters. Ligand $\mathbf{1 0}$ is a stronger $\sigma$-donor and stronger $\pi$-acceptor.

### 6.2.2 Ligand Exchange Study

Both (Py) ${ }_{2} \mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}\left(\mathrm{R}: \mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$ react rapidly with ligands $\mathbf{1}$ and $\mathbf{2}$ to cleanly generate purple diamagnetic cobalt(I) trimethylsilylmethyl complexes which can be easily identified by their characteristic ${ }^{1} \mathrm{H}$ NMR peaks ${ }^{\text {XXXIII }}$ : one is a triplet at $\delta=10.1$ $\mathrm{ppm}(\mathrm{Py} H 4)$, the other one is a singlet at $\delta=-1.2 \mathrm{ppm}(\mathrm{N}=\mathrm{CMe})$. The product from the reaction between ligand 2 and $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ was not obtained in crystalline form, but (1)CoR crystallizes well and was characterized by single-crystal X-ray diffraction. The structure is shown in Figure 6.2 and the comparison with the X-ray structure of (7)CoR is summarized in Table 6.1. The DIP skeleton in (1)CoR is similar to that in (7)CoR: $\mathrm{Co}(1)$ $\mathrm{N}(1), \mathrm{C}(1)-\mathrm{N}(2)$, and $\mathrm{C}(1)-\mathrm{C}(2)$ bond lengths are virtually identical, indicating a similar amount of electron transfer from the cobalt center to the conjugated $\pi$ system of DIP. In both cases, the alkyl groups are bent out of the $\mathrm{CoN}_{3}$ plane (defined by the central pyridine, cobalt and two imine bonds) by a similar amount (the trans NCoC angle is around $165^{\circ}$ ), which is most likely due to steric effects as (7)CoMe has a virtually linear NCoMe arrangement. ${ }^{216}$ In (1)CoR, the angle of Si-C-Co is around $10^{\circ}$ smaller and the torsion angle between the N -aryl ring and the imine bond is also around $5-10^{\circ}$ smaller

XXXIII The products from the $\cdot \mathrm{CH}_{2} \mathrm{SiMe}_{3}$ released end up as TMS and $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ detected by ${ }^{1} \mathrm{H}$ NMR.
than that in (7)CoR, which is probably due to the smaller repulsion between the bulky $\mathrm{SiMe}_{3}$ group and the 2,6-dimethylphenyl group.


Figure 6.2. X-ray structure of (1)CoR (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): $\mathrm{Co}(1)-\mathrm{N}(1): 1.834(2) ; \mathrm{Co}(1)-\mathrm{N}(2): 1.9165(15) ; \mathrm{C}(1)-\mathrm{N}(2): 1.330(2) ; \mathrm{C}(1)-\mathrm{C}(2): 1.434(3) ;$ $\mathrm{Co}(1)-\mathrm{C}(14): 1.964(3) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2): 80.63(5) ; \mathrm{Si}-\mathrm{C}(14)-\mathrm{Co}(1): 128.55(15) ; \mathrm{N}(1)-$ $\mathrm{Co}(1)-\mathrm{C}(14): 165.07(10)$.

Table 6.1. Comparison of the X-ray structures of (7) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ and (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$. (labelling of the atoms as in Figure 6.2; distances in $\AA$; angles in deg)

|  | $(1) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ | $(7) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ |
| ---: | ---: | ---: |
| $\mathrm{Co}(1)-\mathrm{N}(1)$ | $1.834(2)$ | 1.837 |
| $\mathrm{Co}(1)-\mathrm{N}(2)$ | $1.9165(15)$ | 1.920 and 1.929 |
| $\mathrm{C}(1)-\mathrm{N}(2)$ | $1.330(2)$ | 1.327 |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.434(3)$ | 1.436 |
| $\mathrm{Co}(1)-\mathrm{C}(14)$ | $1.964(3)$ | 1.984 |
| $\mathrm{~N}(1)-\mathrm{Co}(1)-\mathrm{N}(2)$ | $80.63(5)$ | 80.72 and 80.28 |
| $\mathrm{Si}-\mathrm{C}(14)-\mathrm{Co}(1)$ | $128.55(15)$ |  |
| $\mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{C}(14)$ | $165.07(10)$ | 139.56 |
| $\mathrm{C}(1)-\mathrm{N}(2)-\mathrm{C}(5)-\mathrm{C}(6)$ |  | 165.91 |
|  | 88.86 | 94.31 and 100.29 |
|  |  |  |

Steric shielding (relative to ligand 7) is further reduced in ligands 3 and 4. Although the reaction with both $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}$ seems to generate the cobalt(I) monoalkyl complexes, the results are complicated. On the one hand, both ligand $\mathbf{3}$ and $\mathbf{4}$ reacted with excess $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ to generate diamagnetic cobalt(I) monoalkyl complexes, but the Py H4 resonances of these products were found at "atypical" chemical shifts
compared to similar cobalt(I) alkyl complexes (Figure 6.3B and Figure 6.4B,C). For ligand 4, the newly generated cobalt(I) complex was very unstable, and started to decompose within 5 min (monitored by ${ }^{1} \mathrm{H} \mathrm{NMR}$ ). After 30 mins , an unknown purple precipitate started to form, and further identification was not successful. ${ }^{\text {XxXIV }}$ For ligand 3, the attempt to isolate the cobalt(I) product was also not successful and only decomposition was observed. On the other hand, both ligand 3 and 4 reacted with (TMEDA) $\mathrm{CoR}_{2}$ to generate a "normal" tridentate cobalt(I) alkyl complex (Figure 6.3A and Figure 6.4A) with chemical shifts at "normal" positions for (DIP)cobalt(I) alkyl complexes. However, further isolation was not successful due to instability of the products.

As stated above, there is a big difference between the ${ }^{1} \mathrm{H}$ NMR spectra of products generated from the reaction with $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and from (TMEDA)CoR ${ }_{2}$. A further experiment was carried out by adding free pyridine to the product generated from (TMEDA)CoR ${ }_{2}$ and ligand 4 (Figure 6.4D). The pyridine H 4 resonance in the resulting ${ }^{1} \mathrm{H}$ NMR spectrum is much closer to that obtained from direct reaction between the ligands and excess $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$. Therefore, the difference between the reactions with $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and (TMEDA)CoR ${ }_{2}$ is probably due to the difference in coordination properties between pyridine and TMEDA. Pyridine is relatively small and may coordinate to the cobalt(I) center to form (DIP)CoR(Py), while TMEDA has higher steric
xxxiv This unknown purple precipitate was suspected to be the (4) ${ }_{2}$ Co complex, due to the lower steric hindrance at imine-nitrogen position of ligand 4 and the possible disproportion of the $(4) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ might also lead to the generation of cobalt(0). ${ }^{67}$ (3) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ might have similar decomposition routes.
hindrance and no significant $\pi$-acceptor character, and will not coordinate to the cobalt(I) center.

Altogether, the decreased steric hindrance of $\mathbf{3}$ and $\mathbf{4}$ does not affect the generation of cobalt(I) alkyl complexes, but it does affect their stabilities.


Figure 6.3. Tentative assignment of ${ }^{1} \mathrm{H}$ NMR resonances for the reaction in $\mathrm{C}_{6} \mathrm{D}_{6}$ of ligand 3 with (A) an equimolar amount of (TMEDA) $\mathrm{CoR}_{2}$; $\mathrm{B}, \mathrm{C}$ ) excess $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ at two different concentrations. (* denotes $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$; the assignment of "h" peak is corrected from the published one)


Figure 6.4. Tentative assignment of ${ }^{1} \mathrm{H}$ NMR resonances for the reaction in $\mathrm{C}_{6} \mathrm{D}_{6}$ of ligand 4 with (A) excess (TMEDA) $\mathrm{CoR}_{2} ;(\mathrm{B}, \mathrm{C})$ excess $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ at two different concentrations; (D) mixture (A) with added Py. (* denotes $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$; assignment of "h" peak is corrected from the published one).

Ligand 5 comes from the earlier research where it was shown to be a better $\pi$-acceptor than standard ligand $\mathbf{2}$. The procedure for the synthesis of ligand $\mathbf{5}$ was kindly provided by Jon M. Malinoski (Brookhart group, UNC Chapel Hill). ${ }^{194}$ The structure was confirmed by single-crystal X-ray diffraction (Figure 6.5). The two N -aryls point away from the plane of the central pyridine ring in opposite directions, probably due to the high polarity of the $\mathrm{CF}_{3}$ groups. As a result, the two imine arms form a pseudo trans conformation.


Figure 6.5. X-ray structure of 5 (30\% thermal ellipsoids; hydrogen atoms omitted for clarity). Selected bond distances ( $\AA$ ) and torsion angles (deg): C(2)-C(5): 1.492(3); C(5)$\mathrm{N}(7): 1.267(3) ; \mathrm{N}(1)-\mathrm{C}(2)-\mathrm{C}(5)-\mathrm{N}(7): 134.98$.

When this better $\pi$-acceptor ligand 5 reacted with labile cobalt dialkyl complexes, the ${ }^{1} \mathrm{H}$ NMR spectrum of the immediate mixture of ligand 5 and $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ showed that a diamagnetic compound was generated (see Figure 6.6B and Figure 6.7B), but this species was not stable. After 2 h at room temperature in the NMR tube (Figure 6.7C), a black suspension had precipitated out. After hydrolysis of this mixture, ${ }^{19}$ F NMR showed the presence of free ligand 5 and some other fluorine-containing compounds. The Co(I) alkyl seems not to be stable enough for isolation, possibly due to a side reaction involving the trifluoro methyl group of the ligand. In addition, ${ }^{19} \mathrm{~F}$ NMR showed that there is no reaction between (TMEDA)CoR ${ }_{2}$ and ligand 5 after immediate mixing; longer standing resulted in decomposition.


Figure 6.6. ${ }^{1} \mathrm{H}$ NMR spectra for reaction in $\mathrm{C}_{6} \mathrm{D}_{6}$ of ligand 5 with excess $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ : (A) pure 5; (B) after addition of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$, showing a few tentative assignments. (* denotes $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$; assignment of h peak is corrected from the published one)


Figure 6.7. ${ }^{19} \mathrm{~F}$ NMR spectra for the reaction of ligand 5 with excess $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ : (A) pure 5; (B) after addition of (Py) $)_{2} \mathrm{CoR}_{2}$; (C) 2h after mixing; (D) after hydrolysis

As the above results indicate, the ligand-exchange reactions with ligands $\mathbf{1 - 5}$ involve a change in oxidation state of cobalt from II to I. Thus it is not a simple liganddisplacement reaction but involves the reduction of the cobalt center. The strong $\pi$ acceptor property of the DIP ligand accounts for the ease of this reduction. Thus we suspected that a ligand with weaker $\pi$-acceptor ability might not undergo this reduction and may cause only a simple ligand-exchange reaction which may allow the isolation of the cobalt(II) dialkyl complex. Pybox ligand 6 (previously calculated to be a weak $\pi$ acceptor but a comparable $\sigma$-donor, ${ }^{195}$ see Chapter 4) was used for this purpose. Indeed,
when it was reacted with $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ in an NMR tube, formation of a cobalt(I) alkyl complex was not observed. Instead, broad peaks characteristic of a paramagnetic product were observed in the ${ }^{1} \mathrm{H}$ NMR spectrum. Unfortunately, the reaction was not clean enough to allow isolation of the product. When Pybox 6 reacted with (TMEDA) $\mathrm{CoR}_{2}$, the same paramagnetic compound could be clearly identified but the reaction was an equilibrium (Figure 6.8) with an equilibrium constant of $0.9(1)$ (for computation of the equilibrium constant, see Table C. 1 in the Appendix C). The free ligand peaks are sharp, but TMEDA peaks are broad, possibly due to the exchange with (TMEDA)CoR ${ }_{2}$. This mixture decomposed in hours at room temperature, but was stable for longer times at -35 ${ }^{\circ} \mathrm{C}$.


Figure 6.8. ${ }^{1} \mathrm{H}$ NMR spectrum of "(6)CoR $\mathrm{C}_{2}$ ", still containing some (TMEDA) $\mathrm{CoR}_{2}$

When poor $\pi$-acceptor properties were maintained but the $\sigma$-donor properties were further reduced by using ligands $\mathbf{8}$ and $\mathbf{9}$, no reaction with (TMEDA) $\mathrm{CoR}_{2}$ was detected by ${ }^{1} \mathrm{H}$ NMR. This clearly showed that a certain $\sigma$-donor strength is required for successful ligand exchange.

The biscarbene 10 with better $\sigma$-donor and better $\pi$-acceptor properties reacted with both $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and (TMEDA)CoR ${ }_{2}$. Unfortunately, it did not generate any detectable products and only unidentified black solid was observed. As the reaction of the same type
of bis(carbene)pyridine ligand with (TMEDA)NiMe 2 or (TMEDA) $\mathrm{PdMe}_{2}{ }^{196}$ leads to alkyl migration from the metal center to coordinated imidazol-2-ylidenes followed by ring opening of the ligand, the same reaction might happen in our case and the possible intermediate generated might not be stable.

### 6.2.3 ${ }^{1} \mathrm{H}$ NMR of (6)CoR $\mathbf{C l}_{2}$

The ${ }^{1} \mathrm{H}$ NMR assignments for (6) $\mathrm{CoR}_{2}$ (Figure 6.8) are based on integration and comparison with (6) $\mathrm{FeR}_{2}$ (Table 6.2). The arrangement of peak positions of $\mathrm{SiMe}_{3}, \mathrm{Py}$ $\mathrm{H} 3, \mathrm{CH}_{2} \mathrm{O}$ and $\mathrm{CMe}_{2}$ are similar in the spectra of both the iron and the cobalt complexes. The significant difference is the signal due to pyridine H4. Thus the relative positions of the Py H3 and Py H4 signals in DIP cobalt and iron complexes were further studied by analyzing the known ${ }^{1} \mathrm{H}$ NMR spectra of $\mathrm{CoCl}_{2}, \mathrm{FeCl}_{2}, \mathrm{CoR}_{2}$ and $\mathrm{FeR}_{2}$ complexes of ligands in Figure 6.1; results are summarized in Table 6.3.

Table 6.2. Comparison of ${ }^{1} \mathrm{H}$ NMR shifts (ppm) for $(\mathbf{6}) \mathrm{MR}_{2}$ complexes $(\mathrm{M}=\mathrm{Co}, \mathrm{Fe})^{\mathrm{a}}$

|  | $(6) \mathrm{CoR}_{2}$ |  | $(6) \mathrm{FeR}_{2}{ }^{\mathrm{b}}$ |  |
| :--- | :---: | ---: | :---: | ---: |
|  | $\delta(\mathrm{ppm})$ | $\Delta v_{1 / 2}(\mathrm{~Hz})$ | $\delta(\mathrm{ppm})$ | $\Delta v_{1 / 2}(\mathrm{~Hz})$ |
| $\mathrm{SiMe}_{3}$ | 21.8 | 120 | 9.3 | 277 |
| $\mathrm{Py} \mathrm{H}_{3}$ | 44.4 | 80 | 25.1 | 224 |
| $\mathrm{Py} \mathrm{H}_{4}$ | -66.5 | 34 | 337 | 1074 |
| $\mathrm{CH}_{2} \mathrm{O}$ | -5.6 | 36 | -0.46 | 432 |
| $\mathrm{CMe}_{2}$ | -16.9 | 110 | -6.4 | 222 |

[^18]Table 6.3. Summary of ${ }^{1} \mathrm{H}$ NMR shifts (ppm) of the central pyridine ring protons in DIP iron and cobalt complexes ${ }^{\text {a }}$

| Entry | Complexes | Py $H_{3}$ | Py $H_{4}$ |
| :--- | :--- | ---: | ---: |
| 1 | $(\mathbf{1}) \mathrm{CoCl}_{2}{ }^{197}$ | N.R. | N.R. |
| 2 | $(\mathbf{1}) \mathrm{FeCl}_{2}{ }^{197}$ | 86.2 | 39.6 |
| 3 | $(\mathbf{1}) \mathrm{FeR}_{2}{ }^{151}$ | 58.12 | 279.42 |
| 4 | $(\mathbf{2}) \mathrm{CoCl}_{2}{ }^{197}$ | 111.4 | 36.14 |
| 5 | $(\mathbf{2}) \mathrm{FeCl}_{2}{ }^{197}$ | 83.7 | 40.1 |
| 6 | $(\mathbf{2}) \mathrm{FeR}_{2}{ }^{151}$ | 57.55 | 283.07 |
| 7 | $(\mathbf{5}) \mathrm{CoCl}_{2}{ }^{\mathrm{c}}$ | 113.7 | 33.4 |
| 8 | $(\mathbf{5}) \mathrm{FeCl}_{2}{ }^{\mathrm{c}}$ | 83.7 | 85.7 |
| 9 | $(\mathbf{6}) \mathrm{CoCl}_{2}{ }^{\mathrm{b}}$ | 78.4 | 11.7 |
| 10 | $(\mathbf{6}) \mathrm{FeCl}_{2}^{\mathrm{b}}$ | 61.5 | -7.65 |
| 11 | $(\mathbf{6}) \mathrm{FeR}_{2}{ }^{\mathrm{c}}$ | 25.1 | 337 |
| 12 | $(\mathbf{7}) \mathrm{CoCl}_{2}{ }^{197}$ | 117.1 | 49.91 |
| 13 | $(\mathbf{7}) \mathrm{FeCl}_{2}{ }^{197}$ | 81.7 | 81.1 |
| 14 | $(7) \mathrm{FeR}_{2}{ }^{151}$ | 52.39 | 306.41 |
| 15 | $(\mathbf{9}) \mathrm{CoCl}_{2}{ }^{\mathrm{c}}$ | 106 | 26.0 |
| 16 | $(\mathbf{9}) \mathrm{FeCl}_{2}{ }^{\mathrm{c}}$ | 86.6 | 39.9 |

${ }^{a}{ }^{1} \mathrm{H}$ NMR was measured in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. ${ }^{\text {b }}$ prepared by me (see experimental part) and ${ }^{1} \mathrm{H}$ NMR was performed in $\mathrm{CD}_{2} \mathrm{Cl}_{2} .{ }^{\mathrm{c}}$ See Section 9.1 on experimental part of Chapter 3 in Chapter 9.

As Table 6.3 indicates, in iron and cobalt dichloride complexes, the Py H3 signal moves downfield when replacing iron by cobalt for all ligands examined, while the change of the Py H4 chemical shifts does not show a consistent trend. For all ligands except Pybox 6, the Py H4 peak moves to higher field while in Pybox 6 complexes, the signals moved downfield. I would expect a similar variation of the pyridine $H 4$ chemical shift in their cobalt or iron dialkyl complexes. Thus Py H4 chemical shifts of (6) $\mathrm{CoR}_{2}$ in its high spin state and with tridentate coordination mode of ligand $\mathbf{6}$ would be expected to be larger than 337 ppm (entries 9-11).

The replacement of chlorine by alkyl induces a shift of the Py H3 peak to high field and of Py H4 shift to down field, which is suspected to have some correlation with the stronger $\pi$-back donation of the iron alkyl (entries 2-3, 5-6, 10-11, 13-14). A similar effect would also be expected for cobalt. Thus, replacement of chlorine by alkyl should lead to a downfield shift of Py $H 4$ when the coordination environments in the two metal complexes are otherwise equal. Compared with the corresponding cobalt dichloride, the chemical shift of the Py H4 peak in (6)CoR $\mathrm{C}_{2}$ would be expected to be much larger than 11.7 ppm if the coordination mode of the ligand $\mathbf{6}$ in this complex is tridentate and the cobalt center is high-spin (the multiplicity of the complex will be quartet).

However, based on the ${ }^{1} \mathrm{H}$ NMR spectrum we observed, the Py H4 peak in $(6) \mathrm{CoR}_{2}$ moves significantly to higher field. Thus, a bidentate coordination of ligand $\mathbf{6}$ and/or a low-spin state of the cobalt center seem likely.

### 6.2.4 Low temperature NMR study

The reactions of ligand $\mathbf{1}$ with both $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}$ were further studied by low-temperature NMR, aiming at detecting a hypothetical (1) $\mathrm{CoR}_{2}$ intermediate. The ${ }^{1} \mathrm{H}$ NMR spectrum for the reaction of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ with ligand $\mathbf{1}$ at low temperature showed broad peaks which could not be interpreted. However, reaction with (TMEDA) ${ }_{2} \mathrm{CoR}_{2}$ gave an interpretable ${ }^{1} \mathrm{H}$ NMR (Figure 6.9). At $-35{ }^{\circ} \mathrm{C}$, there is no reaction (Figure $6.9(1)$ ). At $0{ }^{\circ} \mathrm{C}$, a lot of product can be seen (Figure 6.9(3)). In the spectrum, apart from two reactants and one product, there are no peaks of other paramagnetic intermediates which can be detected. In other words, no intermediate between reactants and products was observed.


Figure 6.9. ${ }^{1} \mathrm{H}$ NMR of reaction of (TMEDA) $\mathrm{CoR}_{2}$ with ligand $\mathbf{1}$ at: 1$\left.)-35{ }^{\circ} \mathrm{C} ; 2\right)-20{ }^{\circ} \mathrm{C}$; 3) $0{ }^{\circ} \mathrm{C}$; 4) $25^{\circ} \mathrm{C}$.

### 6.3 Mechanism study by DFT

As the above illustrated, there is a significant difference between the reactions of ligand 1 and ligand 6 with $\mathrm{L}_{2} \mathrm{CoR}_{2}$ complexes (Scheme 6.1): the former involves a redox reaction and the latter does not. In order to explore the origin of this difference, these two systems were studied further by DFT using the b3-lyp functional (with parallel calculation using b-p for comparison).

L: Pyridine, TMEDA
$\mathrm{R}=-\mathrm{CH}_{2} \mathrm{SiMe}_{3}$


Scheme 6.1. Illustration of $\mathrm{L}_{2} \mathrm{CoR}_{2}$ with ligand $\mathbf{1}$ or $\mathbf{6}$

First, the structure of the (6)CoR ${ }_{2}$ complex $\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$ was explored by DFT. The ${ }^{1} H$ NMR spectrum showed that the complex has effective $\mathrm{C}_{2 \mathrm{v}}$ symmetry. Thus, the binding of the ligand in this complex can be tridentate or bidentate with rapid exchange of the two arms. Based on analysis of the ${ }^{1} \mathrm{H}$ NMR spectrum of cobalt and iron complexes, (6) $\mathrm{CoR}_{2}$ was estimated to be either in a high-spin state with a bidentate coordinate mode or in a low-spin state with a tridentate coordination mode. In order to approach the structure of $(\mathbf{6}) \mathrm{CoR}_{2}$, the geometries of $(\mathbf{6}) \mathrm{CoR}_{2}$ and $(\mathbf{1}) \mathrm{CoR}_{2}$ were optimized at both b3-lyp and b-p. However, the results are not simple. Both functionals predicted the expected geometries for both high-spin state and low-spin state. However, the energy difference between these two spin states was predicted differently: b-p predicted the low-spin state of $(\mathbf{6}) \mathrm{CoR}_{2}$ to be $10 \mathrm{kcal} / \mathrm{mol}$ lower than high-spin state while b3-lyp predicted the high-spin state to be $10 \mathrm{kcal} / \mathrm{mol}$ lower in energy. Thus which functional can best describe the spin state of $(\mathbf{6}) \mathrm{CoR}_{2}$ needs to be further explored. A
good way to decide this issue is to compare the property prediction with experimental results. For (6)CoR 2 , two pieces of experimental data are available: the chemical shifts in the ${ }^{1} \mathrm{H}$ NMR spectrum and the equilibrium constant between $(6) \mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}$.

Both functionals were firstly used to predict the equilibrium constant of the reaction between (TMEDA) $\mathrm{CoR}_{2}$ and ligand 6: b3-lyp predicts the free energy for this reaction to be $2.8 \mathrm{kcal} / \mathrm{mol}$ while b-p predicts it to be $-12.97 \mathrm{kcal} / \mathrm{mol}$ (Table C. 2 in the Appendix C). Clearly the prediction by b-p is far off and the b3-lyp predicts a value reasonably consistent with the experimental value $(\Delta G=0.04 \mathrm{kcal} / \mathrm{mol}) .{ }^{\mathrm{XXXV}}$ In contrast, the exchange equilibrium for $\mathbf{1}$ is predicted to be less favourable than for $\mathbf{6}$ (free energy is calculated to be $10 \mathrm{kcal} / \mathrm{mol}$ larger than for $\mathbf{6}$; see Table C. 2 in the Appendix C), which agrees with the observation that no paramagnetic intermediate for the reaction of (TMEDA)CoR ${ }_{2}$ with ligand $\mathbf{1}$ was detected by low temperature NMR (see Section 6.2.4). As the prediction of paramagnetic ${ }^{1} \mathrm{H}$ NMR shifts worked quite well for $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}$, we decided to apply it also to (6)CoR ${ }_{2}$. As mentioned in Chapter 5, the B3LYP functional works better than BP86 in predicting the ${ }^{1} \mathrm{H}$ NMR chemical shifts of cobalt(II) dialkyl complexes in high-spin states. Therefore, B3LYP was used for the

[^19]prediction of ${ }^{1} \mathrm{H}$ NMR chemical shifts of $(\mathbf{6}) \mathrm{CoR}_{2}$, but BP86 calculations were still done at the same time for comparison. The ${ }^{1} \mathrm{H}$ NMR chemical shifts for both high-spin and low-spin states of $(\mathbf{6}) \mathrm{CoR}_{2}$ were calculated and compared with experimental data (Table 7.1). For B3LYP, the calculated ${ }^{1} \mathrm{H}$ NMR shifts of high-spin (6)CoR ${ }_{2}$ are more consistent with the experimentally observed values, particularly the Py H 4 proton which is predicted to be at -134 ppm for high-spin (HS) state and +163 ppm for low-spin state (LS) (observed: -66.5 ppm). The effective $\mathrm{C}_{2 \mathrm{v}}$ symmetry in solution can be explained by rapid exchange between two alternative $\kappa^{2}$ (bidentate coordination mode) structures. In contrast, BP predictions are consistently off (see Table C. 3 in the Appendix C), though the high-spin state still gives better agreement. Thus, we tentatively identify our complex (6) $\mathrm{CoR}_{2}$ as being high spin with a $\kappa^{2}$-bound ligand. Structure labelling of various (6) $\mathrm{CoR}_{2}$ conformations is shown in Figure 6.10.

Table 6.4. Paramagnetic ${ }^{1} \mathrm{H}$ NMR shifts for Co complexes calculated at B3LYP ${ }^{\text {a }}$

| System | H | Aiso (MHz) | $\delta_{\text {orb }}(\mathrm{ppm})^{\text {a }}$ | $\delta_{\text {pred }}(\mathrm{ppm})$ | $\delta_{\text {obs }}(\mathrm{ppm})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (6) $\mathrm{CoR}_{2}$ | Py H3 | 0.266 | 8.526 | 43.5 | 44.4 |
| ( $\mathrm{HS}^{2}{ }^{\text {* }}$ ) | Py H4 | -1.081 | 7.722 | -134.6 | -66.5 |
|  | OCH2 | 0.143 | 4.153 | 22.9 | -5.6 |
|  | $\mathrm{NCMe}_{2}$ | 0.045 | 1.313 | 7.2 | -16.9 |
|  | $\mathrm{CoCH}_{2}$ | 1.785 | 1.203 | 236.2 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.067 | -0.209 | 8.6 | 21.8 |
| (6) $\mathrm{CoR}_{2}$ | Py H3 | 0.159 | 8.526 | 12.7 | 44.4 |
| $\left(\mathrm{LS} \mathrm{K}{ }^{3}\right)$ | Py H4 | 5.885 | 7.722 | 162.7 | -66.5 |
|  | OCH2 | -0.515 | 4.153 | -9.4 | -5.6 |
|  | $\mathrm{NCMe}_{2}$ | -0.074 | 1.313 | -0.6 | -16.9 |
|  | $\mathrm{CoCH}_{2}$ | 2.890 | 1.203 | 77.3 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.100 | -0.209 | 2.4 | 21.8 |

[^20]

Figure 6.10. Structures and different names of $(\mathbf{6}) \mathrm{CoR}_{2}$ complexes depending on the coordination mode of the ligand (in parenthesis is the relative electronic energy $(\mathrm{kcal} / \mathrm{mol})$ of (6) $\mathrm{CoR}_{2}$ the high-spin state calculated at b3-lyp/TZVP)

Based on ligand-exchange results with $\mathbf{1}$ and $\mathbf{6}$, the following mechanism for the reaction of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ with DIP-type ligands is proposed (Scheme 6.2). First, the DIP-ligand exchanges with pyridine in $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ to generate the high spin $\kappa^{2}$ intermediate, which can be easily converted to the low spin $\kappa^{3}$ state. Loss of one alkyl radical produces the corresponding cobalt(I) complex.



Scheme 6.2. Proposed mechanism for the formation of (DIP)CoR from $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$.

Because we are mainly concerned with how easily $\mathrm{Co}(\mathrm{II})$ dialkyl is converted to the $\mathrm{Co}(\mathrm{I})$ alkyl complex, the energy profiles for (6) $\mathrm{CoMe}_{2},(\mathbf{1}) \mathrm{CoMe}_{2},(\mathbf{6}) \mathrm{CoR}_{2}$ and (1) $\mathrm{CoR}_{2}$ from the high-spin $\kappa^{2}$ intermediates were calculated using the b3-lyp functional. As the whole conversion involves the spin change from $S=3 / 2$ to $S=1 / 2$, spin crossing was further explored. There are two possibilities where the spin flip happens: the spin flips before the second imine-arm coordinates to the metal center or simultaneously during the conversion from high-spin $\kappa^{2}$ to low-spin $\kappa^{3}$. Both possibilities were examined. The minimum-energy crossing point (MECP) (for basic theory see the Appendix C) approach ${ }^{198}$ was used to locate the crossing points between the $S=3 / 2$ and $S=1 / 2$ states starting from points closer to the $\kappa^{2}$ and $\kappa^{3}$ geometries of DIP cobalt complexes (the cross marks in Figure 6.11). The electronic energies for the whole reactions are plotted in Figure 6.11 (for energies of the individual compounds, see Table C. 4 in the Appendix C).



Figure 6.11. Reaction profiles for $\mathrm{CoMe}_{2}$ and $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ fragments bound to ligands 1 and $6(\triangle \mathrm{E}, \mathrm{b} 3-\mathrm{lyp} / \mathrm{TZVP}, \mathrm{kcal} / \mathrm{mol})$. Points marked $\times$ are minimum-energy crossing points (MECP) between HS and LS states; the others are local minima.

Compared with the total activation energies in Figure 6.11, spin flips are quite easy in these systems and do not cause significant barriers in the potential-energy profiles. As a
spin flip before the second imine arm of the DIP ligand binds to the cobalt center requires less energy to arrive at the low spin $\kappa^{3}$ cobalt dialkyl stage, this path was chosen in the calculation of the free-energy profiles (Figure 6.12, for energies of each individual compound, see Table C. 4 in the Appendix C). Structures of optimized complexes in Figure 6.12 are shown in Figure C. 3 and Figure C. 4 in the Appendix C.


Figure 6.12. Reaction profiles for $\mathrm{CoMe}_{2}$ and $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ fragments bound to ligands 1 and $6(\Delta \mathrm{G}, \mathrm{b} 3-\mathrm{lyp} / \mathrm{TZVP}, \mathrm{kcal} / \mathrm{mol})$. Points marked $\times$ are minimum-energy crossing points (MECP) between HS and LS states; the others are local minima. Thermal
corrections to the energies of crossing points are rough estimates by averaging the two thermal corrections to adjacent high-spin $\kappa^{2}$ or $\kappa^{2^{*}}$ and to adjacent low-spin $\kappa^{2}$ or $\kappa^{2^{*}}$ minima.

As Figure 6.12 indicates, to form the low-spin $\kappa^{2}$ complex, Pybox 6 needs around 5 $\mathrm{kcal} / \mathrm{mol}$ more than 1 for $\mathrm{CoMe}_{2}$, and only $2 \mathrm{kcal} / \mathrm{mol}$ more than $\mathbf{1}$ for $\mathrm{CoR}_{2}$. The subsequent coordination of the second imine arm to form the low-spin $\kappa^{3}$ structure is different in different cases. As for $\mathrm{CoMe}_{2}$, the formation of low spin $\kappa^{3}$ structure is more favourable for ligand $\mathbf{1}$, but is around $12 \mathrm{kcal} / \mathrm{mol}$ uphill for ligand $\mathbf{6}$, probably due to the larger steric hindrance in $\mathbf{6}$. For $\mathrm{CoR}_{2}$, the formation of low-spin $\kappa^{3}$ states from low-spin $\kappa^{2}$ state is unfavourable for both ligand $\mathbf{1}$ and ligand $\mathbf{6}$, and requires $4 \mathrm{kcal} / \mathrm{mol}$ more in energy for ligand $\mathbf{6}$ than ligand $\mathbf{1}$. Apparently, the observation of ( $\mathbf{6}) \mathrm{CoR}_{2}$ can be partly explained by the greater reluctance of the second imine arm to approach the cobalt center in $(\mathbf{6}) \mathrm{CoR}_{2}$. Once the low spin $\kappa^{3}$ intermediate formed, loss of a $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ radical is favourable for both $\mathbf{1}$ and $\mathbf{6}$ in the $\mathrm{CoR}_{2}$ case (although loss of Me is not).

In all, as Figure 6.12 indicated, loss of the alkyl radical from high-spin (6) $\mathrm{CoR}_{2}$ requires $6 \mathrm{kcal} / \mathrm{mol}$ more than from (1) $\mathrm{CoR}_{2}$, which is believed to be consistent with the fact that between them only (6) $\mathrm{CoR}_{2}$ was detected by ${ }^{1} \mathrm{H}$ NMR.

### 6.4 Conclusions

The "CoR ${ }_{2}$ " fragment in $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}$ can be transferred to DIP-type ligands as long as the ligand has certain steric protection and certain strength of $\sigma$-donor ability. Strong $\pi$-acceptors favour the formation of a cobalt(I) alkyl complex. The proposed mechanism for the formation of (DIP)CoR from $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ involves the exchange of the ligand to form the high-spin $\kappa^{2}$ cobalt(II) dialkyl, then a spin flip, followed by binding of the second arm, and loss of an alkyl radical to form the final products. A DFT study of this mechanism supports the experimental results.

# Chapter 7. Binuclear reduction of organic halides by cobalt(0) intermediates 

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There are two main types of oxidative addition mechanisms by transition-metal complexes. The most common type, mononuclear oxidative addition, involves a change in metal oxidation state by two and an increase of the coordination number by two (Eq.7.1 in Scheme 7.1). A second, much less common type, binuclear oxidative addition, involves two separate metal centers and produces two separate metal complexes; the oxidation state of each metal center changes by one (Eq. 7.2 in Scheme 7.1). Although main-group metals can also be involved in this second type of reaction (e.g. direct synthesis of organolithium reagents using the metal and the corresponding organic halides), the reaction is usually heterogeneous and happens primarily at the metal surface.
xxxvi Part of Figures, part of Tables and part of Schemes are copied directly from the published papers if available. Part of the text of the corresponding experimental part in Chapter 9 is copied directly from the published papers if available.

Here we are interested in homogeneous oxidative addition at transition metal centers. Binuclear oxidative addition is found mostly with first-row transition metals because they prefer high-spin states and more easily undergo 1-e oxidation.

$$
\begin{align*}
& \mathrm{M}^{\mathrm{n}+}+\mathrm{C}-\mathrm{X} \longrightarrow \mathrm{C}^{\mathrm{M}^{(\mathrm{n}+2)}} \mathrm{X}  \tag{Eq. 7.1}\\
& 2 \mathrm{M}^{\mathrm{n}+}+\mathrm{C}-\mathrm{X} \longrightarrow \mathrm{M}_{\mathrm{C}}^{(\mathrm{n}+1)}+\mathrm{M}^{(\mathrm{n}+1)} \tag{Eq. 7.2}
\end{align*}
$$

Scheme 7.1. Oxidative addition of transition-metal complexes

In this chapter, I concentrate on binuclear oxidative addition of aryl halides and possible applications of the resulting products. The structures of ligands that are relevant to the research described in this chapter are collected in Table 7.1.

Table 7.1. Ligands used in Chapter 7


| Name | Ar |
| :---: | :---: |
| $\mathbf{1}$ | $2,6-\mathrm{Me}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}$ |
| $\mathbf{2}$ | $2,4,6-\mathrm{Me}_{3}-\mathrm{C}_{6} \mathrm{H}_{2}$ |
| $\mathbf{3}$ | $2,6-\mathrm{Et}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}$ |
| $\mathbf{4}$ | $2,6-{ }^{-} \mathrm{Pr}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}$ |

### 7.1 Binuclear oxidative addition

There are only a few well-defined examples for the breaking of carbon-halogen bonds by transition metals in the binuclear mode ${ }^{73,199-202}$ and they seem to be limited to $\mathrm{Cr}, \mathrm{Fe}$ and (low-spin) Co centers.

Recently, ${ }^{199 b}$ Chirik and coworkers have done extensive studies on the chemistry of diiminepyridine (DIP) iron complexes. (4) $\mathrm{Fe}\left(\mathrm{N}_{2}\right)_{2}$ was found to be efficient at breaking alkyl-bromine or vinyl bromine bonds (Scheme 7.2). ${ }^{199 a}$ Later on, the same complex was even found to be able to cleave acyl and ether C-O bonds of esters, ${ }^{73}$ and to activate the $\mathrm{N}-\mathrm{N}$ bond of diazoalkanes. ${ }^{199 b}$


Scheme 7.2. Reaction of $(4) \mathrm{Fe}\left(\mathrm{N}_{2}\right)_{2}$ with EtBr

Similar to complexes of DIP-type ligands, transition metal complexes with $\beta$ diketiminate ligands have also attracted a lot of attention; its strong $\sigma$-donor ability makes the $\beta$-diketiminate ligand special. Smith and coworkers used $\beta$-diketiminato chromium(II) complexes for single-electron oxidative addition of $\mathrm{CH}_{3} \mathrm{I}$ to generate the
corresponding $\mathrm{Cr}(\mathrm{III})$ iodide and $\mathrm{Cr}(\mathrm{III})$ alkyl species as shown in Scheme 7.3. ${ }^{200}$ In addition, simple chromium(II) sulphate in aqueous solution reacts with benzyl bromide in a similar manner. ${ }^{201}$


Scheme 7.3. Reaction of a $\mathrm{Cr}(\mathrm{II})$ complex with $\mathrm{CH}_{3} \mathrm{I}$

Low-spin cobalt(II) complexes were explored systematically by Halpern and coworkers decades ago. ${ }^{202}$ Examples include $\mathrm{Co}(\mathrm{CN})_{5}{ }^{3-}, \quad \mathrm{Co}($ saloph $) \mathrm{B}$ (saloph $=\mathrm{N}, \mathrm{N}^{\prime}-$ bis(salicylidene)-o-phenylenediamine, $B=$ amine or phosphine ligand), and bis(dioximato)cobalt(II) complexes. They were found to react with organic halides to form $\mathrm{Co}(\mathrm{III}) \mathrm{R}$ and $\mathrm{Co}(\mathrm{III}) \mathrm{X}$. Activated alkyl halides such as benzyl bromide or alkyl bromide with an electron-withdrawing group next to the bromine atom were the main substrates studied.

For all three types of metal complexes, the substrates that undergo addition have relatively reactive C-X bonds (C-I or activated C-Br). Only a single example of aryl
halide addition was reported by Halpern and coworkers: the reaction of 2-iodopyridine and $\mathrm{Co}(\mathrm{CN})_{5}{ }^{3-}$ (Scheme 7.4) was proposed to go through an atom-transfer mechanism. ${ }^{202 \mathrm{a}}$


Scheme 7.4. Reaction of $\mathrm{Co}(\mathrm{CN})_{5}{ }^{3-}$ with 2-iodopyridine

In contrast, inexpensive aryl chlorides have not been reported as substrates for this type of reaction. During my research on the reactivity of cobalt(I) alkyl complexes, the complex (1)Co( $\mathrm{N}_{2}$ ) (Figure 7.1) was found to be able to perform this type of reaction, especially for aryl chloride substrates, which will be illustrated in this chapter.


Figure 7.1. Structure of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$

### 7.2 CC coupling reactions

Carbon-carbon coupling reactions, such as Suzuki-Miyaura reactions, ${ }^{203}$ are very useful in organic synthesis for constructing carbon skeletons, and a variety of catalysts have been developed to facilitate these reactions. ${ }^{204}$ Palladium and nickel are the most-used metals and have been used frequently to make pharmaceuticals because of their high efficiency and wide substrate tolerance. ${ }^{205}$ The main mechanism for breaking the aryl carbon-halogen bond is oxidative addition by insertion of the metal center into the carbon-halogen bond (Scheme 7.5). ${ }^{206}$


Scheme 7.5. Mechanism for the catalytic carbon-carbon coupling reactions (Suzuki reaction)

Because of the close side-on approach of the C-X bond to the metal required for oxidative addition, these catalysts are sensitive to steric hindrance at the halide substrate. In particular, application to $\mathrm{C}_{\mathrm{sp} 3}-\mathrm{C}_{\mathrm{sp} 3}$ coupling is problematic. In addition, the high price of these metals and environmental concerns has pushed researchers to find alternatives.

One intensively studied metal is copper. ${ }^{207}$ Although the efficiency is generally much lower, copper has some distinct advantages: lower cost, lower air sensitivity, and lower toxicity. There are several mechanisms proposed for the breaking of aryl-carbon halogen bonds by copper, including widely accepted oxidative addition/reductive elimination, ${ }^{208}$ electron transfer ${ }^{209}$ (in carbon-heteroatom coupling reactions) and iodine atom transfers ${ }^{209}$ (in carbon-heteroatom coupling reactions).

On the other hand, the combination of a cobalt(II) salt with a reducing metal such as zinc or manganese has recently been used to catalyze carbon-carbon bond formation, especially for coupling between organic halides and organometallic reagents such as Grignard reagents. ${ }^{210}$ These somewhat-ill-defined catalysts can catalyze $\mathrm{C}_{\mathrm{sp} 2}-\mathrm{C}_{\mathrm{sp} 2}$ bond formation efficiently, but the more interesting aspect of the cobalt catalyst is its ability to accommodate alkyl halide substrates and form $\mathrm{C}_{\mathrm{sp} 3}-\mathrm{C}_{\mathrm{sp} 3}$ bonds. Although mechanisms similar to those of palladium centers were proposed, evidence for the involvement of radicals was also obtained. ${ }^{211} \operatorname{Cobalt}(0)$ or cobalt(I) centers are proposed as the species that enter the catalytic cycle; however, the nature of the real active species is still not clear.

### 7.3 Reactivity studies of less-hindered (DIP)CoR ( $\mathrm{R}=$ alkyl)

Featuring most prominently in the Fe and Co chemistry of DIP ligands is ligand 4. Highly hindered (4)CoR was the main cobalt(I) alkyl species in the literature due to the fact that (4) $\mathrm{CoCl}_{2}$, reported first by the group of Brookhart and the group of Gibson in 1998, ${ }^{16,17}$
is an efficient catalyst in ethylene polymerization; (4)CoR was shown to be an intermediate during activation of precursors with MAO. ${ }^{81}$ Steric hindrance seems to be a requirement for achieving high catalytic efficiency (see Chapter 1). Up to now, there are two main types of catalysis which have been studied for (DIP)CoR complexes: ethylene polymerization ${ }^{55,81 a, 216}$ and olefin hydrogenation. ${ }^{85,216}$ As ethylene polymerization is not the focus of this thesis (for more background, see Chapter 1), here I will concentrate on hydrogenation. Hydrogenation with (4)CoR has been studied by both the group of Gibson ${ }^{212}$ and the group of Budzelaar. ${ }^{85}$ The intermediate (4) CoH is only stable for a few hours and an equilibrium between (4)CoH and a $\mathrm{C}-\mathrm{H}$ activated complex was observed. In contrast, the reaction of the less-hindered (3)CoR with dihydrogen only led to unknown paramagnetic compounds, although olefins can still be hydrogenated using (3)CoR. ${ }^{85}$ Thus, steric hindrance seems to play an important role in the chemistry of (DIP) $\mathrm{Co}(\mathrm{I})$ complexes. ${ }^{213}$ In the present chapter, I focus on the even less-hindered ligand $\mathbf{1 .}$

### 7.4 Cobalt(0) intermediates

When purple (1)CoR $\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$ reacted with dihydrogen gas in the absence of dinitrogen, a lot of black solids were generated; however, in the presence of dinitrogen gas or in THF solvent, formation of these black solids was suppressed. Under a dinitrogen atmosphere, a green solution was obtained and a paramagnetic complex could
be detected by ${ }^{1} \mathrm{H}$ NMR (broad peaks at around 5 ppm and 17 ppm ) together with around $5-10 \%$ diamagnetic impurities ${ }^{\mathrm{XXXVII}}$ (Figure 7.2).


Figure 7.2. ${ }^{1} \mathrm{H}$ NMR spectrum of the green solution generated by adding 2.0 mL of $\mathrm{H}_{2}(\mathrm{~g})$ to (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ in benzene- $d_{6}$ under a nitrogen atmosphere (* denotes diamagnetic impurities)

XXXVII For possible approaches to identify these unknown side products, see the Outlook section in Chapter 8

As the ${ }^{1} \mathrm{H}$ NMR spectrum does not provide enough information on the product generated, EPR characterization of this green complex was subsequently done; ${ }^{214}$ the spectrum is shown in Figure 7.3. The X-band EPR spectrum in frozen toluene (at 77 K ) reveals a rhombic $g$-tensor $\left(g_{x}=1.967, g_{y}=2.019, g_{z}=2.130\right)$ with resolved cobalt hyperfine couplings along $g_{x}(77 \mathrm{MHz})$ and $g_{z}(60 \mathrm{MHz})$. These values suggest that this paramagnetic compound is a primarily ligand-centered radical yet experiencing substantial (spin-orbit) influence from cobalt. Thus this complex was suspected to be (1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ and has a ligand-centered radical character which agrees with (DIP) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ complexes reported by Chirik. ${ }^{215}$


Figure 7.3. Experimental and simulated X-band EPR spectrum of $(\mathbf{1}) \operatorname{Co}\left(\mathrm{N}_{2}\right)$ in frozen toluene at 70 K (generated by reacting (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with $\mathrm{H}_{2}$ in toluene at RT under a nitrogen atmosphere). Frequency 9.376539 GHz , modulation amplitude 4 gauss, microwave power 0.2 mW

In order to further verify the nature of this paramagnetic green solution, (1) $\operatorname{Co}\left(\mathrm{N}_{2}\right)$ was also prepared according to the procedure reported by Chirik. ${ }^{215}$ The crude product showed the same ${ }^{1} \mathrm{H}$ NMR spectrum as that obtained by hydrogenation of (1)CoR. The further reaction with chlorobenzene generated the same product mixture with the same ratio of two products $((\mathbf{1}) \mathrm{CoCl}$ and (1)CoPh, see section 7.5) as the green solution derived from (1)CoR $+\mathrm{H}_{2}$. In addition, (1)Co( $\mathrm{N}_{2}$ ) synthesized by these two methods showed the same NN stretching frequency ( $v_{\mathrm{NN}} 2084 \mathrm{~cm}^{-1}$ ) in the IR spectra of their KBr pellets (for the IR spectrum, see Figure D. 3 in Appendix C; the NN stretching frequency $v_{\mathrm{NN}}$ in toluene was reported to be $2093 \mathrm{~cm}^{-1}$ reported by Chirik $\left.{ }^{215}\right)^{\text {XXXVIIII }}$. Therefore, We assume the green solution generated by hydrogenolysis of (1)CoR contains $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)^{\mathrm{XXXIX}}$. Because the hydrogenation of (1)CoR to generate (1) $\operatorname{Co}\left(\mathrm{N}_{2}\right)$ is much more convenient than the sodium amalgam method, I stick to this method in the following reactions. As (1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ was generated in situ (no separate isolation is done), the amount of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ will be assumed to be equal to that of (1)CoR used.

The generation of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ from (1)CoR involves a one-oxidation-state change and most likely goes through (1) CoH as an intermediate. Although I was unable to isolate this intermediate, trapping reactions clearly supported this. Hydrogenolysis of (1)CoR in the

[^21]presence of diphenylacetylene resulted in the generation of the corresponding (1) $\mathrm{CoC}(\mathrm{Ph})=\mathrm{CHPh}$ product (Figure 7.4). Figure 7.4a shows that a new triplet at around 10.2 ppm emerged, although there was still some starting material (1)CoR (Py H4: 10.0 ppm, triplet) left. Further addition of dihydrogen gas consumed all (1)CoR and led to fairly pure $(\mathbf{1}) \mathrm{CoC}(\mathrm{Ph})=\mathrm{CHPh}$. In contrast, the reaction of $(\mathbf{1}) \mathrm{CoR}$ in the presence of excess phenylacetylene generated a different cobalt(I) complex through insertion of the intermediate (1) $\mathrm{CoC} \equiv \mathrm{CPh}$ into another molecule of $\mathrm{PhC} \equiv \mathrm{CH},{ }^{\mathrm{XL}}$ and the ${ }^{1} \mathrm{H}$ NMR spectrum strongly indicates the structure as $(1) \mathrm{CoC}(\mathrm{Ph})=\mathrm{C}(\mathrm{H}) \mathrm{C} \equiv \mathrm{CPh}$ by comparison with (4) CoBz. ${ }^{216}$

[^22]

Figure 7.4. ${ }^{1} \mathrm{H}$ NMR spectra for the reaction of $(\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ under nitrogen in the presence of $\mathrm{Ph}_{2} \mathrm{C}_{2}$, with a) 1.5 mL of $\mathrm{H}_{2}(\mathrm{~g})$; b) 3.6 mL of $\mathrm{H}_{2}(\mathrm{~g})$,

Additional convincing evidence was obtained from the trapping reaction using $p$ chlorobenzonitrile, which cleanly furnished the corresponding (1) $\mathrm{CoN}=\mathrm{CHPh}-4-\mathrm{Cl}$ as the only product. The structure of this complex was verified by single-crystal X-ray diffraction (Figure 7.5).


Figure 7.5. X -ray structure of (1)CoN=CHPh-4-Cl (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): $\mathrm{Co}(1)-\mathrm{N}(1): 1.804(4) ; \mathrm{Co}(1)-\mathrm{N}(2): 1.896(4) ; \mathrm{Co}(1)-\mathrm{N}(3): 1.899(4) ; \mathrm{Co}(1)-\mathrm{N}(4)$ : $1.726(4) ; \mathrm{C}(12)-\mathrm{N}(2): 1.336(6) ; \mathrm{C}(12)-\mathrm{C}(13): 1.423(7) ; \mathrm{C}(18)-\mathrm{N}(3): 1.330(6) ; \mathrm{C}(17)-$ $\mathrm{C}(18): 1.453(7) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2): 81.46(17) ; \mathrm{N}(4)-\mathrm{Co}(1)-\mathrm{N}(2): 98.79(19) ; \mathrm{N}(4)-\mathrm{Co}(1)-$ $\mathrm{N}(1): 178.1$ (2); $\mathrm{C}(41)-\mathrm{N}(4)-\mathrm{Co}(1): 169.9(5) ; \mathrm{N}(4)-\mathrm{C}(41)-\mathrm{C}(42): 124.3(6) ; \mathrm{N}(2)-\mathrm{Co}(1)-$ $\mathrm{N}(3): 162.9(17) ; \mathrm{C}(18)-\mathrm{N}(3)-\mathrm{Co}(1): 116.8(3) ; \mathrm{C}(12)-\mathrm{N}(2)-\mathrm{Co}(1): 116.2$ (3).

In Figure 7.5 , the angle of $\mathrm{C}(41)-\mathrm{N}(4)-\mathrm{Co}(1)$ is close to $180^{\circ}$, which indicates significant ionic bonding between the cobalt center and the imine nitrogen atom. The imine bond length ( $1.33 \AA$ ) of the DIP ligand skeleton indicates a one-electron transfer from cobalt to the DIP ligand. The structure of DIP in this complex is similar to that in (2) $\mathrm{CoCl} .{ }^{216}{ }^{1} \mathrm{H}$ NMR chemical shifts of the coordinated DIP ligand (especially Py H3 and Py H4) are closer to those of the free ligand than those in cobalt(I) alkyl derivatives, which probably can be rationalized by a larger singlet-triplet separation ${ }^{\mathrm{XLI}}$ (Figure 7.6). ${ }^{83}$


Figure 7.6. ${ }^{1} \mathrm{H}$ NMR spectra of $(\mathbf{1}) \mathrm{Co}(\mathrm{N}=\mathrm{CH}) \mathrm{PhCl}(2$, black) vs free ligand $(1$, red $)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$

[^23]
### 7.5 Oxidative addition of organic halides

### 7.5.1 Model reaction

When (1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ reacted with one equivalent of 4-chlorotoluene, the solution color changed from green to purple and the ${ }^{1} \mathrm{H}$ NMR spectrum clearly showed two diamagnetic cobalt(I) complexes (two triplets at around 10 ppm and two singlets at around -1 ppm ) as shown in Figure 7.7. However, these two complexes could not be separated successfully.


Figure 7.7. ${ }^{1} \mathrm{H}$ NMR spectrum of product mixture from the reaction between $(\mathbf{1}) \operatorname{Co}\left(\mathrm{N}_{2}\right)$ and 4-chlorotoluene

In order to further verify the constitution of these two complexes in Figure 7.7, an authentic sample of each compound was prepared independently: (1) CoCl was made by reducing (1) $\mathrm{CoCl}_{2}$ with Na amalgam. ${ }^{215}$ (1) $\mathrm{CoPhMe}-4$ was prepared by reacting (1) $\mathrm{CoCl}_{2}$ with 4-MePhLi at room temperature; its structure was verified by single-crystal X-ray diffraction (Figure 7.8). This is the only structurally characterized DIP cobalt aryl complex reported to date. The structure in Figure 7.8 is similar to the corresponding cobalt(I) alkyl complex ${ }^{217}$ with the cobalt center having a distorted square-planar geometry. The tolyl ring is not perpendicular to the $\mathrm{N}_{3}$ plane but makes an angle of $67.94^{\circ}$ with it.


Figure 7.8. X-ray structure of (1)CoPh-4-Me (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): $\mathrm{Co}(1)-\mathrm{N}(1): 1.829(2) ; \mathrm{Co}(1)-\mathrm{N}(2): 1.905(2) ; \mathrm{Co}(1)-\mathrm{N}(3): 1.910(2) ; \mathrm{Co}(1)-\mathrm{C}(1):$
$1.945(3) ; \mathrm{N}(2)-\mathrm{C}(14): 1.329(4) ; \mathrm{N}(3)-\mathrm{C}(13): 1.330(4) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{N}(2): 80.84(11) ; \mathrm{N}(1)-$ $\mathrm{Co}(1)-\mathrm{N}(3): 80.97(11) ; \mathrm{N}(1)-\mathrm{Co}(1)-\mathrm{C}(1): 172.45(12)$.

The identification of each complex in the mixture was done by comparing peaks of the corresponding ${ }^{1} \mathrm{H}$ NMR spectra of the pure complexes with those of the product mixture. The two products are not formed in a 1:1 ratio but in about (1)CoAr: $(\mathbf{1}) \mathrm{CoCl}=0.59: 1.00$ and this ratio is reproducible.

### 7.5.2 Reaction conditions

Encouraged by these results, the stoichiometry of the reaction was first studied by varying the ratio of cobalt complex: aryl halides ( $0.5,1.0,2.0$ ), using $p$ trifluoromethylphenylchloride $\left(\mathrm{CF}_{3} \mathrm{PhCl}\right)$ as the aryl halide substrate. The advantage of this substrate is that it has a clear ${ }^{19} \mathrm{~F}$ signal, and that signals due to the reactant and possible products are unlikely to overlap. The results showed that the relative ratio of two products $((\mathbf{1}) \mathrm{CoAr}$ and $(\mathbf{1}) \mathrm{CoCl})$ was not affected by the ratio of reactants. However, the conversions of the two reactants are indeed affected by increasing the amount of aryl halide: the yield of cobalt complexes (the total amount of (1) CoAr and (1) CoCl relative to (1)CoR used) changed slightly from $78 \%$ to $85 \%$, ${ }^{\text {XLII }}$ while the conversion of the aryl halides decreased dramatically from $96 \%$ to $28 \%$. With the ratio of two reactants kept at
${ }^{\text {XLII }}$ Error margin probably $\sim 5 \%$. The ratio of (1)CoAr to (1)CoCl in the ${ }^{1} \mathrm{H}$ NMR spectrum is used to determine the amount of cobalt products and the ratio of $\mathrm{CF}_{3} \mathrm{PhCl}$ to (1)CoAr in the ${ }^{19} \mathrm{~F}$ NMR spectrum is used to determine the total amount of remaining aryl halide. The amount of $\mathrm{CF}_{3} \mathrm{PhCl}$ consumed is assumed to be equal to the amount of (1) CoCl produced.
$1: 1$, further reduction of the concentration of reactants (to one half) did not change the ratio of the two products. However, the change of solvent from benzene- $d_{6}$ to THF- $d_{8}$ slowed down the reaction rate significantly (from hours in benzene- $d_{6}$ to days in THF- $d_{8}$ ) and produced a lower yield of cobalt(I) aryl ( 0.68 in THF- $d_{8}$ vs 0.77 in benzene- $d_{6}$ ), probably due to the stronger coordination of THF to the cobalt center than dinitrogen (in other words, it is harder for the aryl radical to approach the cobalt( 0 ) center, thereby resulting in higher yield of the side products such as ArH or ArAr ). In addition, the reaction of hindered $(4) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with $\mathrm{CF}_{3} \mathrm{PhCl}$ generated only a small amount of cobalt(I) aryl product, together with a trace amount of (4) CoH ((4) $\mathrm{CoAr}:(4) \mathrm{CoCl}:(4) \mathrm{CoH}=$ 0.14:1.00:0.11). Thus it seems that ligand $\mathbf{1}$ possesses a good combination of steric and electronic properties for the generation of cobalt(I) aryl products through this binuclear mode.

Because the cobalt(I) aryl product is an organometallic reagent which might react with excess organic halides, test reactions between cobalt(I) aryls or alkyls and organic halides were subsequently done. When iodobenzene (which is relatively reactive) was added to (1) CoPh , the ${ }^{1} \mathrm{H}$ NMR spectrum indicated no reaction even after one week. In contrast, when (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ reacted with excess methyl iodide, trimethylethylsilane was detected by ${ }^{1} \mathrm{H}$ NMR (Figure 7.9, a quartet peak at 0.45 ppm ). The connection of the ethyl group to silicon was supported by H-Si HMBC (Figure D. 1 in the Appendix D). However, there is no reaction with butyl chloride or hexyl bromide. Further C-C coupling reactions will be explored later in this chapter.


Figure 7.9. ${ }^{1} \mathrm{H}$ NMR spectrum from the reaction between $(\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with MeI in benzene- $d 6$

Apparently, (1)CoR compounds do not activate aryl halides, but can be reactive toward alkyl halides. Therefore, it is safe to carry out reactions of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with excess $\operatorname{ArX}$, but for reactions with alkyl halides, a ratio of $\mathrm{RX}:(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)=0.5$ was used to avoid further reactions.

### 7.5.3 Scope of reactions

As $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ can successfully break the aryl carbon-chlorine bond in 4-chlorotoluene, a variety of aryl chlorides and bromides with different electronic and steric properties were explored. Separation of the products was not possible, so instead, the ratio of the two products $((\mathbf{1}) \mathrm{CoAr}$ and $(\mathbf{1}) \mathrm{CoCl})$ was determined from the ${ }^{1} \mathrm{H}$ spectra of the reaction mixtures, in particular from the characteristic ${ }^{1} \mathrm{H}$ resonances for Py H 4 (triplets around 10 ppm ) and imine Me (singlet around -1 ppm ), ${ }^{83}$ and results are shown in Table 7.2; all the ${ }^{1}$ H NMR assignments are summarized in Table D. 1 in the Appendix D.

As expected for reduction of aryl halides, the rates of reactions of phenyl halides increase in the order of $\mathrm{Cl}<\mathrm{Br}<\mathrm{I}$ (entries 1-3). However, the relative amount of (1)CoAr obtained decreases in this order, from 0.59 to 0.24 . Electron-withdrawing groups accelerate the reaction (entries 3, 7-9, 20), and also increase the amount of (1)CoAr formed. Among them, the relatively slow reaction of 4-chloroacetophenone (entry 7) is probably due to the coordination of this substrate to the cobalt center though the carbonyl oxygen before the breaking of the carbon-chlorine bond (migration of Co from the carbonyl oxygen to the chlorine atom should cost some energy). The correlation of the substituent Taft parameter with the ratio of $(\mathbf{1}) \mathrm{CoAr} /(\mathbf{1}) \mathrm{CoCl}$ was plotted in Figure 7.10. The fairly good correlation $(\rho=0.91)$ suggests that a partial negative charge is developed in the transition state.

Table 7.2. Reaction with organic halides ${ }^{\mathrm{a}}$

| Entry | Organic halides (ArX or RX) | [(1)CoAr]:[(1)CoX] ${ }^{\text {c }}$ | Rxn time ${ }^{\text {d }}$ |
| :---: | :---: | :---: | :---: |
| 1 | PhI | 0.24 | seconds |
| 2 | PhBr | 0.25 | 1 minute |
| 3 | PhCl | 0.59 | hours |
| 4 | 2,4,6-(Me) $3_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Br}$ | $\sim 0$ | seconds |
| 5 | 2,4,6-( ${ }^{\mathrm{t} \mathrm{Bu})_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Br}}$ | $0.27^{\text {e }}$ | seconds |
| 6 | 2,6-(Me) $2_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Cl}$ | $\sim 0$ | days |
| 7 | $p$-(MeCO) $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl}$ | 0.91 | 30 minutes |
| 8 | $p$-(MeOOC) $-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl}$ | 0.83 | seconds |
| 9 | $p-\left(\mathrm{CF}_{3}\right) \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl}$ | 0.77 | seconds |
| 10 | $p-\mathrm{FC}_{6} \mathrm{H}_{4} \mathrm{Cl}$ | 0.40 | seconds |
| 11 | $3,5-(\mathrm{MeO})_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Cl}$ | 0.59 | seconds |
| 12 | 1,4-(Cl) $2_{2} \mathrm{C}_{6} \mathrm{H}_{4}$ | 0.59 | seconds |
| 13 | $p-\mathrm{MeC}_{6} \mathrm{H}_{4} \mathrm{Cl}$ | 0.59 | hours |
| 14 | $p$-(MeO) $\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl}$ | 0.50 | hours |
| 15 | MeI | $0.71{ }^{\text {b }}$ | seconds |
| 16 | $n$-butyl chloride | 0.13 | seconds |
| 17 | $n$-Hexyl bromide | $0.30^{\text {b }}$ | seconds |
| 18 | Benzyl bromide | $0.14{ }^{\text {b }}$ | seconds |
| 19 | Benzyl chloride | $0.45{ }^{\text {b }}$ | minutes |
| 20 | 2,6-dichloropyridine | 1.00 | seconds |
| 21 | $\left(\mathrm{C}_{5} \mathrm{~F}_{11}\right)\left(\mathrm{CH}=\mathrm{CH}_{2}\right) \mathrm{CF}-\mathrm{F}$ | 0.59 | minutes |
| 22 | $n$-Octanyl fluoride | N.R. |  |
| 23 | Allyl chloride | 1.0 | seconds |
| 24 | Cyclopropylmethyl chloride | 0.5 | seconds |

a: Reaction conditions: (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(0.0140 \mathrm{~g}, 0.027 \mathrm{mmol}), \mathrm{H}_{2}(2.0 \mathrm{~mL}) \mathrm{ArX}(0.027$
mmol, 1.0 eq.), $0.4 \mathrm{~mL} \mathrm{C} \mathrm{C}_{6} \mathrm{D}_{6}$ as solvent. b: RX ( $0.014 \mathrm{mmol}, 0.5 \mathrm{eq}$.) was used. The product ratio was determined according to the relative area ratio of the imine methyl peaks. c: From ${ }^{1} \mathrm{H}$ NMR; estimated error margin $\approx 5 \%$. d: qualitative indication. e: the identity of the cobalt aryl product was corrected as (1) $\mathrm{CoCH}_{2} \mathrm{CMe}_{2}$ (3,5-di(tertbutyl)phenyl) instead of (1)CoAr in the original report; ${ }^{217}$ formation of the rearranged alkyl derivative is probably due to the isomerization of the $2,4,6$-tri(tert-butyl)phenyl radical. ${ }^{218}$


Figure 7.10. The ratio of $(\mathbf{1}) \mathrm{CoAr} /(\mathbf{1}) \mathrm{CoCl}$ vs $\sigma_{\mathrm{p}}{ }^{-}$parameter of substituent ${ }^{175}$ (correlation coefficient $\rho=0.91$ )

The sensitivity of these reactions to steric hindrance was not very high: even $\mathrm{BrC}_{6} \mathrm{H}_{2}$ -$2,4,6-{ }^{t} \mathrm{Bu}_{3}$ gave a significant amount of (1) $\mathrm{CoCH}_{2} \mathrm{CMeC}_{6} \mathrm{H}_{3}-3,5-{ }^{t} \mathrm{Bu}_{2}$ (entry 5), which will be discussed later. However, 2,6-dimethyl substituted aryl halides form very little (1) CoAr (entries 4,6), probably due to the highly unstable aryl radical generated.

The reaction with alkyl halides $\mathrm{RX}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I})$ showed similar selectivity trends: for activated halides (benzyl) and for bromides, the reaction is faster, but less (1)CoR is formed. The reason for the lower yield in the reaction with hexyl bromide and butyl chloride (entries 16 and 17) is partially due to the lower stability of the corresponding cobalt(I) alkyl product which can undergo $\beta-\mathrm{H}$ elimination. Unexpectedly, methyl iodide produced a high yield of (1)CoMe. Unactivated $\mathrm{C}\left(\mathrm{sp}^{3}\right)$ - F bonds are not active $\left(n-\mathrm{C}_{8} \mathrm{H}_{17} \mathrm{~F}\right.$,
entry 22), but the allylic fluoride $n-\mathrm{C}_{6} \mathrm{~F}_{13} \mathrm{CH}=\mathrm{CH}_{2}$ (entry 21) produced a reasonable amount of an alkyl complex, tentatively identified as $(\mathbf{1}) \mathrm{Co}\left(\sigma-\mathrm{CH}_{2} \mathrm{CH}=\mathrm{CFC}_{5} \mathrm{~F}_{11}\right)\left({ }^{1} \mathrm{H}\right.$ NMR spectrum, see Figure D. 2 in the Appendix D). The reaction of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with an allyl chloride produced (1) $\operatorname{Co}\left(\eta^{3}\right.$-allyl) instead of $(\mathbf{1}) \operatorname{Co}\left(\eta^{1}\right.$-allyl) and a $1: 1$ ratio of (1) $\mathrm{Co}\left(\eta^{3}\right.$-allyl) to (1) CoCl was obtained (entry 23). One exceptional character of this cobalt(I) allyl complex is its ${ }^{1} \mathrm{H}$ NMR spectrum (for ${ }^{1} \mathrm{H}$ NMR spectrum of this reaction, see Figure D. 5 in the Appendix D): the ${ }^{1} \mathrm{H}$ NMR spectrum of $(\mathbf{1}) \mathrm{Co}\left(\eta^{3}\right.$-allyl) does not show the characteristic triplet around 10 ppm and singlet around -1 ppm . Instead, a "normal" diamagnetic spectrum with the ${ }^{1} \mathrm{H}$ chemical shifts of the coordinate DIP ligand similar to that of a free ligand was observed. The reaction of $(\mathbf{1}) \operatorname{Co}\left(\mathrm{N}_{2}\right)$ with cyclopropylmethyl chloride generated the ring-opening product (1)Co( $\eta^{3}$-crotyl) complex; this complex showed a similar ${ }^{1} \mathrm{H}$ NMR spectrum to that of $(\mathbf{1}) \mathrm{Co}\left(\eta^{3}\right.$-allyl) in a ratio of 0.5 relative to (1) CoCl (entry 24 ); a small amount of an unidentified free olefin was observed (for the ${ }^{1} \mathrm{H}$ NMR spectrum of this reaction, see Figure D. 6 in the Appendix D).

### 7.6 Mechanistic study

As the breaking of alkyl carbon-halogen bonds by transition metals has been studied extensively, ${ }^{219}$ the mechanism for binuclear oxidative addition of aryl halides, especially aryl chlorides, is the main focus of the following sections.

### 7.6.1 Proposed Mechanism

For simplicity, we assume here that all oxidative additions of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ follow a similar mechanism. Substrate-dependent mechanisms cannot be excluded, but so far, we have no indication for that.

The activation of 2,4,6-tri(tertbutyl)phenyl bromide clearly indicates that mononuclear oxidative addition of the aryl halide, followed by transfer of the aryl radical or its isomer to $(1) \mathrm{Co}\left(\mathrm{N}_{2}\right)$, is unlikely because the required "side-on" $\mathrm{C}-\mathrm{Br}$ coordination of the aryl bromide to the (1)Co fragment is impossible for steric reasons. Obvious alternatives are atom transfer (direct halogen-atom abstraction by Co ) and electron transfer (1-e reduction of the halide, which loses a halide anion). In both cases, the initial product would be LCoX and a free Ar radical. The Halpern group found that, for low-spin cobalt(II) systems, atom transfer is much faster for bromides than for chlorides $\left(\mathrm{k}_{\mathrm{RBr}} / \mathrm{k}_{\mathrm{RCl}} \sim 10^{3}\right)$, whereas for electron-transfer-mediated reactions, the rate difference is much smaller $\left(\mathrm{k}_{\mathrm{RBr}} / \mathrm{k}_{\mathrm{RCl}} \sim 2\right) .{ }^{202 \mathrm{e}}$ Our results show rate differences $\mathrm{k}_{\mathrm{RI}} / \mathrm{k}_{\mathrm{RBr}}$ and $\mathrm{k}_{\mathrm{RBr}} / \mathrm{k}_{\mathrm{RCl}}$ on the order of 100, suggesting an atom-transfer mechanism.

Finally, the classical three-member oxidative-addition transition-state at (1)Co, similar to the transition state for the breaking of phenyl bromide by a palladium catalyst in Suzuki reaction (Figure 7.11), ${ }^{220}$ was searched for by DFT. However, all searches resulted in a transition state indicative of a radical mechanism.


Figure 7.11. Transition state for the breaking of phenyl bromide at a $\operatorname{Pd}(0)$ center. Bond length is in $\AA$. (coordinates are taken from ref. 220a).

Atom transfer at a low-spin cobalt(II) complex has been proposed by Halpern. ${ }^{5 \mathrm{~d}}$ Halide abstraction by a $\mathrm{Co}(\mathrm{III})$ complex bearing redox-active ligands has also been reported, ${ }^{28}$ and generation of free radical through irradiating cobalt(III) alkyls has been observed ${ }^{221}$. The radical mechanism I propose and studied by DFT is illustrated in Scheme 7.6 using chlorobenzene as an example.


Scheme 7.6. Proposed mechanism for oxidative addition of phenyl chloride

It involves the hydrogenation of the precursor cobalt(I) alkyl to generate a cobalt(I) hydride, which is apparently not stable and can be converted into a cobalt( 0 ) dinitrogen complex in the presence of dinitrogen gas. After displacement of the coordinated dinitrogen, chlorobenzene is cleaved to generate the cobalt(I) chloride product $((\mathbf{1}) \mathrm{CoCl})$ and a phenyl radical $(\mathrm{Ph} \bullet)$. This phenyl radical may meet another cobalt( 0 ) center to generate a cobalt(I) phenyl product $((\mathbf{1}) \mathrm{CoPh})$. The observed product ratio $((\mathbf{1}) \mathrm{CoAr}:(\mathbf{1}) \mathrm{CoCl}<1)$ indicated that this combination is not highly efficient. As the hydrogenation of cobalt(I) alkyl complexes has been experimentally and computationally studied by the groups of Gibson ${ }^{212}$ and Budzelaar ${ }^{85}$ and this step is fast at room temperature in our system, only the breaking of the aryl carbon-halogen bond with the (1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ intermediate was studied by DFT using chlorobenzene as the model. The resulting energy profile is shown in Figure 7.12.


Figure 7.12. Calculated free-energy profile (b3-lyp/TZVPP//b3-lyp/TZVP) for the binuclear oxidative addition of $\mathrm{ClC}_{6} \mathrm{H}_{5}$ at two $\mathrm{Co}(0)$ centers according to Scheme 7.6. Bond lengths (for the TS) in $\AA$

The displacement of $\mathrm{N}_{2}$ from (1)Co( $\mathrm{N}_{2}$ ) by $\mathrm{ClC}_{6} \mathrm{H}_{5}$ to form a terminally Cl-bound chlorobenzene complex $(\mathbf{1}) \mathrm{Co}\left(\mathrm{ClC}_{6} \mathrm{H}_{5}\right)$ is endergonic by about $10 \mathrm{kcal} / \mathrm{mol}$ (Figure 7.12) and the homolytic breaking of the $\mathrm{C}-\mathrm{Cl}$ bond costs another $10 \mathrm{kcal} / \mathrm{mol}$; the transition state optimized by DFT showed the right imaginary frequency. Following this imaginary frequency leads to the cobalt(I) chloride complex together with a phenyl radical. Finally, the total calculated overall free-energy barrier for this process is $23.4 \mathrm{kcal} / \mathrm{mol}$, which is
consistent with the experimental observations (slow reaction, hours to complete at room temperature).

### 7.6.2 Ratio of (1)CoAr/(1) CoCl

With the above mechanism defined, the ratios of the two products in Table 7.2 can be explained in terms of the stability of the aryl radical intermediate. For phenyl iodide and phenyl bromide, the relatively weaker aryl carbon-halogen bonds lead to higher reaction rate (entries 1-3); the resulting higher concentration of phenyl radicals leads to the lower yield of (1)CoAr and higher yields of side products (e.g. homocoupled biphenyl). When the substituent at the 4-position of the cobalt-bound aryl ring is electron-withdrawing (entries 7-9), it stabilizes the corresponding aryl radical, thus slowing down the homocoupling reaction, and increasing the yield of (1)CoAr. 2,6-Dichloropyridine seems to follow the same trend. When there are ortho alkyl substituents, the corresponding aryl radical can further isomerize to form a stable alkyl radical (for the 2,4,6-tri(tertbutyl)phenyl radical, a relatively stable alkyl radical; for its isomerization, see Scheme 7.7) and further react with another cobalt( 0 ) center to form a cobalt(I) alkyl product (the lower yield of this product is probably due to the higher barrier of this step, which results in higher yield of the hydrogen abstraction product or homocoupled compounds).


Scheme 7.7. Isomerization of 2,4,6-tri(tert-butyl)phenyl radical

However, for both 2,6-dimethylphenyl chloride and 2,4,6-trimethylphenyl bromide, no (1)CoAr or (1)CoR was detected (Scheme 7.8). Thus methyl groups at ortho positions of phenyl radical hindered the formation of (1)CoAr. In addition, the barrier for isomerization from aryl radical to alkyl radical is suspected to be too high. Thus homocoupling of the aryl radical is the suspected to be favorable in this system.


Scheme 7.8. Possible reactions of 2,4,6-trimethylphenyl radical

### 7.7 Applications to C-C coupling reactions

The product mixture of $(\mathbf{1}) \mathrm{CoCl}$ and $(\mathbf{1}) \mathrm{CoPh}$ generated by reaction of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with 1.0 eq. PhCl was further reacted with benzyl chloride $(\mathrm{BnCl})$, resulting in formation of a lot of pink solid cobalt(II) dihalide complexes (see the following discussion about this solid; the pink color was caused by the liquid color). After hydrolysis by water, the organic layer was analyzed by GC/MS. Three products were detected: $\mathrm{Bn}-\mathrm{Bn}, \mathrm{PhBn}$ and PhPh . Calibration for these three products showed that the ratio $\mathrm{BnBn}: \mathrm{PhBn}: \mathrm{PhPh}$ was 1:3.5:0.03. Although there is no immediate reaction between pure (1) CoCl with benzyl chloride, after 30 min some solid precipitated; however, no BnBn was detected by ${ }^{1} \mathrm{H}$ NMR. Thus, the generation of three products ( $\mathrm{BnBn}, \mathrm{BnPh}$ and PhPh ) strongly suggests that (1)CoAr performs CC coupling reactions with BnCl most likely via a radical mechanism (in other words, these three products formed from benzyl radical and phenyl radical).

A variety of other (1)CoAr obtained from the reactions in Table 7.2 were then reacted with alkyl halides and the products were analyzed by GC-MS (Table 7.3). The identification of products was done by comparing their mass spectra with those in the MS database.

Table 7.3. Reaction of a mixture of $(\mathbf{1}) \mathrm{CoAr}+(\mathbf{1}) \mathrm{CoCl}$ with alkyl halides ${ }^{\mathrm{d}}$ :
Entry
Entry
a: Product was detected by GC/MS and the regiochemistry of the CC-coupling product is assumed. ${ }^{\text {XLIII }} \mathrm{b}$ : there are two peaks corresponding to molecular ion of 418.11. Thus two isomers were suspected. c : Using 2.0 equiv of BnBr relative to $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ d: mixture of (1) $\mathrm{CoAr}+(\mathbf{1}) \mathrm{CoCl}$ generated from (1) $\mathrm{CoN}_{2}$ as described in Table 7.2, then 0.5 eq. RX was added to it. e: using separately prepared pure (1) CoPh instead of the mixture with (1) CoCl . f: using separately prepared pure (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ and 1.8 equiv. of $\mathrm{CH}_{3} \mathrm{I}$; the product was identified by NMR and GC/MS. g: no cross-coupled product was identified, but some BnBn was detected which is possibly due to the trace amount of impurity in BnCl .h: assigned tentatively (it could also be $\mathrm{Ar}_{2}$ )

Activated alkyl halides (benzyl or allyl) reacted smoothly, with bromides more reactive than chlorides (entries 1-9), but aryl halides did not react (entry 11), probably due to the difficult generation of aryl radical or stronger aryl-halogen bond. For cobalt aryls with an electron-withdrawing group at the 4-position of the aryl (entries 16-17), no color change was observed on addition of alkyl halide and no CC cross-coupling product was detected by GC/MS, probably due to the decreased reduction potential of the cobalt center in the complexes and the lower oxidative potential of benzyl chloride. Electron poor (1) $\mathrm{Co}(\mathrm{Py}-$ 6-Cl) showed similar low activity (entry 14). Replacing benzyl chloride by more reactive

[^24]benzyl bromide produced only BnBn . Thus (1) CoCl was suspected to be more reactive than (1)Co(Py-6-Cl). By adding more BnBr (another 1.5 eq.), a cross-coupled product was detected by GC/MS (entry 15, will be discussed in more detail later).

### 7.8 Mechanistic consideration for CC-coupling reactions of (1)CoAr

### 7.8.1 Experimental considerations

When a mixture of $(\mathbf{1}) \mathrm{Co}(\mathrm{Py}-6-\mathrm{Cl})$ and $(\mathbf{1}) \mathrm{CoCl}(1: 1)$ generated by reacting of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with 1.0 eq. 2,6-dichloropyridine reacted with 0.5 eq. BnBr , a pink solution with a dark suspension was observed. After centrifugation, the pink supernatant solution was determined by NMR to be a mixture of cobalt(I) complexes ((1)Co(Py-6$\mathrm{Cl}):(\mathbf{1}) \mathrm{CoBr}^{\mathrm{XLIV}}:(\mathbf{1}) \mathrm{CoCl}=1.0: 0.67: 0.44$; for the ${ }^{1} \mathrm{H}$ NMR spectrum, see Figure D. 7 in the Appendix D) and the dark-colored solid was identified to be mainly (1) CoBrCl together with other DIP cobalt(II) dihalides (for the ${ }^{1} \mathrm{H}$ NMR spectrum, see Figure D. 8 in the Appendix D). By adding excess BnBr to the above pink solution, a cross-coupled product suspected to be 2-chloro-6-benzylpyridine was detected by GC/MS. In addition, the distribution of products from the reaction of (1) CoPh and $(\mathbf{1}) \mathrm{CoCl}$ with BnCl clearly showed that the coupling reaction most likely occur through a radical mechanism. ${ }^{\text {xLV }}$
${ }^{\text {xLIV }}$ The generation of ( $\left.\mathbf{1}\right) \mathrm{CoBr}$ is probably through the exchange of chlorine in (1)CoCl by bromine facilitated by benzyl radical.
${ }^{\text {XLV }}$ The generation of three products is suspected from the random combination of the benzyl radical and the phenyl radical.

Thus, based on the above experimental results, we propose a radical mechanism for this CC-coupling reaction in the following section.

### 7.8.2 Proposed mechanism

$\mathrm{Co}^{(0)}$ is a strong enough reductant to cleave the aryl carbon-halogen bond, but cobalt(I) is not (see Section 7.5.2). The fact that no cross-coupled product could be detected for the reaction of (1)CoPy-6-Cl with 0.5 eq. of BnBr indicates the lower reduction potential of (1)CoAr with an electron withdrawing substituent at cobalt-bound aryl ring. Thus, the mechanism we propose here involves the abstraction of halide by (1)CoAr to form intermediate (1)CoArX (Step 1 in Scheme 7.9), together with the release of benzyl radical (Step 2 in Scheme 7.9). The (1)CoArX quickly loses the aryl radical (which is consistent with the easy loss of an alkyl radical from (1) $\mathrm{CoR}_{2}$ in Chapter 6) which will encounter the aforementioned benzyl radical or the other aryl radical to form a crosscoupled product or homo-coupled products (Step 3 in Scheme 7.9). This mechanism can be illustrated using (1)CoPh and BnCl in Scheme 7.9:


Scheme 7.9. A possible mechanism for CC coupling reaction of (1) CoPh with benzyl chloride

In Scheme 7.9, the reaction of Step 1 is faster than Step 3 for (1)CoAr with electron rich Ar, while it is slower for (1)CoAr with electron poor Ar such as 2-(1)Co-Py-6-Cl. Thus the presence of $(\mathbf{1}) \mathrm{CoCl}$ is problematic for the coupling of $(\mathbf{1}) \mathrm{Co}-\mathrm{Py}-6-\mathrm{Cl}$ with benzyl bromide and a larger amount of BnBr is needed.

### 7.9 Extension to C-O bond-cleavage reactions

(1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ can also be used to break the C-O bond of diphenyl carbonate but at a rather slow rate (weeks). (1)CoOPh was detected as the only cobalt(I) product based on the ${ }^{1} \mathrm{H}$ NMR spectrum. The reaction with ethyl benzoate showed similar results but required even longer time. Compared with the $(4) \mathrm{Fe}\left(\mathrm{N}_{2}\right)_{2}$ complex reported by Chirik (Scheme 7.10), ${ }^{73}$ in our system, only the acyl C-O bond was cleaved (Scheme 7.11) and no cleavage of the ester C-O bond was observed.


Scheme 7.10. Reaction of $(4) \mathrm{Fe}\left(\mathrm{N}_{2}\right)_{2}$ with ethyl benzoate


Scheme 7.11. Reaction of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with diphenyl carbonate.

However, when hydrogen gas was injected after the addition of diphenyl carbonate, the reaction was immediate and ${ }^{1} \mathrm{H}$ NMR indicated two triplets (one at 9.2 ppm , indicating the presence of $(\mathbf{1}) \mathrm{CoOPh}$; the other at 8.8 ppm ; the ratio of these two peaks is $2: 1)$. When more $\mathrm{H}_{2}(\mathrm{~g})$ was added, and the reaction was allowed to proceed longer at room temperature, the peak at 8.8 ppm nearly disappeared. Based on the peak integration, this compound might be (1) $\mathrm{Co}\left(\mathrm{OCH}_{3}\right)$ (there is a singlet peak at 3.8 ppm and its peak area indicated three H relative to that of the peak at 8.8 ppm ; in addition, it is expected to be a right product from the reaction of $(\mathbf{1}) \mathrm{CoH}$ with a ketone or an aldehyde), but this would not be expected to react with dihydrogen.

### 7.10 Conclusions

The oxidative addition of aryl halides, especially aryl chlorides, at two cobalt centers was achieved using (1) $\operatorname{Co}\left(\mathrm{N}_{2}\right)$ complexes generated in situ by hydrogenation of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ in the presence of dinitrogen. The reaction with a variety of aryl halides
strongly suggests a radical mechanism. The result of a DFT study on this radical mechanism is consistent with experimental conditions. The corresponding cobalt(I) aryls generated can subsequently perform C-C cross-coupling with alkyl iodides, benzyl halides and allyl chlorides through a radical mechanism. The further application to C-O bond breaking was less successful, leading only to a (1)CoOPh product.

The current system showed that the binuclear oxidative addition happens at two separate metal centers and the amount of (1)CoAr product is relatively smaller than that of (1) CoCl . However, (1)CoAr is more useful than (1) CoCl . To use two different metal centers, one good at cleaving aryl carbon-chlorine bonds and the other good at trapping the aryl radical, will be the ideal case. Future work could be aimed at finding an optimum combination of two metal centers. Alternatively, the main effort can be devoted to exploration of a possible reagent to convert (1) CoCl into the $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ complex without affecting the (1)CoAr product. In addition, as the current system for the CC-coupling reaction is not yet catalytic, finding a way to make it catalytic would be valuable.

# Chapter 8. Conclusions, Speculations and Outlook 

### 8.1 Conclusions

Diiminepyridine (DIP) ligands have received intense attention during the past decades after their iron and cobalt dihalide complexes were found to be highly efficient in ethylene polymerization. Further improvement of these catalysts has not been very successful, although a lot of effort has already been put into it. The research in this thesis has made some contributions to the understanding of this system by examining complex structures and ligand properties:

1) A study of the suspected correlation between structures of five-coordinate cobalt(II) and iron(II) dihalides complexes and catalytic activity has been done. The low energy barriers for the distortion of the structures by DFT clearly do not support the existence of a direct causal relation. However, the high steric hindrance of 2,6-diisopropylphenyliminylpyridine, of which iron(II) dialkyl complexes show large displacements of the metal center from the ligand N3 plane, may prohibit possible side reactions of the corresponding precursor or active species and indirectly result in higher catalytic activity of complexes based on this ligand.
2) Ligand parameters aiming at quantifying the electronic properties of DIPtype ligands show that the standard DIP ligands are both good $\sigma$-donors and good $\pi$-acceptors.

An optimum combination of $\sigma$-donor and $\pi$-acceptor abilities, together with a fair amount of steric shielding, will be a useful guideline to search for the next generation of DIP-like catalysts.

Cobalt(I) alkyl complexes are intermediates along the path of activation of the (DIP) $\mathrm{CoCl}_{2}$ precatalyst by MAO. Although they are diamagnetic, the ${ }^{1} \mathrm{H}$ NMR spectra are somewhat unusual, especially the position of the pyridine H 4 and imine Me resonances. The presence of singlet biradical character is considered the best way to describe their electronic structure and explain their diamagnetic behaviour. Accepting this description for the moment, there are three possible interpretations of the unusual chemical shifts:
a) thermal population of a low-lying triplet state; ${ }^{82}$
b) spin admixture ${ }^{245}$ or Temperature-Independent Paramagnetism (TIP): ${ }^{121,174}$ the ground state is not a "pure singlet" but can best be represented as a mixture of mainly singlet with some triplet mixed in through spin-orbit coupling;
c) the molecule is a true singlet, and no higher spin states are involved. However, in the expression in Eq. 2.1 in Chapter 2 for $\sigma_{p}$ contribution to the chemical shifts in the section 2.1.1, the presence of low-lying excited configurations results in unusually large (de)shielding contributions.

Discriminating between these possibilities can not be done within this thesis. Thus, an examination of the influence of the ligand variation on the position of the peaks can be helpful. However, the study of cobalt(I) complexes has so far been mostly restricted to highly hindered DIP systems (e.g. 2,6-\{(2,6-diisopropylphenylimino)ethyl $\}$ pyridine), probably because other cobalt(I) complexes are harder to synthesize. The current research provides an alternative way to synthesize these complexes and reveals some clues on how the pyridine H 4 resonance is affected:

1) Three labile cobalt(II) dialkyl complexes $\left((\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}\right.$, (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and $\left.(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}\right)$ have been successfully prepared. Reactions with DIP-type ligands showed that for ligands with stronger $\pi$-acceptor ability, cobalt (I) alkyl complexes are the only observable product while for a ligand with comparable $\sigma$-donor but worse $\pi$-acceptor properties (Pybox), only a cobalt(II) dialkyl was detected. Thus a good $\pi$-acceptor ability is required to generate the cobalt(I) alkyl product. In addition, the instability of the cobalt(I) product from the reaction with PhDIP indicates that a certain amount of steric protection is necessary for high stability.
2) For less-hindered N -phenyl and N-benzyl DIP ligands, the products from the reactions with $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and with (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ are different, and the results suggest formation of labile pyridine-coordinated cobalt(I) complexes in the former case. The upfield shifting of the pyridine H4 peak appears to be caused by the equilibrium between a pyridine-coordinated cobalt(I) alkyl species and a cobalt(I) alkyl species without pyridine
coordination. In addition, the research in Chapter 7 provides several types of cobalt(I) complexes (cobalt(I) aryl, cobalt(I) imine and cobalt(I) allyl complexes) which showed quite different pyridine H 4 shifts: a) the replacement of a cobaltbound alkyl by a cobalt-bound aryl shifts the pyridine H4 peak from 10.0 ppm downfield to 10.26 ppm ; b) the ${ }^{1} \mathrm{H}$ NMR spectrum of (DIP) $\mathrm{CoN}=\mathrm{C}(\mathrm{H}) \mathrm{PhCl}-4$ showed the pyridine H 4 peak at 7.9 ppm ; c) a (DIP) $\mathrm{Co}\left(\eta^{3}\right.$-allyl) complex showed a "normal" Py H4 chemical shift (7.4 ppm). By including the N-isopropyl DIP cobalt(I)-alkyl complex (its Py H4 peak at 9.15 ppm ) and N -isopropyl DIP cobalt(I)-chloride complex (its Py H4 peak at 41.6 ppm ) reported by Chirik, ${ }^{82}$ a systematic comparison of chemical shifts of the pyridine H 4 in different cobalt(I) complexes with the energy gap between singlet and triplet states calculated by DFT should now be possible, which might lead to the discrimination of the above three interpretations for this unusual Py H4 shift.
3) A good correlation between ${ }^{1} \mathrm{H}$ chemical shifts predicted by DFT and the experimental data for truly paramagnetic cobalt(II) dialkyl complexes indicates that NMR prediction by DFT is a good tool in assigning the peaks and sometimes discriminating the structures of paramagnetic complexes.

Finally, the study on less-hindered DIP cobalt(I) alkyl complexes in Chapter 7 provides more insights into cobalt( 0 ) chemistry. The research in Chapter 7 of this thesis established that the paramagnetic complex generated by hydrogenation of less hindered cobalt(I) alkyl complexes is (DIP)Co( $\mathrm{N}_{2}$ ) or (DIP)Co(solvent). Applying this paramagnetic complex to the breaking of aryl-halide bonds species produced quite
interesting chemistry. First, binuclear oxidative addition was observed instead of the more usual mononuclear oxidative addition typically found with palladium and nickel systems. Second, the involvement of a radical mechanism, rather than standard oxidative addition and reductive elimination, was supported by both experimental evidence and DFT calculations. This is quite fascinating because aryl radicals are normally hard to generate. Finally, the further C-C coupling of the cobalt(I) aryl product with alkyl iodides or benzyl halides or allyl chloride can be successful and a radical mechanism for coupling was strongly supported by $\mathrm{GC} / \mathrm{MS}$ results. The ability for $\mathrm{C}_{\mathrm{sp} 3}-\mathrm{C}_{\mathrm{sp} 3}$ coupling makes this procedure quite promising. Although the current system is not catalytic, it did provide an opportunity to explore this chemistry and could form a basis for further improvement.

### 8.2 Speculations

For the DIP iron dichloride precatalyst, the active species in ethylene polymerization by MAO were shown to be the iron(II) alkyl cation complexes ${ }^{246}$ (Scheme 8.1).


Scheme 8.1. Active species for (DIP) $\mathrm{FeCl}_{2}$ complex in ethylene polymerization by MAO

For cobalt, I would expect a similar mechanism. In other words, a cobalt(II) monoalkyl cation might be the active species, although a $\operatorname{Co}(\mathrm{III})$ center was suspected to be the active species by the group of Gibson. ${ }^{81}$ As there was no report on the (DIP) $\mathrm{CoR}_{2}$ complexes before the current work, the observation of a (Pybox) $\mathrm{CoR}_{2}$ complex in this thesis might provide some insight into the activation of cobalt catalysts.

Firstly, the lower stability of (Pybox) $\mathrm{CoR}_{2}$ relative to (Pybox) $\mathrm{FeR}_{2}$ might be the reason why (DIP) $\mathrm{CoCl}_{2}$ has lower efficiency than its iron analog in ethylene polymerization if they go through the same mechanism. If this is the case, the active species in the cobalt case has a shorter lifetime.

Secondly, the preference of bidentate coordination of DIP in cobalt dialkyl complexes might be another reason why cobalt complexes have lower efficiency than iron systems. On the path of generating active species ([(DIP)MR] $]^{+}, \mathrm{M}: \mathrm{Fe}, \mathrm{Co}$ ), the DIP ligand can coordinate to the cobalt center in a bidentate mode, and organometallic reagents such as MAO, which will easily attack the remaining imine arm, thus can destroy the intermediates of cobalt complexes. The highly hindered arm might slow down this step; as a result, more species, which are active, are generated. In iron complexes, DIP always takes the tridentate binding mode.

Finally, the metal deviation from the N3 plane induced by steric hindrance at the N -aryl ring can indirectly protect one side of the metal center, just like the Cp ligand in metallocenes, leaving the other side free to bind the incoming ethylene.

### 8.3 Outlook

The results described in this thesis suggest a number of opportunities for further research.

## 1. Ligand descriptors

As described in Chapter 1 (Section 1.10), the steric hindrance of DIP ligands seems to play an important role in the application of their metal dihalide catalysts in ethylene polymerization and oligomerization (e.g. molecular weight distribution, rate of deactivation). The electronic properties of DIP ligands are important in the activation of their cobalt or iron dihalide catalysts (the active species of (DIP)FeX ${ }_{2}$ has been accepted as $[(\mathrm{DIP}) \mathrm{FeR}]^{+}$, see also Scheme 8.1 in Section 8.2 ); however, once DIP metal dihalides have been activated, the steric properties are likely to be more relevant to the following catalytic activity. In Chapter 5, I have found a reasonable approach to quantify the electronic properties of DIP ligands, although a steric contribution is included in those ligand parameters. A proper separate description of ligand steric properties is still needed to predict or interpret their catalytic behaviour. Up to now, there are three popularly-used concepts to generate steric parameters which have been developed mainly for monodentate ligands such as monophosphines and monocarbenes:

1) Tolman cone angle, ${ }^{155}$ originally developed for monophosphine ligands, works mainly for the ligands with similar skeletons. As the skeletons of DIP ligands are significantly different from that of monophosphine ligands (the substituents in monophosphine ligands point away from the metal center to form a cone, while
the substituents in DIP ligand at N -aryl ring surround the metal), the Tolman cone angle approach is probably not suitable for the DIP ligand.
2) The solid angle approach ${ }^{247}$ is an alternative to the Tolman cone angle, but it does not offer significant improvement over Tolman cone angles, its main advantage being that it can be calculated by a computer. It is mainly suitable for monophosphines and related ligands. As the DIP ligand has a very non-conical shape, any attempt to represent it by a single "converge" number may give misleading results.
3) Percentage buried volume ${ }^{248}$ which was originally developed for the steric description of N -heterocyclic carbene ligands showed a good correlation with the Tolman cone angle for monophosphine ligands and can be further extended to cyclopentadienyl ( Cp ) ligands and bisphosphine ligands. As the 3-dimensional skeleton of a DIP ligand has some similarity to that of a N -heterocyclic carbene (Figure 8.1), percent buried volume might be used as the basis to describe the steric properties of DIP ligands, although, like cone angle and solid angle, this descriptor too is only a single number used to describe a complex, non-conical shape.


Figure 8.1. Comparison of ligand skeletons of a N-heterocyclic carbene and a DIP ligand.

## 2. Application of "CoR ${ }_{2}$ " sources

As illustrated in Chapter 5 and Chapter 6, two convenient sources of " $\mathrm{CoR}_{2}$ " have been established. These can be exploited to explore cobalt-alkyl chemistry of other types of ligands than just the simple DIP ligands studied here. For example, the reaction with DIP ligands supported on various media ${ }^{55}$ can be meaningful in terms of recycling the complex. Bidentate ligands with strong non-innocent character such as bisimine ${ }^{13}$ or imine-pyridine ${ }^{249}$ ligands can be interesting to explore. In addition, these " $\mathrm{CoR}_{2}$ " sources can be further used to explore the stability of different labile organic cobalt reagents. As described in Chapter 5, there is a significant stability difference between $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ and $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{Me}_{2} \mathrm{Ph}\right)_{2}$. As neither compound contains $\beta$ hydrogens, a weaker ability to stabilize the cobalt center in the latter case is suspected. In addition, attempted synthesis of $(\mathrm{Py})_{2} \mathrm{CoPh}_{2}$ using the same procedure as $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ was unsuccessful, which might be due to easy $\mathrm{C}-\mathrm{C}$ coupling (see footnote in Section 5.4). Further exploration of the stability of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}(\mathrm{R}$ : any alkyl group) or the decay of $(\mathrm{Py})_{2} \mathrm{CoAr}_{2}$ (Ar: any aryl group) can be useful for the exploration
of synthesis and application of other labile cobalt alkyl precursors. Finally, labile ligands other than pyridine such as 4-dimethylaminopyridne are worth testing in the future, in order to improve their stability.

## 3. Less hindered (DIP)CoR

As described in Chapter 6, the reaction of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ with PhDIP did not result in a stable cobalt(I) complex, due to the weak steric protection in PhDIP. Understanding the possible decomposition routes will help the design of new methods for accessing less hindered DIP complexes.

## 4. Binuclear oxidative addition and CC coupling

The work described in Chapter 7 forms only the beginning of an explanation of $\mathrm{Co}-\mathrm{C}$ and C-C bond formations. Several features of the binuclear oxidative addition in Chapter 7 are not yet clear.

4A) The mechanism for formation of (DIP) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ from (DIP) CoH needs to be addressed. The overall reaction involves the reduction of the cobalt center from cobalt(I) to cobalt( 0 ) and the breaking of a cobalt(I) hydride bond. It is not clear yet what becomes of the hydrogen originally bound to Co ; evolution of $\mathrm{H}_{2}$ seems reasonable, but needs to be confirmed. I suspect a similar mechanism to the homolytic pathway proposed by Gray and coworker in studying hydrogen evolution catalyzed by cobaloxime, ${ }^{250}$ and a bimolecular mechanism, which involves loss of $\mathrm{H}_{2}$ through attack of a cobalt-bound hydride of one (DIP) CoH to the cobalt center of another (DIP)CoH, shown in Scheme
8.2. However, locating the binuclear transition state by DFT calculations is probably not trivial.


Scheme 8.2. A mechanism involving binuclear transition state for the conversion of (DIP)CoH into (DIP) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$.

Obtaining experimental evidence for the mechanism of conversion of (DIP) CoH into (DIP)Co( $\mathrm{N}_{2}$ ) is difficult. A kinetic study of this conversion to obtain the information on the reaction order is not trivial because the less hindered (DIP)CoH is unstable. Using $\mathrm{D}_{2}$ instead of $\mathrm{H}_{2}$ will most likely slow down this conversion. However, the concentration of
any intermediate along the conversion path will probably be too low to be detected by e.g. ${ }^{2}$ D NMR. In addition, these intermediates are suspected to be paramagnetic. Finally, as mentioned in Chapter 7, there are around $5-10 \%$ of diamagnetic and highly asymmetric cobalt(I) side products identified by ${ }^{1} \mathrm{H}$ NMR. Obtaining their crystal structures will not be easy, but knowledge of their structures might result in ideas about the reaction mechanism.
$4 \boldsymbol{B})$ The yield of (DIP)CoAr (in terms of cobalt consumed) is still low due to the generation of the (DIP)CoX side product. Finding an appropriate reagent to convert (DIP) CoCl completely into (DIP)CoAr would be a major improvement. One direct solution is the arylation of (DIP)CoCl, but this is not very useful because a) not many aryl metal reagents are commercially available and b) this is contrary to the purpose of using that (DIP)CoAr as a useful arylating reagent and c) the further reaction of (DIP)CoAr with a main group metal aryl reagent can be a problem. Alternatively, (DIP) CoCl in the presence of (DIP)CoAr can be reduced into (DIP) $\mathrm{CoN}_{2}$ by a suitable 1e reducing reagent (e.g. $\mathrm{Na}-\mathrm{Hg}$ ), or it can be converted by a suitable hydride source into (DIP) CoH which will automatically decay into (DIP) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$. Both the reducing reagent and the hydride source should not attack the desired (DIP)CoAr product. However, the two hydride sources I tested did not work: NaH in toluene did not react, whereas, $\mathrm{NaBHEt}_{3}$ not only reacted with (DIP)CoCl, but also with (DIP)CoAr.
$4 C)$ The formation of (iPrDIP)CoH from the reaction of (iPrDIP)Co( $\mathrm{N}_{2}$ ) with aryl halides is worth exploring further (Section 7.5.2 in Chapter 7). There is no obvious hydrogen
source in the reactant that can react with (iPrDIP) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$, so $\mathrm{C}-\mathrm{H}$ bond activation (of an aryl halide or the THF solvent) or $\beta$-hydrogen elimination from an unknown cobalt(I) alkyl intermediate are suspected. Labelling experiments might be performed and ${ }^{2} \mathrm{D}$ NMR might be able to verify this idea. However, the broadness of the $\mathrm{H}(\mathrm{Co})$ resonance may make it difficult to monitor this reaction. In addition, how (iPrDIP) CoH disappears in the presence of aryl halide can be further studied by synthesizing (iPrDIP)CoH separately and studying its reaction with aryl halides.

4D) The most exciting result in this thesis is the formation of $\mathrm{C}-\mathrm{C}$ bonds using welldefined cobalt complexes in what seems to be a radical-mediated coupling reaction. This can be used to explore the mechanism for C-C coupling catalyzed by cobalt catalysts generated in situ by mixing a cobalt salt, a main group metal reagent and a ligand. ${ }^{210}$

However, the reaction presented here still has a number of drawbacks, and further work could focus on developing a truly catalytic variation based on this chemistry. Finding a way to convert (DIP) $\mathrm{CoCl}_{2}$ back to (DIP)CoAr in the presence of ArX and BnX is a possible way to go.

## Oxidation state of the cobalt center in (DIP)Co(I) and the pure singlet energy

Several aspects of the electronic structure and properties of (DIP)CoR complexes are still not entirely clear. This includes the reasons for the anomalous ${ }^{1} \mathrm{H}$ peak positions mentioned in Section 1.14 in Chapter 1 and Section 8.1. Experimental measurement of the oxidation state of the cobalt center in (DIP)CoR complexes by e.g X-ray absorption near edge structure (XANES ${ }^{251}$ ) using the cobalt K-edge or L-edge can be performed to
assist in understanding the bonding in these complexes. In addition, fractional occupancy approaches mentioned in Section 2.4.4 in Chapter 2 can be explored in this DIP cobalt(I) system to get more accurate singlet-triplet energy gaps and further correlate this with ${ }^{1} \mathrm{H}$ NMR results.

At this point, considering extensive studies on cobalt complexes worldwide, further application of the research in this thesis to other fields such as electrochemistry (e.g. the study of the reduction potential of cobalt(I) complexes by cyclic voltammetry ${ }^{252}$ ), photochemistry (e.g. photochemical study of cobalt(I) complex or cobalt(II) complexes), and organic synthesis (e.g. synthesis of the aryl derivatives), would be expected in the future.

## Chapter 9. Experimental Section

## General procedure for single-crystal X-ray diffraction measurement

The data collection of the single-crystal was set following the procedure in Section 2.3.2 in Chapter 2. Because the complexes consist mostly of organic $\mathrm{C}, \mathrm{N}, \mathrm{O}, \mathrm{Cl}, \mathrm{P}$ atoms of lower scattering ability, data tended to be weak at higher $2 \theta$ angles. Thus the intensity of the scattered X-ray decreases rapidly as the $2 \theta$ angle increases. In addition, the complexes prefer to co-crystallize with solvent molecules and the serious disorder of the solvent molecule also leads to the rapid decrease of intensity with increasing $\theta$. Therefore, absorption models were built based on lower-angle data and then applied to all the data collected. The structures were solved according to the procedure in Section 2.3.3 in Chapter 2.

### 9.1 Experimental section for Chapter 3:

General: All experiments were done under argon atmospheres using the standard Schlenk line techniques, unless otherwise noted. Triphenylphosphine, 2,6diacetylpyridine, sodium, anilines and anhydrous $\mathrm{FeCl}_{2}$ and $\mathrm{CoCl}_{2}$ were purchased from Aldrich. All dry solvents were obtained from the solvent-purification instrument branded with "Pure Solv" (Innovative Technology, inc.). 2-Acetyl-6-bromopyridine, ${ }^{145}$ 2-[2,6-diisopropylphenylimino]-6-bromopyridine, ${ }^{146}$ 6-Bis[ $4^{\prime}, 4^{\prime}$-dimethyloxazolin- $2^{\prime}$-yl]pyridine 15, ${ }^{222}$ 2,4,6-trimethylphenylazide, 2,6-diisopropylphenylazide and phenylazide, ${ }^{223}$ ligand
$7,{ }^{224} \mathrm{CoCl}_{2}(\mathrm{THF})_{1.5}{ }^{225}$ and $\mathrm{FeCl}_{2}(\mathrm{THF})_{1.5}{ }^{226}$ were prepared according to literature methods.
${ }^{1} \mathrm{H},{ }^{13} \mathrm{C},{ }^{19} \mathrm{~F}$ and ${ }^{31} \mathrm{P}$ NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All data were collected at room temperature; chemical shifts ( $\delta$ ) are reported in ppm. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ chemical shifts were referenced to residual proton solvent signals $\left(\mathrm{CDCl}_{3}:{ }^{1} \mathrm{H} 7.26,{ }^{13} \mathrm{C} 77.0 ; \mathrm{CD}_{2} \mathrm{Cl}_{2}:{ }^{1} \mathrm{H} 5.33,{ }^{13} \mathrm{C} 54.2\right)$. Listing assignments: $\mathrm{Ms}=$ $2,4,6-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2}, \mathrm{Ar}=2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}$.

Elemental analysis was done at Guelph Chemical Laboratories Ltd, Canada.

## Synthesis of ligands

$\left.\mathbf{2 - [ 2 , 6}-{ }^{i} \mathbf{P r}_{\mathbf{2}} \mathbf{C}_{\mathbf{6}} \mathbf{H}_{\mathbf{3}} \mathbf{N}=\mathbf{C M e}\right]-\mathbf{6}-\mathbf{P h}_{\mathbf{2}} \mathbf{P}-\mathbf{C}_{\mathbf{5}} \mathbf{H}_{\mathbf{3}} \mathbf{N}^{\mathbf{1 4 2}}: 1.3 \mathrm{~g}(0.056 \mathrm{~mol}) \mathrm{Na}$ was added in small pieces to 200 mL of liquid ammonia. To the deep-blue solution was added $6.13 \mathrm{~g}(0.023$ mol) triphenylphosphine in small portions. The resulting solution was stirred for 2 h , during which time it turned dark red. Then $1.25 \mathrm{~g}(0.023 \mathrm{~mol})$ dry ammonium chloride was added to the solution, which turned a lighter orange. After $30 \mathrm{~min}, 7.8 \mathrm{~g} 2-[2,6-$ diisopropylphenylimino]-6-bromopyridine $(0.022 \mathrm{~mol})$ was added to the solution in small portions, followed by 20 mL of dry THF. The next morning, all ammonia had evaporated. The resulting THF solution was heated at $50^{\circ} \mathrm{C}$ for 2 h , and then cooled again to room temperature. 80 mL water and $50 \mathrm{ml} \mathrm{CH}_{2} \mathrm{Cl}_{2}$ were added, the organic layer was separated and the water layer extracted with two more portions of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and evaporated using a rotary evaporator to give a
red residue. Crystallization from toluene/ether/ $\mathrm{CH}_{3} \mathrm{OH}$ gave $8.0 \mathrm{~g}(80 \%)$ of the product as a yellow powder.
${ }^{1} \mathrm{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.27(\mathrm{~d}, 1 \mathrm{H}, J 7.9 \mathrm{~Hz}, \mathrm{Py} H 3), 7.71\left(\mathrm{t}, 1 \mathrm{H}, J_{\mathrm{av}} 7.5\right.$ Hz, Py H4), 7.48-7.57 (m, 4 H, Ph o), 7.36-7.45 (m, $6 \mathrm{H}, \mathrm{Ph} m, p$ ), 7.29 (d, $1 \mathrm{H}, J 6.9 \mathrm{~Hz}$, Py H5), 7.08-7.22 ( $\left.\mathrm{AB}_{2} \mathrm{~m}, 3 \mathrm{H}, \mathrm{Ar} m, p\right), 2.77$ (sept, $2 \mathrm{H}, J 6.9 \mathrm{~Hz}, \mathrm{C} H \mathrm{Me}_{2}$ ), 2.13 (s, 3 H , $\mathrm{N}=\mathrm{CMe}$ ), 1.18 and 1.19 ( $2 \mathrm{~d}, 6 \mathrm{H}$ each, $J 6.9 \mathrm{~Hz}, \mathrm{CH} M e_{2}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 167.4(C=\mathrm{N}), 162.3\left(\mathrm{~d}, J_{\mathrm{P}} 3 \mathrm{~Hz}\right.$, Py C6), 156.5 (d, $J_{\mathrm{P}}$ $11 \mathrm{~Hz}, \operatorname{Py} C 6), 146.4(\operatorname{Ar} i), 136.4\left(\mathrm{~d}, J_{\mathrm{P}} 10 \mathrm{~Hz}, \operatorname{Ph} i\right), 136.0$ (d, $J_{\mathrm{P}} 3 \mathrm{~Hz}$, Py C4), 135.7 (d, $J_{\mathrm{P}} 20 \mathrm{~Hz}, \mathrm{Ph} o$ ), 129.1 (d, $\left.J_{\mathrm{P}} 20 \mathrm{~Hz}, \mathrm{Py} C 5\right), 129.0(\mathrm{Ph} p), 128.4\left(\mathrm{~d}, J_{\mathrm{P}} 7 \mathrm{~Hz}, \mathrm{Ph} m\right), 123.5$ $\left.(\operatorname{Ar} p), 122.9(\operatorname{Ar} m), 119.6(\operatorname{Py} C 3), 28.2\left(\mathrm{CHMe}_{2}\right), 23.2,22.8(\mathrm{CHMe})_{2}\right), 17.2(\mathrm{~N}=\mathrm{CMe})$.
${ }^{31} \mathrm{P}$ NMR (121.5 MHz, $\mathrm{CDCl}_{3}$ ): -2.2.
Anal. Calcd for $\mathrm{C}_{31} \mathrm{H}_{33} \mathrm{~N}_{2} \mathrm{P}$ (464.58): C 80.14; H 7.16; N 6.03; P 6.67. Found: C 80.36; H 6.85; N 6.17; P 6.76.

2-[2,6- $\left.{ }^{\boldsymbol{i}} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathbf{N}=\mathbf{C M e}\right]-6-\left[\mathbf{2 , 4 , 6}-\mathrm{Me}_{3} \mathrm{C}_{6} \mathbf{H}_{2} \mathbf{N}=\mathbf{P P h}_{2}\right]-\mathrm{C}_{5} \mathbf{H}_{3} \mathbf{N}(\mathbf{8})^{\mathbf{1 4 2}}$ : To a solution of $2.73 \mathrm{~g}(5.8 \mathrm{mmol})$ of $2-\left[2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{CMe}\right]-6-\mathrm{Ph}_{2} \mathrm{P}-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ in 20 ml of dry toluene was added 3 g of 2,4,6-trimethylphenylazide, resulting in vigorous evolution of dinitrogen. After stirring for 2 h at room temperature, the solution was heated at $60^{\circ} \mathrm{C}$ for 2 h . After cooling, the toluene was evaporated in vacuo. Addition of 8 mL of pentane resulted in precipitation of a yellow solid, which was filtered off, washed with pentane and dried in vacuo, giving 3.2 g ( $90 \%$ ) of a yellow powder.
${ }^{1} \mathrm{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.38$ (d, $1 \mathrm{H}, J 7.7 \mathrm{~Hz}, \operatorname{Py} H 3$ ), 8.18 (t, $1 \mathrm{H}, J_{\text {av }} 6.4 \mathrm{~Hz}$, Py H4), 7.91 (dd, $\left.1 \mathrm{H}, J 7.9 \mathrm{~Hz}, J_{\mathrm{P}} 4.0 \mathrm{~Hz}, \mathrm{Py} H 5\right), 7.78-7.88$ (m, 4H, Ph o), 7.35-7.54 (m,
$6 \mathrm{H}, \mathrm{Ph} m, p$ ), 7.06-7.19 ( $\mathrm{AB}_{2} \mathrm{~m}, 3 \mathrm{H}, \mathrm{Ar} m p$ ), 6.75 (s, 2H, Ms $m$ ), 2.69 (sept, 2H, J 6.8 Hz , $\mathrm{C} H \mathrm{Me}_{2}$ ), $2.20(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ms} p$ ), 2.04 ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{Ms} o$ ), $1.94(\mathrm{~s}, 3 \mathrm{H}, \mathrm{N}=\mathrm{CMe}$ ), 1.13, 1.15 (2 d, 6 H each, $J 6.9 \mathrm{~Hz}, \mathrm{CH} M e_{2}$ ).
${ }^{13} \mathrm{C}$ NMR (75.5 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 166.7(C=\mathrm{N}), 156.2\left(\mathrm{~d}, J_{\mathrm{P}} 129 \mathrm{~Hz}\right.$, Py $\left.C 6\right), 155.9\left(\mathrm{~d}, J_{\mathrm{P}}\right.$ $18 \mathrm{~Hz}, \operatorname{Py} C 2), 146.2(\operatorname{Ar} i), 144.1(\mathrm{Ms} i), 136.5\left(\mathrm{~d}, J_{\mathrm{P}} 9 \mathrm{~Hz}, \operatorname{Py} C 4\right), 135.6(\mathrm{Ar} o), 133.6$ (d, $\left.J_{\mathrm{P}} 101 \mathrm{~Hz}, \mathrm{Ph} i\right), 132.5\left(\mathrm{~d}, J_{\mathrm{P}} 9 \mathrm{~Hz}, \mathrm{Ph} o\right), 132.1\left(\mathrm{~d}, J_{\mathrm{P}} 7 \mathrm{~Hz}, \mathrm{Ms} o\right), 131.1\left(\mathrm{~d}, J_{\mathrm{P}} 2 \mathrm{~Hz}\right.$, Ph $p$ ), 129.4 (d, $J_{\mathrm{P}} 20 \mathrm{~Hz}, \operatorname{Py} C 5$ ), 128.4 (Ms $m$ ), 128.0 (d, $J_{\mathrm{P}} 12 \mathrm{~Hz}, \operatorname{Ph} m$ ), 127.5 (Ms $p$ ), $123.7(\operatorname{Ar} p), 123.0(\operatorname{Ar} m), 121.9\left(\mathrm{~d}, J_{\mathrm{P}} 3 \mathrm{~Hz}, \mathrm{Py} C 3\right), 28.2\left(C \mathrm{HMe}_{2}\right), 23.2,22.8$
( CHMe$)_{2}$ ), 21.3 ( $\mathrm{Ms} o$ ), $20.5(\mathrm{Ms} p), 17.0(\mathrm{~N}=\mathrm{CMe})$.
${ }^{31} \mathrm{P}$ NMR (121.5 MHz, $\mathrm{CDCl}_{3}$ ): -12.5.
Anal. Calcd for $\mathrm{C}_{40} \mathrm{H}_{44} \mathrm{~N}_{3} \mathrm{P}$ (597.77): C 80.37; H 7.42; N 7.03; P 5.18. Found: C 80.67; H 7.76; N 6.62; P 4.89.

2-[2,6- $\left.{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{C M e}\right]-6-\left[2,6-\mathrm{iPr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{PPh}_{2}\right]-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ (9): This was prepared like ligand 8, but using $1.02 \mathrm{~g}(2.2 \mathrm{mmol})$ of $2-\left[2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{CMe}\right]-6-\mathrm{Ph}_{2} \mathrm{P}-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ in 3 mL dry toluene and 2.5 g of 2,6-diisopropylphenylazide. $1.15 \mathrm{~g}(82 \%)$ of a yellow powder was obtained.
${ }^{1} \mathrm{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.39(\mathrm{~d}, 1 \mathrm{H}, J 7.7 \mathrm{~Hz}, \operatorname{Py} H 3), 7.96\left(\mathrm{t}, 1 \mathrm{H}, J_{\mathrm{av}} 6.2 \mathrm{~Hz}\right.$, Py H4), 7.85-7.90 (m, 1H, Py H5), 7.74-7.80 (m, 4H, Ph o), 7.40-7.56 (m, 6H, Ph m,p), 7.06-7.17 (m, 3H, Ar m,p), 6.97 (d, 2H, J 7.2 Hz, PNAr m), 6.81 (t, 1H, $J_{a v} 7.5 \mathrm{~Hz}, \mathrm{PNAr}$ p), 3.34 (sept, 2H, J6.8 Hz, PNAr CHMe $)$, 2.67 (sept, $2 \mathrm{H}, J 6.9 \mathrm{~Hz}, \mathrm{C} H \mathrm{Me}_{2}$ ), 1.86 (s, $\left.3 \mathrm{H}, \mathrm{N}=\mathrm{CMe}), 1.13\left(\mathrm{t}, 12 \mathrm{H}, J_{a v} 6.3 \mathrm{~Hz}, \mathrm{CHMe}\right)_{2}\right), 0.88\left(\mathrm{~d}, 12 \mathrm{H}, J 6.8 \mathrm{~Hz}, \mathrm{PNAr} \mathrm{CH} M e_{2}\right)$.
${ }^{13} \mathrm{C}$ NMR (75.5 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 166.8(C=\mathrm{N}), 155.7\left(\mathrm{~d}, J_{\mathrm{P}} 128 \mathrm{~Hz}\right.$, Py $\left.C 6\right), 156.03(\mathrm{~d}$, $\left.J_{\mathrm{P}} 18 \mathrm{~Hz}, \operatorname{Py} C 2\right), 146.2(\mathrm{Ar} i), 143.9(\mathrm{PNAr} i), 142.6\left(\mathrm{~d}, J_{\mathrm{P}} 7 \mathrm{~Hz}, \operatorname{PNAr} o\right), 136.4\left(\mathrm{~d}, J_{\mathrm{P}} 9\right.$ $\mathrm{Hz}, \mathrm{Py} C 4), 135.6(\mathrm{Ar} o), 132.8\left(\mathrm{~d}, J_{\mathrm{P}} 103 \mathrm{~Hz}, \mathrm{Ph} i\right), 132.6\left(\mathrm{~d}, J_{\mathrm{P}} 9 \mathrm{~Hz}, \mathrm{Ph} o\right), 131.2(\mathrm{Ph}$ p), 129.0 (d, $\left.J_{\mathrm{P}} 20 \mathrm{~Hz}, \operatorname{Py} C 5\right), 128.0\left(\mathrm{~d}, J_{\mathrm{P}} 12 \mathrm{~Hz}, \mathrm{Ph} m\right), 123.6(\operatorname{Ar} p), 122.9(\mathrm{Ar} m)$, 122.5 (d, $J_{\mathrm{P}} 3 \mathrm{~Hz}, \mathrm{Py} C 3$ ), 121.9 ( $\mathrm{PNAr} m$ ), 119.2 ( $\mathrm{PNAr} p$ ), 28.5 ( $\mathrm{PNAr} C \mathrm{HMe}_{2}$ ), 28.2 $\left(\mathrm{CHMe}_{2}\right), 23.5$ ( PNAr CHMe$)_{2}$ ), 23.1, $\left.22.8(\mathrm{CHMe})_{2}\right), 16.9(\mathrm{~N}=\mathrm{CMe})$.
${ }^{31} \mathrm{P}$ NMR (121.5 MHz, $\mathrm{CDCl}_{3}$ ): -11.1.
Anal. Calcd for $\mathrm{C}_{43} \mathrm{H}_{50} \mathrm{~N}_{3} \mathrm{P}$ (639.85): C 80.72; H 7.88; N 6.57; P 4.84. Found: C 81.07; H 8.21; N 6.61; P 4.54.

2-[2,6- $\left.{ }^{i} \mathbf{P r}_{2} \mathbf{C}_{6} \mathbf{H}_{3} \mathbf{N}=\mathbf{C M e}\right]-6-\left[\mathbf{C}_{6} \mathbf{H}_{5} \mathbf{N}=\mathbf{P P h}_{2}\right]-\mathbf{C}_{5} \mathbf{H}_{3} \mathbf{N}$ (10): This was prepared like ligand 8, but using $2.04 \mathrm{~g}(4.39 \mathrm{mmol})$ of $2-\left[2,6-\mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{CMe}\right]-6-\mathrm{Ph}_{2} \mathrm{P}-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ and 2.52 g of phenylazide. $2.37 \mathrm{~g}(97 \%)$ of a yellow powder was obtained.
${ }^{1} \mathrm{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.45(\mathrm{~d}, 1 \mathrm{H}, J 7.9 \mathrm{~Hz}, \operatorname{Py} H 3), 8.36\left(\mathrm{t}, 1 \mathrm{H}, J_{\text {av }} 6.4 \mathrm{~Hz}\right.$, Py $H 4$ ), 7.92 (dt, $1 \mathrm{H}, J 7.9 \mathrm{~Hz}, J_{\mathrm{P}} 4.0 \mathrm{~Hz}$, Py $H 5$ ), 8.00-8.06 (m, 4H, Ph o), 7.44-7.58 (m, $6 \mathrm{H}, \operatorname{Ph} m, p), 7.09(\mathrm{t}, 2 \mathrm{H}, J 7.4 \mathrm{~Hz}, \mathrm{NPh} m), 6.94(\mathrm{~d}, 2 \mathrm{H}, J 7.9 \mathrm{~Hz}, \mathrm{NPh} o), 6.72(\mathrm{t}, 1 \mathrm{H}, J$ $7.3 \mathrm{~Hz}, \mathrm{NPh} p$ ), 2.73 (sept, 2H, J 6.9 Hz, $\mathrm{C} H \mathrm{Me}_{2}$ ), 2.12 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{N}=\mathrm{CMe}$ ), 1.18, 1.17 ( 2 d , 6 H each, $J 6.9 \mathrm{~Hz}, \mathrm{CH} M e_{2}$ ).
${ }^{13} \mathrm{C}$ NMR (75.5 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 166.3(C=\mathrm{N}), 156.5\left(\mathrm{~d}, J_{\mathrm{P}} 18 \mathrm{~Hz}\right.$, Py $\left.C 2\right), 153.9\left(\mathrm{~d}, J_{\mathrm{P}}\right.$ $129 \mathrm{~Hz}, \mathrm{Py} C 6), 151.0$ (d, $J_{\mathrm{P}} 2.4 \mathrm{~Hz}, \mathrm{NPh} i$ ), 146.1 (Ar $i$ ), 136.7 (d, $J_{\mathrm{P}} 9 \mathrm{~Hz}, \mathrm{Py} C 4$ ), $135.6(\mathrm{Ar} o), 132.9\left(\mathrm{~d}, J_{\mathrm{P}} 9 \mathrm{~Hz}, \mathrm{Ph} o\right), 131.6\left(\mathrm{~d}, J_{\mathrm{P}} 3 \mathrm{~Hz}, \mathrm{NPh} m\right), 130.3\left(\mathrm{~d}, J_{\mathrm{P}} 98 \mathrm{~Hz}\right.$, Ph i), 130.0 (d, $J_{\mathrm{P}} 20 \mathrm{~Hz}$, Py C5), 128.6 (d, $J_{\mathrm{P}} 2 \mathrm{~Hz}, \mathrm{Ph} p$ ), 128.3 (d, $J_{\mathrm{P}} 12 \mathrm{~Hz}, \mathrm{Ph} m$ ), 123.7
(d, $\left.J_{\mathrm{P}} 8 \mathrm{~Hz}, \mathrm{NPh} o\right), 123.4(\operatorname{Ar} p), 123.0(\mathrm{Ar} m), 122.5\left(\mathrm{~d}, J_{\mathrm{P}} 3 \mathrm{~Hz}, \mathrm{Py} C 3\right), 117.4(\mathrm{NPh} p)$
$28.2\left(\mathrm{CHMe}_{2}\right), 23.2,22.8(\mathrm{CHMe}), 17.2(\mathrm{~N}=\mathrm{CMe})$.
${ }^{31} \mathrm{P}$ NMR (121.5 MHz, $\mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$ ): $\delta$-2.0.
Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{38} \mathrm{~N}_{3} \mathrm{P}$ (555.69): C 79.97; H 6.89; N 7.56; P 5.57. Found: C 80.56; H 7.25; N 7.63; P 5.48.

## Synthesis of iron(II) dichloride and cobalt(II) dichloride complexes

## 

1.1 g of $\mathrm{CoCl}_{2} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ was dissolved in 20 mL isopropanol. A solution of 2.0 g of $\mathbf{3}$ in 15 mL of toluene was added dropwise. The resulting reaction mixture was heated at $80^{\circ} \mathrm{C}$ for 1 h . The green precipitate was filtered over a glass frit to give $2.76 \mathrm{~g}(89 \%)$ of a green powder.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300.1 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$, all signals broad singlets): $35.5(1 \mathrm{H}$, Py $H 4), 16.7(6 \mathrm{H}$, Ms p-Me), $6.4(4 \mathrm{H}, \mathrm{Ms} m),-0.6\left(6 \mathrm{H}, \mathrm{N}=\mathrm{CCH}_{3}\right),-26.2(12 \mathrm{H}, \mathrm{Ms} \mathrm{o}-\mathrm{Me})$.

The following content within $/ * * \backslash$ was done by Peter H.M. Budzelaar.

## /* Synthesis of $\left\{\mathbf{2 , 6}\right.$-bis $\left.\left.\mathbf{2 , 4 , 6}-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{CCF}_{3}\right]-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right\} \mathrm{CoCl}_{2}$ : (7) $\mathrm{CoCl}_{\mathbf{2}}$

To 0.1 g of $\mathrm{CoCl}_{2}(\mathrm{THF})_{1.5}$ was added a solution of 0.23 g 7 in 10 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The initially yellow solution turned green and then dark brown. After stirring for 5 h , the solution was filtered through a glass frit, concentrated in vacuo to ca 1 mL , and carefully
${ }^{\text {XLVI }} \mathrm{As}(3) \mathrm{CoCl}_{2}$ is an known complex, the synthesis described here aims at obtaining its X-ray structure.
layered with 10 mL of toluene. After 24 h , the solution was decanted, leaving large, darkbrown needles of $(7) \mathrm{CoCl}_{2} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$. The yield is not determined
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, CDCl ${ }_{3}$, all signals broad singlets): 113.7 (2H, Py H3), 33.4 ( 1 H , Py H4), 15.8 (6H, Ar p-Me), 3.7 (4H, Ar Hm), -31.9 (12H, Ar o-Me).
${ }^{19}$ F NMR (282.4 MHz, $\mathrm{CDCl}_{3}$ ): -74.1.

## 

This was prepared following the same procedure as for (7) $\mathrm{CoCl}_{2}$. The solution is deepgreen and toluene layering produces large dark-green needles of (7) $\mathrm{FeCl}_{2} \cdot$ (toluene) $)_{1.5}$. Yield is not determined. A similar procedure using benzene for layering gave smaller needles which easily lost solvent, becoming light-green and opaque.
${ }^{1} \mathrm{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{CDCl}_{3}$, all signals broad singlets): $\delta 85.7$ ( 1 H, Py H 4 ), 83.7 ( 2 H , Py H3), 28.5 (6H, Ms p-Me), 13.4 (4H, Ms $m$ ), 12.0 (12H, Ms o-Me).
${ }^{19}$ F NMR (282.4 MHz, $\mathrm{CDCl}_{3}$ ): -256.0.* ${ }^{*}$

## Synthesis of $\left\{2-\left[2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{C M e}\right]-6-\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}=\mathrm{PPh}_{2}\right]-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right\} \mathrm{CoCl}_{2}:(10) \mathrm{CoCl}_{2}$

 Ligand $10(0.54 \mathrm{~g}, 0.97 \mathrm{mmol})$ and $\mathrm{CoCl}_{2}(0.13 \mathrm{~g}, 0.97 \mathrm{mmol})$ were weighed into a 100 mL Schlenk tube and the mixture was evacuated and purged with argon three times. After adding 20 mL dry THF, the resulting brown suspension was stirred overnight at room temperature. The mixture was filtered over a glass frit and the solid was washed with THF. The residue was redissolved in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and layered with pentane at room temperature for two days, giving $0.35 \mathrm{~g}(56 \%)$ of the brown crystalline product, suitable for the X-ray diffraction.${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, all signals broad singlets): 94.6 ( $1 \mathrm{H}, \operatorname{Py~H} 3$ ), $66.7(1 \mathrm{H}$, Py H5), 27.5 (2H, N-Ar $m$ ) 19.2 (1H, Py H4), 16.6 (3H, N=CMe), 5.2 (2H, NPh $m$ ), 4.5 $(4 \mathrm{H}, \mathrm{PPh} m), 0.3(1 \mathrm{H}, \mathrm{NPh} p), 0.0(2 \mathrm{H}, \mathrm{PPh} p),-4.9\left(6 \mathrm{H}, \mathrm{CHMe} e_{2}\right),-10.2(4 \mathrm{H}, \mathrm{PPh} o),-$ $11.3(1 \mathrm{H}, \mathrm{NAr} p),-14.1(2 \mathrm{H}, \mathrm{NPh} o),-17.3(6 \mathrm{H}, \mathrm{CHMe} 2),-30.5(2 \mathrm{H}, \mathrm{CHMe} 2)$.

Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{38} \mathrm{Cl}_{2} \mathrm{CoN}_{3} \mathrm{P}$ (685.53): C 64.83; H 5.59; N 6.13; P 4.52; Cl 10.34. Found: C 64.90; H 5.32; N 5.83; P 3.99; Cl 10.28.

## Synthesis of $\left\{2-\left[2,6-{ }^{i} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{C M e}\right]-6-\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}=\mathbf{P P h}_{2}\right]-\mathrm{C}_{5} \mathrm{H}_{3} \mathbf{N}\right\} \mathrm{FeCl}_{2}:(\mathbf{1 0}) \mathrm{FeCl}_{2}$

This was prepared like (9) $\mathbf{F e C l}_{\mathbf{2}}$, but using $0.10 \mathrm{~g}(0.79 \mathrm{mmol})$ of anhydrous $\mathrm{FeCl}_{2}$ and 0.50 g of $\mathbf{1 0}$. Purification was done by layering with a mixture of diethylether and pentane instead of pure pentane, and gave $0.38 \mathrm{~g}(62 \%)$ of the deep blue crystalline product.
${ }^{1} \mathrm{H}$ NMR ( $300.1 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$, all signals broad singlets): $87.4(1 \mathrm{H}, \mathrm{Py} \mathrm{H} 3), 58.9(1 \mathrm{H}$, Py H5), 46.4 (1H, Py H4), 22.7 (2H, NAr $m$ ), 16.7 (4H, br, PPh $o$ ), 13.3 ( $4 \mathrm{H}, \mathrm{PPh} m$ ), $11.9(2 \mathrm{H}, \mathrm{NPh} m), 6.1\left(8 \mathrm{H}\right.$, suspected as $\mathrm{CH} \mathrm{Me}_{2}$ and $\left.\mathrm{PPh} p\right), 0.1(1 \mathrm{H}, \mathrm{NAr} p),-3.8(6 \mathrm{H}$, $\left.\mathrm{CH} \mathrm{Me}_{2}\right),-8.0(2 \mathrm{H}, \mathrm{br}, \mathrm{NPh} o),-21.1(1 \mathrm{H}, \mathrm{NPh} p),-42.2\left(2 \mathrm{H}, \mathrm{CH} \mathrm{Me}_{2}\right),-79.1(3 \mathrm{H}$, $\mathrm{N}=\mathrm{CMe}$ ). The peaks in region between $0-9 \mathrm{ppm}$ cannot be unambiguously assigned due to the solvent peaks overlapping.

Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{38} \mathrm{Cl}_{2} \mathrm{FeN}_{3} \mathrm{P}$ (682.44): C 65.12; H 5.61; N 6.16; P 4.54; Cl 10.39.
Found: C 65.17; H 5.84; N 5.96; P 3.83; Cl 10.93.

## Synthesis of $\left\{2-\left[2,6-{ }^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{C M e}\right]-6-\left[\mathbf{2 , 4 , 6}-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{PPh}_{2}\right]-\right.$

## $\left.\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right\} \mathrm{CoCl}_{2}:(8) \mathrm{CoCl}_{\mathbf{2}}$

Ligand $8(0.66 \mathrm{~g}, 0.97 \mathrm{mmol})$ was dissolved in 20 mL THF and added into a suspension of $\mathrm{CoCl}_{2}(0.13 \mathrm{~g}, 0.97 \mathrm{mmol})$ in 20 mL THF. The resulting green suspension was stirred overnight and filtered over frit filter and washed with THF and dried in high vacuum. The yield was not determined. The crystalline solid can be obtained by dissolving the solid in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution and layering with pentane at room temperature.

Tentive assignments:
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, all signals broad singlets): 106.6 (1H, Py H3), 71.3
(1H, Py H5), 37.0 (3H, Ms $p-\mathrm{Me}$ ), 35.3 ( $2 \mathrm{H}, \mathrm{N}-\mathrm{Ar} m$ ), 27.0 (3H, N=CMe), 25.9 (1H, Py $H 4),-0.5(3 \mathrm{H}),-0.9(6 \mathrm{H}, \mathrm{Ms} o-\mathrm{Me}),-5.7\left(6 \mathrm{H}, \mathrm{CH} \mathrm{Me}_{2}\right),-12.2(1 \mathrm{H}, \mathrm{NAr} p),-16.5(4 \mathrm{H}$, PPh o), -21.4 (br, 6H, CHMe 2 ), -42.2(br, 1H, $\mathrm{CHMe}_{2}$ ).

Anal. Calcd for $\mathrm{C}_{40} \mathrm{H}_{44} \mathrm{Cl}_{2} \mathrm{CoN}_{3} \mathrm{P}$ (727.61): C, 66.03; H, 6.10; N, 5.78; P, 4.26; Cl, 9.75.
Found: C, 65.95; H, 6.14; N 5.40; P, 4.04; Cl, 10.38.

## Synthesis of $\left\{\mathbf{2}-\left[2,6-{ }^{i}{ }^{\mathbf{P}} \mathbf{r r}_{2} \mathrm{C}_{6} \mathbf{H}_{3} \mathbf{N}=\mathbf{C M e}\right]-6-\left[\mathbf{2 , 6}-\mathrm{iPr}_{2} \mathrm{C}_{6} \mathbf{H}_{3} \mathbf{N}=\mathbf{P P h}_{2}\right]-\right.$

## $\left.\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right\} \mathrm{CoCl}_{2}:(9) \mathrm{CoCl}_{2}$

Ligand $9(0.95 \mathrm{~g}, 1.48 \mathrm{mmol})$ was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(40 \mathrm{~mL})$ and added into a blue suspension of $\mathrm{CoCl}_{2}(0.19 \mathrm{~g}, 1.46 \mathrm{mmol})$ in THF ( 30 mL ) at room temperature. The resulting mixture was stirred for 24 h . After filtration, all solvent was evaporated and redissolve in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and layered with pentane at room temperature. The green needles were obtained and the yield was not determined.

Tentative assignments:
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, all signals broad singlets): 111.9 (1H, Py H3), 69.7
(1H, Py H5), $37.9(2 \mathrm{H}, \mathrm{N}-\mathrm{Ar} m), 30.4(1 \mathrm{H}, \mathrm{Py} H 4), 27.1(3 \mathrm{H}, \mathrm{N}=\mathrm{CMe}),-1.4(2 \mathrm{H}, \operatorname{PPh} p)$, -7.4 (6H, CHMe $),-9.9\left(6 \mathrm{H}, \mathrm{CH} \mathrm{Ce}_{2}\right),-14.6(1 \mathrm{H}, \mathrm{NAr} p),-21.5(4 \mathrm{H}, \mathrm{PPh} o),-23.0(6 \mathrm{H}$, $\mathrm{CHMe}),-60.3(1 \mathrm{H}, \mathrm{CHMe} 2)$.

A satisfactory elemental analysis could not be obtained. The X-ray structure determination shows the presence of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallization; partial loss of this cocrystallized solvent is probably responsible for the analysis issues.

## Synthesis of $\left\{2-\left[2,6-{ }^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{C M e}\right]-6-\left[\mathbf{2 , 4 , 6}-\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{PPh}_{2}\right]-\right.$

## $\left.\mathbf{C}_{\mathbf{5}} \mathbf{H}_{\mathbf{3}} \mathbf{N}\right\} \mathrm{FeCl}_{\mathbf{2}}:(\mathbf{8}) \mathrm{FeCl}_{\mathbf{2}}$

This was prepared like (9) $\mathbf{F e C l}_{\mathbf{2}}$, but using 0.13 g anhydrous $\mathrm{FeCl}_{2}(1.0 \mathrm{mmol})$ and $\mathbf{8}(1.0$ mmol ). Crystals of the deep-blue crystalline product were obtained by layering the corresponding dichloromethane solution with pentane.

Tentative assignments:
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, all signals broad singlets): 86.6 (1H, Py H3), $56.4(1 \mathrm{H}$, Py H5), 39.9 (1H, Py H4), 27.4 (4H, PPh $m$ ), 22.2 ( $2 \mathrm{H}, \mathrm{NAr} m$ ), 16.5 (4H, br, PPh $o$ ), $15.7(3 \mathrm{H}, \mathrm{Ms} \mathrm{p-Me}), 13.6$ (12H, Ms o-Me and NAr CHMe 2 ), -2.2 ( $6 \mathrm{H}, \mathrm{CH} \mathrm{Ce}_{2}$ ), -84.3 $\left(3 \mathrm{H}, \mathrm{N}=\mathrm{CMe}_{3}\right)$.

A satisfactory elemental analysis could not be obtained. The X-ray structure determination shows the presence of $1.5 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallization; partial loss of this cocrystallized solvent is probably responsible for the analysis issues.

## Synthesis of $\left\{2-\left[2,6{ }^{-}{ }^{i} \operatorname{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{C M e}\right]-6-\left[2,6{ }^{-}{ }^{\mathbf{i}} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathbf{P P h}_{2}\right]-\right.$

## $\left.\mathbf{C}_{5} \mathbf{H}_{\mathbf{3}} \mathbf{N}\right\} \mathrm{FeCl}_{\mathbf{2}}:(\mathbf{9}) \mathrm{FeCl}_{\mathbf{2}}$

Under an argon atmosphere, $0.133 \mathrm{~g}(1.0 \mathrm{mmol})$ of anhydrous $\mathrm{FeCl}_{2}$ and $0.66 \mathrm{~g}(1.0$ mmol) 9 were weighed into a 50 mL Schlenk tube. 3.5 mL dry THF was added, forming a green suspension. Addition of 10 mL dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ produced a clear blue clear solution. The resulting mixture was stirred overnight and then concentrated in vacuo. Layering with pentane and stand overnight at room temperature produced the blue crystalline product.
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, all signals broad singlets): $83.6(1 \mathrm{H}$, Py $H 3), 52.3(1 \mathrm{H}$, Py H5), $37.7(1 \mathrm{H}, \mathrm{Py} H 4), 22.9(2 \mathrm{H}, \mathrm{NAr} m), 17.8(4 \mathrm{H}, \mathrm{PPh} o), 15.4(2 \mathrm{H}, \mathrm{PNAr} m)$, 13.1(4H, PPh $m),-0.3(6 \mathrm{H}, \mathrm{CHMe} 2),-3.2(6 \mathrm{H}, \mathrm{CHMe}),-12.9(4 \mathrm{H}, \mathrm{CHMe} 2),-22.1(1 \mathrm{H}$, PNAr $p),-79.2(3 \mathrm{H}, \mathrm{N}=\mathrm{CMe})$. Tentative assignment for rest peaks which might belong to the complex: $8.7\left(6 \mathrm{H}, \mathrm{CH} M e_{2}\right), 1.9(2 \mathrm{H}, \mathrm{PPh}), 0.1(2 \mathrm{H}, \mathrm{NAr} p$ and PNAr $)$.

A satisfactory elemental analysis could not be obtained. The X-ray structure determination shows the presence of $3 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ of crystallization; partial loss of this cocrystallized solvent is probably responsible for the analysis issues.

## Synthesis of ( $\mathbf{P y})_{\mathbf{4}} \mathbf{F e C l}_{\mathbf{2}}$

Under an argon atmosphere, anhydrous $\mathrm{FeCl}_{2}(6.26 \mathrm{~g}, 0.05 \mathrm{~mol})$ was weighed into a 100 mL Schlenk tube and 80 mL dry pyridine was added. The resulting yellow suspension was stirred for 4 h at room temperature. After filtration over frit filters and washed with pyridine, around 6 g of yellow powder was obtained and this product was used without further purification.

## Synthesis of $\mathbf{\{ 2 , 6}$-Bis $\left[\mathbf{4}^{\prime}, \mathbf{4}^{\prime}\right.$-dimethyloxazolin-2'-

## yl) pyridine $\} \mathbf{F e}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right):(\mathbf{1 5}) \mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$

Under argon atmosphere, $(\mathrm{Py})_{4} \mathrm{FeCl}_{2}(0.48 \mathrm{~g}, 1.1 \mathrm{mmol})$ was weighed into a 50 mL Schlenk tube and suspended in 20 mL dry Hexane. The resulting yellow suspension was cooled to $-70{ }^{\circ} \mathrm{C}$ and kept at this temperature for 30 min . At $-70{ }^{\circ} \mathrm{C}, 2.2 \mathrm{~mL} \mathrm{LiCH} \mathrm{SiMe}_{3}$ (1.0 M in pentane) was dropped into it. The resulting red mixture was allowed to slowly warm to room temperature and continue to stir at room temperature for another one hour and filtered over celite. The filtrate was cooled to $-35^{\circ} \mathrm{C}$ and kept at this temperature for 30 min . Ligand $15(0.13 \mathrm{~g}, 0.5 \mathrm{mmol})$ in 20 diethyl ether was added dropwisely. The resulting violet solution was continued to stir for another 1 h at room temperature. After filtering over celite, most of solvent was evaporated and 1 mL diethylether was added to dissolve them and cooled to $-35^{\circ} \mathrm{C}$ for overnight. A lot of deep violet crystals were generated. Yield was more than $23 \%$ based on the amount of ligand $\mathbf{1 5}$ used. The X-ray quality crystal was obtained by cooling $\mathrm{Et}_{2} \mathrm{O} /$ hexane saturated solution at $-35^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene-d6, 300 MHz$): \delta 337\left(1 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 1074 \mathrm{~Hz}\right.$, Py H4), 25.1 (2H, br, $\left.\Delta v_{1 / 2} 224 \mathrm{~Hz}, \operatorname{Py} H 3\right), 9.3\left(18 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 277 \mathrm{~Hz}, \operatorname{Si} M e_{3}\right),-0.46\left(12 \mathrm{H}, \mathrm{br}, \Delta v_{1 / 2} 432\right.$ $\left.\mathrm{Hz}, \mathrm{CH}_{2} \mathrm{O}\right),-6.4\left(4 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 222 \mathrm{~Hz}\right) . \mathrm{CH}_{2}(\mathrm{Fe})$ was not observed.

Anal. Calcd for $\mathrm{C}_{23} \mathrm{H}_{41} \mathrm{FeN}_{3} \mathrm{O}_{2} \mathrm{Si}_{2}$ (503.61): C, 54.85; H, 8.21; N, 8.34; O, 6.35; Si,
11.15; Fe, 11.09. Found: C, 54.72; H, 7.97; N 8.76; O, 6.15; Si, 11.65; Fe, 11.40.

## X-ray structure determinations

All data were collected at room temperature on a Bruker four-circle diffractometer with an APEX detector, and were corrected for absorption using SADABS ${ }^{102}$ (the measurement of the crystal was assisted by Peter H.M. Budzelaar). Structures were analyzed for the presence of solvent-accessible voids using PLATON. ${ }^{106}$ Complexes of DIP-type ligands tend to include solvent in the structure when crystallizing, and this often leads to poor crystal quality. We found various solvents in the structures of all complexes studied, resulting in particularly poor crystal quality for complexes (3) $\mathrm{CoCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$, (8) $\mathrm{FeCl}_{2}$ and (10) $\mathrm{FeCl}_{2}$. Nevertheless, connectivity is not in doubt and gross features of the structure should still be accurate enough to classify the metal environment as TBP or SP line (see below). Details of the data collection and structure determinations are collected in notes on individual structures and the refinement results are shown in Table 9.1 and Table 9.2.:
(3) $\mathbf{C o C l}_{2} \cdot \mathbf{H}_{2} \mathbf{O}$ : (Figure 9.1) Long needles of the compound were obtained by crystallization from a saturated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution cooled to $-20^{\circ} \mathrm{C}$. A fragment of a transparent light-green needle was glued on top of a thin glass capillary using epoxy glue. The fragment showed some cracks perpendicular to its long dimension, but was the best we were able to obtain. Data quality was poor. Diffraction spots were large (ca $2^{\circ}$ ), and no data was observed past $2 \theta=30^{\circ}$. The structure was solved using Patterson methods. In view of the poor data quality and small amount of data, only the Co and Cl atoms were refined anisotropically. A void of ca $50 \AA^{3}$ near a chloride contained the highest peak in the electron-density difference map. This was assumed to contain a partially occupied
water molecule (occupancy refined to ca 0.7 ). Its hydrogen atoms were not included in the refinement.


Figure 9.1. X-ray structure of $(\mathbf{3}) \mathrm{CoCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O}$. (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms and co-crystallized water have been omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg): $\mathrm{Co}(1)-\mathrm{N}(1): 2.244(15) ; \mathrm{Co}(1)-\mathrm{N}(2)$ : 2.037(15); $\mathrm{Co}(1)-\mathrm{N}(3): 2.214(16) ; \mathrm{Co}(1)-\mathrm{Cl}(1): 2.244(7) ; \mathrm{Co}(1)-\mathrm{Cl}(2): 2.258(6) ; \mathrm{C}(2)-$ $\mathrm{N}(1): 1.27(2) ; \mathrm{C}(2)-\mathrm{C}(3): 1.49(2) ; \mathrm{C}(3)-\mathrm{N}(2): 1.35(2) ; \mathrm{C}(7)-\mathrm{N}(2): 1.37(2) ; \mathrm{C}(7)-\mathrm{C}(8):$ $1.41(2) ; \mathrm{N}(3)-\mathrm{C}(8): 1.27(2) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(1): 76.4(6) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{N}(3): 75.0(6) ; \mathrm{N}(3)-$ $\mathrm{Co}(1)-\mathrm{N}(1): 151.4(6) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{Cl}(1): 120.5(4) ; \mathrm{N}(2)-\mathrm{Co}(1)-\mathrm{Cl}(2): 124.5(4)$.
(7) $\mathrm{CoCl}_{2} \cdot \mathbf{C H}_{2} \mathbf{C l}_{2}$ : Crystals obtained as described in the synthesis of the complex were suitable for diffraction studies. A crystal fragment broken off a larger needle, was mounted inside a thin-walled glass capillary. The structure was solved using direct
methods. One (ordered) molecule dichloromethane of crystallization was found to be present.
(7) $\mathrm{FeCl}_{2} \cdot($ (toluene) $\mathbf{1 . 5}$ : Crystals obtained as described in the synthesis of the complex were suitable for diffraction studies. A crystal fragment broken off a larger needle, was mounted inside a thin-walled glass capillary. The quality of the data set was poor, with virtually no data observed above $2 \theta=40^{\circ}$. The structure was solved using direct methods. Two disordered toluene molecules were found, one located on an inversion centre and one in a general position. They were refined as idealized rigid hexagons with a methyl carbon attached at a fixed distance of $1.50 \AA$, and assigned one common isotropic temperature factor.

8•(toluene) $)_{0.5}$ : (Figure 9.2) An initial small triclinic unit cell was easily identified, but there were weak indications of a supercell structure. Therefore, a full sphere of data was collected based on this doubled cell. Eventually, refinements using this doubled cell were unsuccessful and the structure was refined in the original small cell. The structure was solved using direct methods. One molecule of toluene was found to be disordered about an inversion center. It was refined as a rigid hexagon with the methyl carbon placed at a fixed distance of $1.50 \AA$, and assigned one common isotropic temperature factor. One of the phenyl rings bound to phosphorus was also found to be ca $50: 50$ disordered, its two orientations differing only by a twist around the P-phenyl bond. As this aryl ring is fairly close to the disordered toluene solvent molecule, the supercell indications noted above might be a sign of partial order in the arrangements of phenyl rings and toluene
molecules in adjacent cells. However, we could not develop a satisfactory refinement model for this using the supercell in either P1 or P-1.


Figure 9.2. X-ray structure of 8. (thermal ellipsoids are drawn at $30 \%$ probability, hydrogen atoms and co-crystallized toluene have been omitted for clarity). Selected bond distances $(\AA)$ : $\mathrm{N}(3)-\mathrm{P}(1): 1.533(7) ; \mathrm{C}(2)-\mathrm{P}(1): 1.828(8) ; \mathrm{N}(1)-\mathrm{C}(2): 1.348(8) ; \mathrm{N}(1)-\mathrm{C}(6)$ : 1.340(10); C(6)-C(7): 1.495(9); N(2)-C(7): 1.265(9).
(10) $\mathrm{CoCl}_{2} \cdot$ (solvent): the crystal was obtained by layering dichloromethane solution with pentane solvent. A dark brown fragment broken from a big needle was sealed in a thin glass capillary. The structure was solved using direct method. However, there is a big void ( $665.0 \AA^{3}$ ) which most likely contains dichloromethane; however, it cannot be modeled as disordered or discrete ordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecules. Thus we use PLATON/SQUEEZE ${ }^{228}$ option to account for the solvent electron density.
(10) $\mathrm{FeCl}_{2}$ : (Figure 9.3) The crystal was obtained by layering dichloromethane solution with pentane solvent. A blue fragment of plate was put in glass capillary and the data was collected according to the standard procedure. The absorption correction was done using SADABS. ${ }^{102}$ Integration of actual data was done using SAINT. ${ }^{101}$


Figure 9.3. X-ray structure of (10) $\mathrm{FeCl}_{2}$ (thermal ellipsoids drawn at $30 \%$ probability, hydrogen atoms and co-crystallized $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ omitted for clarity). Selected bond distances $(\AA \AA)$ and angles $(\operatorname{deg}): \mathrm{Fe}(1)-\mathrm{N}(1): 2.284(4) ; \mathrm{Fe}(1)-\mathrm{N}(2): 2.115(4) ; \mathrm{Fe}(1)-\mathrm{N}(3): 2.161(4)$; $\mathrm{Fe}(1)-\mathrm{Cl}(1): 2.161(4) ; \mathrm{Fe}(1)-\mathrm{Cl}(2): 2.261(2) ; \mathrm{C}(2)-\mathrm{N}(1): 1.273(7) ; \mathrm{C}(2)-\mathrm{C}(3): 1.473(8)$; $\mathrm{C}(3)-\mathrm{N}(2): 1.341(7) ; \mathrm{C}(7)-\mathrm{N}(2): 1.324(7) ; \mathrm{C}(7)-\mathrm{P}(1): 1.821(6) ; \mathrm{P}(1)-\mathrm{N}(3): 1.593(5)$; $\mathrm{N}(1)-\mathrm{Fe}(1)-\mathrm{N}(2): 73.3(2) ; \mathrm{N}(2)-\mathrm{Fe}(1)-\mathrm{N}(3): 81.9(2) ; \mathrm{N}(1)-\mathrm{Fe}(1)-\mathrm{N}(3): 154.3(2) ; \mathrm{N}(2)-$ $\mathrm{Fe}(1)-\mathrm{Cl}(1): 98.29(13) ; \mathrm{N}(2)-\mathrm{Fe}(1)-\mathrm{Cl}(2): 137.68(13)$.
(8) $\mathrm{FeCl}_{2}$ : (Figure 9.4) Crystals were obtained by layering a dichloromethane solution with hexane. A long needle $\left(0.7^{*} 0.2 * 0.1\right)$ was sealed in a thin glass capillary. Visual inspection of the data revealed that the diffraction spots were large and streaky, and no data was observed beyond $2 \theta=30^{\circ}$. It was clear the crystal was of poor quality, but despite repeated attempts, no better crystals could be obtained. The structure was solved using Patterson methods. The analysis showed the presence of significant voids in the structure, which presumably contain some solvent (dichloromethane and/or cyclohexane). However, atoms for these molecules could not be located.


Figure 9.4. X-ray structure of $(\mathbf{8}) \mathrm{FeCl}_{2}$ (thermal ellipsoids of one of the two molecules are drawn at $30 \%$ probability, hydrogen atoms and co-crystallized $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ or other solvent have been omitted for clarity). Selected bond distances ( $\AA$ ) and angles (deg):
$\mathrm{Fe}(1)-\mathrm{N}(3): 2.131(8) ; \mathrm{Fe}(1)-\mathrm{N}(5): 2.152(7) ; \mathrm{Fe}(1)-\mathrm{N}(4): 2.259(7) ; \mathrm{Fe}(1)-\mathrm{Cl}(5): 2.378(3) ;$ $\mathrm{Fe}(1)-\mathrm{Cl}(4): 2.267(3) ; \mathrm{N}(4)-\mathrm{C}(25): 1.322(10) ; \mathrm{C}(24)-\mathrm{C}(25): 1.489(13) ; \mathrm{N}(5)-\mathrm{C}(24):$ $1.346(11) ; \mathrm{N}(5)-\mathrm{C}(10): 1.346(12) ; \mathrm{P}(1)-\mathrm{C}(10): 1.803(10) ; \mathrm{P}(1)-\mathrm{N}(3): 1.606(7) ; \mathrm{N}(3)-$ Fe(1)-N(5): 80.7(3); N(5)-Fe(1)-N(4): 72.2(3); N(3)-Fe(1)-N(4): 148.0(2); N(5)-Fe(1)$\mathrm{Cl}(4): 151.8(2) ; \mathrm{N}(5)-\mathrm{Fe}(1)-\mathrm{Cl}(5): 91.7(2)$.
(9) $\mathbf{F e C l}_{2} \cdot \mathbf{3} \mathbf{C H}_{2} \mathbf{C l}_{\mathbf{2}}$ : (Figure 9.5) Crystals were obtained by layering dichloromethane solution with pentane. A long dark-blue needle was sealed in a thin glass capillary. The structure was solved by direct methods. Three poorly ordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecules were found in the structure. PLATON indicated the presence of additional small voids $\left(41 \AA^{3}\right)$, possibly containing water molecules. These voids were far away from the $\mathrm{FeCl}_{2}$ fragment. I did not succeed in refining water molecules in these positions. For the three $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecules, all $\mathrm{C}-\mathrm{Cl}$ bond lengths were constrained to be same using the SADI option of SHELXL. ${ }^{105}$ The intramolecular $\mathrm{Cl}-\mathrm{Cl}$ distances were similarly constrained to enforce equal $\mathrm{Cl}-\mathrm{C}-\mathrm{Cl}$ angles. The most seriously disordered $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ molecule was modeled as disordered over two orientations, $\mathrm{Cl}(13)-\mathrm{C}(92)-\mathrm{Cl}(14)$ (orientation 1) and $\mathrm{Cl}(84)-\mathrm{C}(94)-\mathrm{Cl}(83)$ (orientation 2); their occupancies were refined to be $0.300(5) / 0.699(5)$.


Figure 9.5. X-ray structure of (9) $\mathrm{FeCl}_{2}$ (thermal ellipsoids are drawn at $30 \%$ probability, hydrogen atoms and co-crystallized $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ have been omitted for clarity). Selected bond distances $(\AA)$ and angles (deg): $\mathrm{Fe}(1)-\mathrm{N}(2): 2.261(5) ; \mathrm{Fe}(1)-\mathrm{N}(3): 2.086(4) ; \mathrm{Fe}(1)-\mathrm{N}(4)$ : 2.127(5); $\mathrm{Fe}(1)-\mathrm{Cl}(8): 2.251(2) ; \mathrm{Fe}(1)-\mathrm{Cl}(9): 2.313(2) ; \mathrm{N}(2)-\mathrm{C}(6): 1.291(7) ; \mathrm{C}(51)-\mathrm{C}(6):$ $1.480(8) ; \mathrm{C}(51)-\mathrm{N}(3): 1.347(7) ; \mathrm{C}(55)-\mathrm{N}(3): 1.347(6) ; \mathrm{P}(5)-\mathrm{C}(55): 1.815(6) ; \mathrm{P}(5)-\mathrm{N}(4):$ $1.600(5) ; \quad \mathrm{N}(3)-\mathrm{Fe}(1)-\mathrm{N}(2): \quad 73.85(17) ; \quad \mathrm{N}(3)-\mathrm{Fe}(1)-\mathrm{N}(4): \quad 81.49(17) ; \quad \mathrm{N}(4)-\mathrm{Fe}(1)-$ $\mathrm{N}(2): 149.10(18) ; \mathrm{N}(3)-\mathrm{Fe}(1)-\mathrm{Cl}(8): 154.22(14) ; \mathrm{N}(3)-\mathrm{Fe}(1)-\mathrm{Cl}(9): 94.96(14)$.
(15) $\mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ : (Figure 9.6) Crystal was obtained by cooling the $\mathrm{Et}_{2} \mathrm{O} / \mathrm{Hexane}$ solution at $-35^{\circ} \mathrm{C}$. A irregular fragment (approximate $0.25^{*} 0.30 * 0.40 \mathrm{~mm}$ ) was sealed in a thin-wall glass capillary. The standard procedure for data collection and processing were used. The structure was solved by the Patterson method with SHELXS97. ${ }^{104}$


Figure 9.6. X-ray structure of (15) $\mathrm{Fe}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ (thermal ellipsoids are drawn at $30 \%$ probability, one molecule and hydrogen atoms were omitted for clarity). Selected bond distances $(\AA)$ and angles (deg): $\mathrm{N}(8)-\mathrm{C}(13): 1.279(3) ; \mathrm{C}(8)-\mathrm{C}(13): 1.432(3) ; \mathrm{N}(7)-\mathrm{C}(8)$ : $1.370(3) ; \mathrm{N}(7)-\mathrm{C}(12): 1.371(3) ; \mathrm{C}(12)-\mathrm{C}(18): 1.443(3) ; \mathrm{N}(10)-\mathrm{C}(18): 1.272(3) ; \mathrm{Fe}(1)-$ $\mathrm{N}(8): 2.2348(16) ; \mathrm{Fe}(1)-\mathrm{N}(7): 2.0089(16) ; \mathrm{Fe}(1)-\mathrm{N}(10): 2.2599(16) ; \mathrm{Fe}(1)-\mathrm{C}(25)$ : 2.0794(19); $\mathrm{Fe}(1)-\mathrm{C}(51): 2.0647(19) ; \mathrm{N}(7)-\mathrm{Fe}(1)-\mathrm{N}(8): 75.12(6) ; \mathrm{N}(7)-\mathrm{Fe}(1)-\mathrm{N}(10)$ : 74.76(6); $\mathrm{N}(8)-\mathrm{Fe}(1)-\mathrm{N}(10): 149.88(6) ; \mathrm{N}(7)-\mathrm{Fe}(1)-\mathrm{C}(25): 120.50(7) ; \mathrm{N}(7)-\mathrm{Fe}(1)-\mathrm{C}(51)$ : 118.48(7); C(51)-Fe(1)-C(25): 121.02(8).

## Computational methods

All geometries were optimized at the $\mathrm{b} 3-\mathrm{lyp}^{229} / \mathrm{SV}(\mathrm{P})^{230}$ level using the Turbomole package ${ }^{231}$ in combination with an external optimizer: the standalone Baker optimizer ${ }^{232}$
for the local minima, and BOptimize ${ }^{147}$ for the constrained optimizations used to explore the potential-energy surface using the two-angle criterion $\omega$. The Turbomole b3-lyp functional is similar to the Gaussian B3LYP functional, but uses $\mathrm{VWN}(\mathrm{V})$ instead of VWN(III) for the correlation part of the functional. ${ }^{233}$ High-spin states were assumed for all dichlorides, and the spin-unrestricted formalism was used for all open-shell calculations. Improved single-point energies were then calculated at $\operatorname{SV}(\mathrm{P})$ geometries using the TZVP basis set. ${ }^{234}$ Energies mentioned in the text are pure electronic energies: the vibrational analyses required for calculations of zero-point energies and enthalpy and entropy corrections would be very expensive for the larger systems, and are meaningless for the constrained optimizations.

Table 9.1. Details of crystal-structure determinations for Chapter 3

|  | $\begin{aligned} & \hline 8 \\ & \cdot 0.5 \text { toluene } \end{aligned}$ | $\begin{aligned} & \text { (3) } \mathrm{CoCl}_{2} \\ & \cdot \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\begin{aligned} & (7) \mathbf{C o C l}_{\mathbf{2}} \\ & \cdot \mathbf{C H}_{2} \mathbf{C l}_{2} \end{aligned}$ | $\begin{aligned} & \hline(10) \mathrm{CoCl}_{2} \\ & \cdot(\text { solvent } \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
| Formula | $\begin{aligned} & \mathrm{C}_{40} \mathrm{H}_{44} \mathrm{~N}_{3} \mathrm{P} \\ & \cdot 0.5 \mathrm{C}_{7} \mathrm{H}_{8} \end{aligned}$ | $\begin{aligned} & \mathrm{C}_{27} \mathrm{H}_{31} \mathrm{Cl}_{2} \mathrm{CoN}_{3} \\ & \cdot \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\begin{aligned} & \mathrm{C}_{27} \mathrm{H}_{25} \mathrm{Cl}_{2} \mathrm{CoF}_{6} \mathrm{~N}_{3} \\ & \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{aligned}$ | $\begin{aligned} & \mathrm{C}_{3} 7 \mathrm{H}_{38} \mathrm{Cl}_{2} \mathrm{CoN}_{3} \mathrm{P} \\ & \text { • solvent } \end{aligned}$ |
| Mol wt | 643.82 | 543.38 | 720.27 | 685.50 |
| Cryst system | Triclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P-1 | P2 $1^{1 / c}$ | P2 $1^{\prime} \mathrm{c}$ | P2 $1^{\prime} \mathrm{c}$ |
| $a / \AA$ | 11.6000(8) | 7.986(3) | 8.5975(4) | 10.4731(4) |
| $b / \AA$ | 14.0850(10) | 13.707(4) | 23.0136(11) | 22.0957(9) |
| $c / \AA$ | 14.3620(17) | 25.479(8) | 16.7577(8) | 17.1785(7) |
| $\alpha /$ deg | 118.2700(13) | 90.00 | 90 | 90 |
| $\beta /$ deg | $110.2500(14)$ | 95.414(5) | 97.6641(12) | 98.3666(9) |
| $\gamma / \mathrm{deg}$ | 92.6000(13) | 90.0 | 90 | 90 |
| $V / \AA^{3}$ | 1875.7(3) | 2776.8(15) | 3286.1(3) | 3933.0(3) |
| Z | 2 | 4 | 4 | 4 |
| $D_{\mathrm{c}} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.14 | 1.300 | 1.456 | 1.158 |
| abs coef $/ \mathrm{mm}^{-1}$ | 0.107 | 0.834 | 0.904 | 0.639 |
| $\mathrm{F}_{000}$ | 690 | 1132 | 1460 | 1428 |
| index ranges | $-14 \leq \mathrm{h} \leq 14$ | $-6 \leq h \leq 6$ | $-10 \leq \mathrm{h} \leq 10$ | $-12 \leq \mathrm{h} \leq 12$ |


|  | $\begin{aligned} & 8 \\ & \cdot 0.5 \text { toluene } \end{aligned}$ | $\begin{aligned} & \text { (3) } \mathrm{CoCl}_{2} \\ & \cdot \mathrm{H}_{2} \mathrm{O} \end{aligned}$ | $\begin{aligned} & (7) \mathrm{CoCl}_{2} \\ & \cdot \mathbf{C H}_{2} \mathrm{Cl}_{2} \end{aligned}$ | $\begin{aligned} & \hline\left(\text { (solvent) } \mathrm{CoCl}_{2}\right. \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | $-17 \leq \mathrm{k} \leq 17$ | $-11 \leq \mathrm{k} \leq 11$ | $-27 \leq \mathrm{k} \leq 26$ | $-26 \leq \mathrm{k} \leq 26$ |
|  | $-17 \leq 1 \leq 17$ | $-21 \leq 1 \leq 21$ | $-20 \leq 1 \leq 20$ | $-20 \leq 1 \leq 20$ |
| $2 \theta_{\text {max }} /$ deg | 51 | 51 | 51 | 51 |
| \# rflctns | 13959 | 6344 | 20825 | 28888 |
| \# unique | 6982 | 1762 | 6093 | 7332 |
| $\#>2 \sigma$ | 5921 | 927 | 4279 | 6518 |
| GOF | 1.048 | 1.004 | 1.224 | 1.018 |
| \# parameters | 393 | 161 | 385 | 425 |
| $R(F \mathrm{O}>4 \sigma(F \mathrm{o}))^{\mathrm{XLVII}}$ | 0.1190 | 0.1065 | 0.1063 | 0.0420 |
| $R$ (all data) | 0.1305 | 0.1768 | 0.1427 | 0.0466 |
| $w R 2$ (all data) | 0.3162 | 0.2652 | 0.2121 | 0.1246 |
| largest peak, hole/e $\AA^{-3}$ | 1.363, | 0.665, | 0.733, | 0.430, |
|  | -1.182 | -0.445 | -0.376 | -0.164 |

${ }^{\text {XLVII }} R(F \mathrm{o}>4 \sigma(F \mathrm{o}))$ is from the output of SHELXL 97, which is a criterion for assessing the refinement quality based on "observed" reflections. However, the " $4 \sigma$ " threshold was not used to exclude data from the refinement.

Table 9.2. Details of crystal-structure determinations for Chapter 3

|  | $\begin{aligned} & (7) \mathrm{FeCl}_{2} \\ & \cdot 1.5 \text { toluene } \end{aligned}$ | $\begin{aligned} & \left(\mathbf{1 0 )} \mathrm{FeCl}_{2}\right. \\ & \cdot \mathbf{C H}_{2} \mathbf{C l}_{2} \end{aligned}$ | $\begin{aligned} & \hline(8) \mathrm{FeCl}_{2} \\ & \cdot \text { (solvent) } \end{aligned}$ | $\begin{aligned} & \text { (9) } \mathrm{FeCl}_{2} \\ & -3 \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{aligned}$ | (Pybox)Fe( $\left.\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Formula | $\begin{aligned} & 2\left(\mathrm{C}_{27} \mathrm{H}_{25} \mathrm{Cl}_{2} \mathrm{~F}_{6} \mathrm{~N}_{3}\right) \\ & -3 \mathrm{C}_{7} \mathrm{H}_{8} \end{aligned}$ | $\begin{aligned} & \mathrm{C}_{37} \mathrm{H}_{38} \mathrm{Cl}_{2} \mathrm{CoN}_{3} \mathrm{P} \\ & \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{aligned}$ | $\mathrm{C}_{40} \mathrm{H}_{44} \mathrm{Cl}_{2} \mathrm{FeN} 3 \mathrm{P} \cdot\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ | $\begin{aligned} & \mathrm{C}_{43} \mathrm{H}_{50} \mathrm{Cl}_{2} \mathrm{FeN}_{3} \mathrm{P} \\ & \cdot 3 \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{aligned}$ | $\mathrm{C}_{23} \mathrm{H}_{41} \mathrm{FeN}_{3} \mathrm{O}_{2} \mathrm{Si}_{2}$ |
| Mol wt | 1540.90 | 767.35 | 759.95 | 1021.36 | 503.62 |
| Cryst system | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $\mathrm{P} 21 / \mathrm{c}$ | P2 $1 / \mathrm{c}$ | P-1 | Cc | $\mathrm{P} 2_{1} / \mathrm{n}$ |
| $a / \AA$ | 12.7827(9) | 10.4789(7) | 12.9108(14) | 13.2575(8) | 10.8062(4) |
| $b / \AA$ | 17.3375(12) | 22.0476(15) | 20.122(2) | 22.9960(12) | 19.1223(8) |
| $c / \AA$ | 17.8208(13) | 17.3356(12) | 17.1707(19) | 17.5282(10) | 27.5846(12) |
| $\alpha /$ deg | 90 | 90 | 95.669(4) | 90 | 90 |
| $\beta /$ deg | 107.0897(12) | 98.285(2) | 89.895(3) | 95.2100(14) | 94.7266(11) |
| $\gamma /$ deg | 90 | 90 | 95.449(3) | 90 | 90 |
| $V / \AA^{3}$ | 3775.1 | 3963.3(5) | 4418.8(8) | 5321.7(5) | 5680.7(4) |
| Z | 2 | 4 | 4 | 4 | 8 |
| $D_{\mathrm{c}} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.356 | 1.286 | 1.151 | 1.275 | 1.178 |
| abs coef $/ \mathrm{mm}^{-1}$ | 0.601 | 0.720 | 0.587 | 0.748 | 0.637 |
| $\mathrm{F}_{000}$ | 1588 | 1592 | 1600 | 2120 | 2160 |
| index ranges | $-15 \leq h \leq 15$ | $-12 \leq \mathrm{h} \leq 12$ | $-15 \leq \mathrm{h} \leq 15$ | $-16 \leq h \leq 16$ | $-13 \leq \mathrm{h} \leq 13$ |


|  | (7) $\mathrm{FeCl}_{2}$ <br> - 1.5 toluene | $\begin{aligned} & \left(\mathbf{1 0 )} \mathrm{FeCl}_{2}\right. \\ & \cdot \mathbf{C H}_{2} \mathbf{C l}_{2} \end{aligned}$ | $\begin{aligned} & \hline(8) \mathrm{FeCl}_{2} \\ & \cdot \text { (solvent) } \end{aligned}$ | $\begin{aligned} & \text { (9) } \mathrm{FeCl}_{2} \\ & \cdot \mathbf{3} \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{aligned}$ | (Pybox)Fe( $\left.\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $-21 \leq \mathrm{k} \leq 21$ | $-24 \leq \mathrm{k} \leq 26$ | $-24 \leq \mathrm{k} \leq 24$ | $-27 \leq \mathrm{k} \leq 27$ | $-23 \leq \mathrm{k} \leq 23$ |
|  | $-21 \leq 1 \leq 21$ | $-20 \leq 1 \leq 20$ | $-20 \leq 1 \leq 20$ | $-21 \leq 1 \leq 21$ | $-33 \leq 1 \leq 33$ |
| $2 \theta_{\text {max }} /$ deg | 51 | 51 | 51 | 51 | 51 |
| \# rflctns | 24335 | 25102 | 32878 | 17265 | 37291 |
| \# unique | 7026 | 7366 | 16453 | 9680 | 10575 |
| $\#>2 \sigma$ | 4376 | 5278 | 6134 | 7711 | 8595 |
| GOF | 1.132 | 0.993 | 1.014 | 1.066 | 1.006 |
| \# parameters | 380 | 431 | 911 | 547 | 593 |
| $R(F \mathrm{O}>4 \sigma(F \mathrm{o})$ ) | 0.0952 | 0.0962 | 0.1165 | 0.0777 | 0.0395 |
| $R$ (all data) | 0.1399 | 0.1319 | 0.2364 | 0.0931 | 0.0491 |
| $w R 2$ (all data) | 0.2738 | 0.2406 | 0.3437 | 0.1929 | 0.1075 |
| largest peak, hole/e $\AA^{-3}$ | $\begin{aligned} & 0.822, \\ & -1.053 \end{aligned}$ | $\begin{aligned} & 1.139 \\ & -0.645 \end{aligned}$ | $\begin{aligned} & 0.716, \\ & -0.616 \end{aligned}$ | $\begin{aligned} & 0.917 \\ & -0.703 \end{aligned}$ | $\begin{aligned} & 0.323 \\ & -0.193 \end{aligned}$ |

### 9.2 Experimental section for Chapter 4:

Computational details: (the text is the verbatim copy from the experimental part of the published paper, with the permission from [Zhu, D.; Budzelaar, P.H.M. Organometallics 2008, 27, 2699] Copyright [2008] American Chemical Society.)

Using the standalone Baker optimizer, structures of free ligands, $\mathrm{MgCl}_{2}$ and $\mathrm{ZnCl}_{2}$ complexes were optimized at restricted $\mathrm{b} 3-\mathrm{lyp}^{229} / \mathrm{SV}(\mathrm{P})^{230}$ but open-shell calculations were done for the rest of the first-row transition-metal halide complexes using the Turbomole package. Open-shell singlet calculation was done for CoMe complexes. The improved single-point electronic energies were calculated at b3-lyp/TZVP ${ }^{234} / / \mathrm{b} 3-$ $\operatorname{lyp} / \mathrm{SV}(\mathrm{P})$. Thus all energies used in the text are pure electronic energies without zeropoint energy corrections or any thermal corrections. Apart from these, BSSE corrections were not done, either. The main reasons not to use the free energy here are partly because it is too expensive to calculate for large molecules and partly because electronic effects are our primary concern. In addition, the energy change here is quite small and the entropy correction, in particular, would introduce a lot of "noise" in the calculation. Total energies, $\hat{S^{2}}$ values and geometries (xyz format) for all structures can be found in the supporting information of the paper published in Organometallics 2008, 27, 2699.

### 9.3 Experimental section for Chapter 5:

Experimental section (the text is the verbatim copy from the experimental part of the published paper unless otherwise specified, with permission from [Zhu, D.; Janssen, F.F.B.J.; Budzelaar, P.H.M. Organometallics 2010, 29, 1897] Copyright [2010] American Chemical Society; $\left.\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3} ; \mathrm{R}^{\prime}=\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)$

General. All experiments were done under argon atmosphere using standard Schlenk techniques, or in a nitrogen-filled dry-box. Pyridine and tetramethylethylenediamine (TMEDA) were obtained from Aldrich and dried by distillation from calcium hydride. Pentane, hexane, toluene, diethyl ether, tetrahydrofuran, benzene and benzene- $d_{6}$ were distilled from sodium/benzophenone. $\mathrm{LiCH}_{2} \mathrm{SiMe}_{3}$ was purchased from Aldrich and crystallized from pentane at $-35^{\circ} \mathrm{C}$. Anhydrous $\mathrm{CoCl}_{2}$, 2-methyl-2phenylpropylmagnesium chloride solution $(0.5 \mathrm{M}$ in diethyl ether), methyl lithium solution (1.6 M in diethyl ether) and phenyl lithium solution (1.8 M in dibutyl ether) were purchased from Aldrich and used as received.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All NMR shifts ( $\delta, \mathrm{ppm}$ ) were referenced to the solvent (benzene- $d_{6},{ }^{1} \mathrm{H}$ NMR: $\mathrm{C}_{6} \mathrm{D}_{5} \mathrm{H} \delta 7.16$ ppm; ${ }^{13} \mathrm{C}$ NMR: $C_{6} \mathrm{D}_{6} \delta 128.0 \mathrm{ppm} ; \mathrm{CDCl}_{3},{ }^{1} \mathrm{H}$ NMR: $\mathrm{CHCl}_{3} \delta 7.26 \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR: $\left.\mathrm{CHCl}_{3} \delta 77.0 \mathrm{ppm}\right)$. Data were collected at room temperature unless otherwise noted. Deconvolution and linewidth determination for broad peaks was done with the SpinWorks package. ${ }^{189}$ Elemental analysis was done in Guelph Chemical laboratories LTD.
$(\boldsymbol{P y})_{4} \boldsymbol{C o C l}_{2}$. Anhydrous $\mathrm{CoCl}_{2}(1.36 \mathrm{~g}, 10.4 \mathrm{mmol})$ was transferred into a 100 mL Schlenk tube under argon atmosphere, followed by adding 15 mL of pyridine. The resulting suspension of initially blue solid in a pink solution was stirred overnight at room temperature, during which the solid became pink. The solid was filtered off using a frit filter and dried in vacuo, giving $3.65 \mathrm{~g}(78 \%)$ of pink crude $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$.

Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{20} \mathrm{Cl}_{2} \mathrm{CoN}_{4}$ (446.24): $\mathrm{C}, 53.83 ; \mathrm{H}, 4.52 ; \mathrm{N}, 12.56 ; \mathrm{Cl}, 15.89$. Found: C, 53.67; H, 4.85; N, 12.81; Cl, 16.10.
$(\boldsymbol{P y})_{2}$ CoR $_{2}$. Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}(0.32 \mathrm{~g}, 0.72 \mathrm{mmol})$ was transferred into a 50 mL Schlenk tube under argon atmosphere, and 10 mL of pentane or hexane was added to form a blue suspension. The resulting suspension was cooled to $-70^{\circ} \mathrm{C}$ and kept at this temperature for $20 \mathrm{~min} . \mathrm{LiCH}_{2} \mathrm{SiMe}_{3}(0.136 \mathrm{~g}, 1.44 \mathrm{mmol})$ was weighed in a dry-box and dissolved in 10 mL of hexane; this solution was added dropwise to the above blue suspension at $-70^{\circ} \mathrm{C}$. The color of the mixture changed to blue-green. It was kept at $-70^{\circ} \mathrm{C}$ for another 20 min , and was then allowed to slowly ( 3 h ) warm to room temperature. During this, the color first changed to red (around $-10^{\circ} \mathrm{C}$ ), and then at around $0^{\circ} \mathrm{C}$ most of the solid dissolved to form a yellow-green solution with some suspended white solid. This was stirred for another hour at room temperature and filtered through a glass frit. Solvents were removed in vacuo, leaving a thick bright-green oil. Addition of a small amount of hexamethylbenzene as an internal standard allowed determination of the yield by NMR: $75 \%$. For most subsequent experiments, a single portion of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ was prepared and used assuming this $75 \%$ yield.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 114\left(4 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 1600 \mathrm{~Hz}\right.$, Py H2), $38.4(4 \mathrm{H}$, br, $\Delta v_{1 / 2} 500 \mathrm{~Hz}$, Py H3), 10.3 ( $18 \mathrm{H}, \mathrm{br}, \Delta v_{1 / 2} 80 \mathrm{~Hz}, \operatorname{SiMe}$ ), $-8.5\left(2 \mathrm{H}, \mathrm{br}, \Delta v_{1 / 2} 190 \mathrm{~Hz}\right.$, Py $\mathrm{H} 4)$; $\mathrm{CH}_{2}(\mathrm{Co})$ not observed.

Evans method for determination of magnetic moment: in a dry-box, one drop of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ was dissolved in about $0.5 \mathrm{~mL} \mathrm{C}_{6} \mathrm{D}_{6}$ in a small vial and $0.0253 \mathrm{~g} \mathrm{C}_{6} \mathrm{Me}_{6}$ (reference and internal standard) was added. The resulting green solution was diluted to 3.1 mL by adding $\mathrm{C}_{6} \mathrm{D}_{6}$. Integration of the ${ }^{1} \mathrm{H}$ NMR spectrum showed the concentration of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ to be $0.22 \mathrm{~mol} / \mathrm{L}$; the chemical-shift difference between $\mathrm{C}_{6} \mathrm{Me}_{6}$ in the paramagnetic solution and in pure $\mathrm{C}_{6} \mathrm{D}_{6}$ was 9.14 ppm , implying a magnetic moment of $4.9 \mu_{\mathrm{B}}$. Two further experiments at different concentrations produced similar values (0.66 $\left.\mathrm{mol} / \mathrm{L}: 4.5 \mu_{\mathrm{B}} ; 0.052 \mathrm{~mol} / \mathrm{L}: 5.0 \mu_{\mathrm{B}}\right)$; average 4.8(3) $\mu_{\mathrm{B}}$.

Hydrolysis: in a dry-box, $0.158 \mathrm{~g}(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and $0.053 \mathrm{~g} \mathrm{C} \mathrm{C}_{6} \mathrm{Me}_{6}$ were weighed into a small vial. Part of this sample was used for a ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$. From the observed molar ratio of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and $\mathrm{C}_{6} \mathrm{Me}_{6}$ (1.13:1, by integration), the purity was calculated to be $91 \%$. To the NMR sample was added 0.05 mL water, the resulting suspension was quickly filtered and the ${ }^{1} \mathrm{H}$ NMR spectrum of the filtrate was immediately recorded. The only visible signals were due to pyridine, tetramethylsilane, and hexamethylbenzene. The observed molar ratio of the $\mathrm{Py}, \mathrm{Me}_{4} \mathrm{Si}$ and $\mathrm{C}_{6} \mathrm{Me}_{6}$ species in solution (1.97:2.12:1, by integration; expected $2.26: 2.26: 1$ ) agreed reasonably well with the expected values for $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$, considering that some pyridine will remain coordinated to Co and/or stay in the water drop and some $\mathrm{Me}_{4} \mathrm{Si}$ will evaporate during filtration.
$(\mathbf{P y})_{2} \mathbf{C o P h}_{2}$.(this paragraph is reported in paper in reference 217) Procedure A: Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}(0.58 \mathrm{~g}, 1.3 \mathrm{mmol})$ was transferred into a 50 mL Schlenk tube under an argon atmosphere, and 16 mL of pentane was added to form a blue suspension. The resulting suspension was cooled to $-60^{\circ} \mathrm{C}$ and kept at this temperature for 20 min . $\mathrm{LiPh}(1.4 \mathrm{~mL}$, 1.8 M in dibutyl ether) was dropped into it to form a yellow suspension. After warming to room temperature over 4 h , the resulting yellow-green suspension was stirred for another 30 min at room temperature. After filtered over celite, a clear brown solution was obtained and most of cobalt was left on top of the celite. No further useful characterization was obtained.

Procedure B: Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}(0.45 \mathrm{~g}, 1.0 \mathrm{mmol})$ was transferred into a 50 mL Schlenk tube under an argon atmosphere, and 8 mL of diethylether was added to form a blue suspension. The resulting suspension was cooled to $-10^{\circ} \mathrm{C}$ and kept at this temperature for 20 min . $\mathrm{LiPh}(1.2 \mathrm{~mL}, 1.8 \mathrm{M}$ in dibutyl ether) was dropped into it to form a dark red suspension. After warming up to room temperature, the suspension turned gray very quickly, together with depositing a lot of black solids. No further characterization was performed.
$(\mathbf{P y})_{2} \mathbf{C o M e}_{2}$. (this paragraph is not reported in the paper in reference 217) Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}(0.80 \mathrm{~g}, 1.79 \mathrm{mmol})$ was transferred into a 25 mL Schlenk tube under an argon atmosphere, and 6 mL of pentane was added to form a blue suspension. LiMe (2.2 $\mathrm{mL}, 1.6 \mathrm{M}$ in diethyl ether) was dropped into it within 30 mins . Green solids suspended in a clear yellow solution was obtained and they were cooled to $-10^{\circ} \mathrm{C}$ and kept at this
temperature for 10 min and 10 mL dry toluene was added into it. After stirring for another 10 mins , the liquid was transferred to another Schlenk tube by syringe. After evaporation of all solvent under high vacuum, a yellow residue was obtained and the similar peaks to those of $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in ${ }^{1} \mathrm{H}$ NMR spectrum were not observed.
(TMEDA)CoR $\boldsymbol{R}_{2}$. (the procedure here is slightly modified from the published procedure in reference 217) The freshly prepared $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ ( 0.82 mmol assuming $75 \%$ yield from $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$; see above) was dissolved in 5 mL pentane and the green solution was cooled to $-30^{\circ} \mathrm{C}$. TMEDA ( 10 eq. $1.25 \mathrm{~mL}, 8.2 \mathrm{mmol}$ ) was slowly added at $-30^{\circ} \mathrm{C}$, resulting in a color change to red and then brown. The resulting mixture was allowed to warm to room temperature and continued to stir for 1 h . After filtration, the solution was evaporated to dryness. The residue was dissolved in 2 mL pentane and centrifuged to remove all possible solid, one drop of TMEDA was added and the solution was cooled to $-35^{\circ} \mathrm{C}$, depositing a dark solid. The cold liquid was pipetted off, and the solid was dried to give a purple-blue solid $\left(0.2186 \mathrm{~g}, 57 \%\right.$ yield based on $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$ used or $76 \%$ yield based on the $\left.(\mathrm{Py})_{2} \mathrm{CoR}_{2}\right)$. The deep bluish purple single crystal was grown by cooling the saturated pentane solution at $-35^{\circ} \mathrm{C}$ overnight.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 80\left(4 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 600 \mathrm{~Hz}, \mathrm{CH}_{2} \mathrm{~N}\right), 78(12 \mathrm{H}, \mathrm{br}$, $\left.\Delta v_{1 / 2} 350 \mathrm{~Hz}, \mathrm{~N} M e\right), 9.6\left(18 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 70 \mathrm{~Hz}, \mathrm{Si}_{2} \mathrm{Se}_{3}\right) ; \mathrm{CH}_{2}(\mathrm{Co})$ not observed.
$(\boldsymbol{P})_{2} \mathbf{C o R}^{\prime}{ }_{2}:$ a number of procedures were tried for the synthesis of this complex, but none gave a completely pure product. Procedure (A) below was used to generate the mixture of $(\mathrm{Py})_{2} \mathrm{MgR}^{\prime}{ }_{2}$ and $(\mathrm{Py})_{2} \mathrm{CoR}_{2}^{\prime}$ from which a crystal was used for the X-ray
structure determination mentioned in the text. Procedure (B) gave a better quality product for which the NMR spectrum could be assigned with some confidence.

Procedure (A): Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}(1.24 \mathrm{~g}, 2.78 \mathrm{mmol})$ was transferred into a 50 mL Schlenk tube, and 26 mL of dry diethyl ether was added to form a blue suspension. The resulting mixture was cooled to $-50^{\circ} \mathrm{C}$. $\mathrm{R}^{\prime} \mathrm{MgCl}(11.8 \mathrm{~mL}$ of a 0.5 M solution in diethyl ether, 5.90 mmol ) was added dropwise. The solution quickly turned green and a white solid was formed. The stirred mixture was slowly (in 30 min .) warmed to room temperature. 1.5 mL of dry pyridine was added, and the resulting green suspension was stirred at room temperature for another 30 min and filtered through a glass frit. The solvents were removed in vacuo, the residue was transferred into a dry box, dry pentane was added and the suspension was filtered through glass wool. On standing overnight at $35{ }^{\circ} \mathrm{C}$, the filtrate deposited whitish crystals of (presumably) $(\mathrm{Py})_{2} \mathrm{MgR}^{\prime}$, dark-green blocks of $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}$, and some sticky dark oily droplets. A fragment of one of the darkgreen blocks was used for single-crystal X-ray structure determination. ${ }^{1} \mathrm{H}$ NMR of the deposited solids in $\mathrm{C}_{6} \mathrm{D}_{6}$ indicated the presence of $(\mathrm{Py})_{2} \mathrm{MgR}^{\prime}{ }_{2}$ and $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ (see below).

Procedure (B): Pink $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}(0.69 \mathrm{~g}, 1.55 \mathrm{mmol})$ was transferred into a 100 mL Schlenk tube, and 26 mL of dry THF was added to form a clear blue solution. This was cooled to $-50^{\circ} \mathrm{C}$, during which pink solid precipitate formed. $\mathrm{R}^{\prime} \mathrm{MgCl}(2.8 \mathrm{~mL}$ of a 0.5 M solution in diethyl ether, 1.4 mmol ) was added dropwise. The resulting mixture was warmed to around $0{ }^{\circ} \mathrm{C}$ in 1 h , during which it turned purplish and a white solid formed. The solution was again cooled to $-50{ }^{\circ} \mathrm{C}$, and $\mathrm{R} \mathrm{MgCl}(3.2 \mathrm{~mL}$ of a 0.5 M solution in
diethyl ether, 1.6 mmol ) was added dropwise. The resulting suspension was stirred at -50 ${ }^{\circ} \mathrm{C}$ for 20 min and warmed to room temperature in 1 h , during which it turned green. 0.6 mL of dry pyridine was added into it and the green mixture was cooled to $-30{ }^{\circ} \mathrm{C}$ and concentrated to about 2 mL . A 20 mL portion of dry pentane was added, the solution was filtered through a glass frit and the filtrate was cooled to $-35{ }^{\circ} \mathrm{C}$. Overnight, a dark and shiny solid crystallized; the mother liquid was pipetted off, leaving $0.15 \mathrm{~g}(20 \%)$ of reasonable pure $(\mathrm{Py})_{2} \mathrm{CoR}_{2}{ }_{2}$. NMR samples always show some decomposition to diamagnetic compounds (pyridine, $\mathrm{PhCMe}_{3}$ ), and within 4 h all signals due to $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ disappear.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $d_{6}, 300 \mathrm{MHz}$; assignment tentative!): $\delta 108\left(4 \mathrm{H}, \Delta v_{1 / 2} 5300\right.$ Hz, Py $H 2$ ), 32.7 ( $4 \mathrm{H}, \Delta v_{1 / 2} 1700 \mathrm{~Hz}$, Py H3), 21.6 (12H, $\Delta v_{1 / 2} 270 \mathrm{~Hz}, \mathrm{CMe}$ ), $10.2(4 \mathrm{H}$, $\left.\Delta v_{1 / 2} 160 \mathrm{~Hz}, \operatorname{Ar} o\right), 7.4\left(4 \mathrm{H}, \Delta v_{1 / 2} 27 \mathrm{~Hz}, \operatorname{Ar} m\right), 3.9\left(2 \mathrm{H}, \Delta v_{1 / 2} 17 \mathrm{~Hz}, \operatorname{Ar} p\right),-8.1\left(2 \mathrm{H}, \Delta v_{1 / 2}\right.$ $590 \mathrm{~Hz}, \mathrm{Py} H 4)$.

## Synthesis of $(\mathrm{Py})_{2} \mathrm{Mg}\left(\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)_{2}$.

Under a nitrogen atmosphere, 5 mL dry pyridine was dissolved in 15 mL dry pentane, and 5 mL 2-methyl-2-phenylpropylmagnesium chloride solution ( 0.5 M in diethyl ether) was added, resulting in the precipitation of a white powder. The resulting yellow solution with white suspended solid was stirred for another 2 h at room temperature and filtered through a glass frit. The filtrate was evaporated to dryness, and the resulting yellow sticky oil was dissolved in toluene and layered with pentane in $-35^{\circ} \mathrm{C}$ overnight, forming a yellow crystalline solid $(0.45 \mathrm{~g}, 80 \%$ yield $)$.
${ }^{1} \mathrm{H}$ NMR ( $25^{\circ} \mathrm{C}$, benzene- $d 6,300 \mathrm{MHz}$ ): $\delta 7.90(\mathrm{~d}, 4 \mathrm{H}, J 4.0 \mathrm{~Hz}$, Py $H 2$ ), $7.78(\mathrm{~d}, 4 \mathrm{H}$, $J 7.7 \mathrm{~Hz}, \operatorname{Ar} o), 7.12(\mathrm{t}, 4 \mathrm{H}, J 7.7 \mathrm{~Hz}, \operatorname{Ar} m), 6.99(\mathrm{t}, 2 \mathrm{H}, J 7.2 \mathrm{~Hz}, \operatorname{Ar} p), 6.78(\mathrm{t}, 2 \mathrm{H}, J$ $7.4 \mathrm{~Hz}, \operatorname{Py} H 4), 6.41(\mathrm{t}, 4 \mathrm{H}, J 6.4 \mathrm{~Hz}, \operatorname{Py} H 3), 1.83(\mathrm{~s}, 12 \mathrm{H}, M e), 0.77\left(\mathrm{~s}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) .{ }^{13} \mathrm{C}$ NMR ( $25^{\circ} \mathrm{C}$, benzene- $d 6,75 \mathrm{MHz}$ ): $\delta 158.3$ ( $\left.\mathrm{Ar} i\right), 148.82$ (Py C2), 137.69 (Py C4), 127.80 (Ar m), 125.92 (Ar o), 124.21 (Py C4), 123.91 (Ar, p), 40.41 (CMe2), 36.62 (CMe2), $34.48(\mathrm{CH} 2)$.

X-ray structure determinations (see also Table 9.3).

General. Refer to the single crystal X-ray diffraction in Chapter 2.
(TMEDA)CoR $\mathbf{2}_{2}$. A deep bluish-purple crystal fragment (ca. $0.5 \times 0.2 \times 0.15 \mathrm{~mm}$ ) was mounted in a thin-walled glass capillary. Data were collected at 293 K on a Bruker 4circle diffractometer with an APEX detector. The crystal system and space group were determined from the cell metric and systematic absences. The structure was solved by the Patterson method with SHELXS97. ${ }^{104}$ This is not a new structure: the structure of the complex was originally determined by Hay-Motherwell, ${ }^{185}$ and we find the same unit cell and coordinates. However, these authors did not report any characterization data other than the X-ray structure, so we used our structure determination as confirmation of the identity of the complex.
$(\boldsymbol{P y})_{2} \mathbf{C o R}^{\prime}{ }_{2}$. A large irregular crystal fragment (ca $0.6 \times 0.5 \times 0.4 \mathrm{~mm}$ ) was broken off an even larger block of green-black $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}$, picked from the results of a crystallization
attempt (nearly colorless crystals of a magnesium complex were also present). The fragment was mounted in a thin-walled glass capillary. Data was collected using $0.30^{\circ}$ scan width, a 15 s scan time and full-sphere coverage. The large scan width and fast scan time, as well as the large size of the crystal, was chosen to allow rapid data collection since Cámpora reported that the iron analogue decayed during data collection. ${ }^{151}$ Indeed, after about $75 \%$ of the full-sphere data was collected, the crystal had visibly changed the shape and did not diffract any more. Analysis of the diffraction data showed that, at completion of the first hemisphere of data, decay was less than $15 \%$. Therefore, only this first hemisphere of data was processed and used in the refinement. The data integration was performed using SAINT ${ }^{101}$ with a decay correction, and an absorption correction was done using SADABS ${ }^{102}$. The structure was solved by the Patterson method using SHELXS97. ${ }^{104}$ Even though the final thermal parameters and error margins look acceptable, the data should be treated with caution because of the crystal decay during data collection.

Table 9.3. Details of crystal structure determinations

|  | $($ TMEDA $) \mathbf{C o R}_{2}$ | $\left(\mathbf{P y}_{\mathbf{2}} \mathbf{C o R}_{2}\right.$ |
| :--- | :--- | :--- |
| Formula | $\mathrm{C}_{14} \mathrm{H}_{38} \mathrm{CoN}_{2} \mathrm{Si}_{2}$ | $\mathrm{C}_{30} \mathrm{H}_{36} \mathrm{CoN}_{2}$ |
| Mol wt | 349.57 | 483.54 |
| Cryst system | monoclinic | triclinic |
| Space group | $\mathrm{C} 2 / \mathrm{c}$ | $\mathrm{P}-1$ |


|  | (TMEDA)CoR ${ }_{2}$ | $(\mathrm{Py})_{2} \mathrm{CoR}^{2}$ |
| :---: | :---: | :---: |
| $a / \AA$ | 25.565(3) | 11.8183(11) |
| $b / \AA$ | 10.1487(10) | 11.8294(12) |
| $c / \AA$ | 17.3758(18) | 12.1892(12) |
| $\alpha /$ deg | 90 | 105.652(2) |
| $\beta /$ deg | 100.104(6) | 109.119(2) |
| $\gamma / \mathrm{deg}$ | 90 | 108.825(2) |
| $V / \AA^{3}$ | 4438.3(8) | 1383.1(2) |
| Z | 8 | 2 |
| $D_{\mathrm{c}} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.046 | 1.161 |
| abs coef $/ \mathrm{mm}^{-1}$ | 0.875 | 0.639 |
| $\mathrm{F}_{000}$ | 1528 | 514 |
| index ranges | $-30 \leq \mathrm{h} \leq 30$ $-12 \leq \mathrm{k} \leq 12$ | $\begin{aligned} & -14 \leq h \leq 14 \\ & -14 \leq k \leq 14 \\ & -14 \leq l \leq 14 \end{aligned}$ |
|  | $-20 \leq 1 \leq 21$ |  |
| $2 \theta_{\text {max }} /$ deg | 51 | 51 |


|  | (TMEDA)CoR 2 | $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ |
| :---: | :---: | :---: |
| \# rflctns | 13479 | 10195 |
| \# unique | 4140 | 5166 |
| $\#>2 \sigma$ | 3163 | 4314 |
| GOF | 1.054 | 1.088 |
| \# parameters | 186 | 324 |
| $R(F \mathrm{O}>4 \sigma(F \mathrm{o})$ ) | 0.0374 | 0.0685 |
| $R$ (all data) | 0.0496 | 0.0772 |
| $w R 2$ (all data) | 0.1090 | 0.2060 |
| largest peak, hole/e $\AA^{-3}$ | $0.266$ <br> $-0.171$ | $\begin{aligned} & 0.555 \\ & -0.241 \end{aligned}$ |

## Computational methods

All geometry optimizations were done with Turbomole ${ }^{231}$ using the SVP ${ }^{230}$ and TZVP ${ }^{234}$ basis sets and the functionals b3-lyp ${ }^{229}$ and $b-p^{110,111}$ (the latter with the RI approximation) in combination with an external optimizer (PQS OPTIMIZE ${ }^{232}$ ). All calculations used the spin-unrestricted formalism with $S_{\mathrm{z}}=3 / 2$ ( $\mathrm{Co}^{\text {II }} \mathrm{HS}$ ). Vibrational analyses were done for all stationary points to confirm their nature, and also to calculate thermal corrections (enthalpy and entropy, gas phase, 298K, 1 bar) and obtain free
energies using the standard formulas of statistical thermodynamics. ${ }^{235}$ Calculations of the orbital contributions to the chemical shift were calculated using Gaussian $03^{118}$ (B3LYP and BP86 functionals, TZVP basis set, GIAO method ${ }^{236}$ ). EPR hyperfine couplings used to estimate Fermi contact shifts (Eq. 5.2) were calculated ${ }^{237}$ using the Orca ${ }^{119}$ program (B3LYP and BP86 functionals, TZVP basis set).

### 9.4 Experimental section for Chapter 6:

Experimental sections (the text is the verbatim copy from the experimental part of published paper unless otherwise specified, with permission from [Zhu, D.; Janssen, F.F.B.J.; Budzelaar, P.H.M. Organometallics 2010, 29, 1897] Copyright [2010] American Chemical Society; $\left.\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3} ; \mathrm{R}^{\prime}=\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)$

General. All experiments were done under argon atmosphere using standard Schlenk techniques, or in a nitrogen-filled dry-box. Pyridine and tetramethylethylenediamine (TMEDA) were obtained from Aldrich and dried by distillation from calcium hydride. Pentane, hexane, toluene, diethyl ether, tetrahydrofuran, benzene and benzene- $d_{6}$ were distilled from sodium/benzophenone. Ligands $\mathbf{1 - 3},{ }^{238} \mathbf{4}^{239}, \mathbf{6}^{222}, \mathbf{8}^{142}$ and $\mathbf{1 0}^{240}$ in Chapter 6 were prepared according to published procedures. The procedure for synthesizing ligand 9 in this Chapter refers to the synthesis of $2-\left[2,6-{ }^{-} \operatorname{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{CMe}\right]-6-[2,4,6-$ $\left.\mathrm{Me}_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{PPh}_{2}\right]-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ in the experimental part of Chapter 3 .
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All NMR shifts ( $\delta, \mathrm{ppm}$ ) were referenced to the solvent (benzene- $d_{6},{ }^{1} \mathrm{H}$ NMR: $\mathrm{C}_{6} \mathrm{D}_{5} \mathrm{H} \delta 7.16$ ppm; ${ }^{13} \mathrm{C}$ NMR: $\mathrm{C}_{6} \mathrm{D}_{6} \delta 128.0 \mathrm{ppm} ; \mathrm{CDCl}_{3},{ }^{1} \mathrm{H}$ NMR: $\mathrm{CHCl}_{3} \delta 7.26 \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR: $\left.C \mathrm{HCl}_{3} \delta 77.0 \mathrm{ppm}\right)$. Data were collected at room temperature unless otherwise noted. Elemental analysis was done in Guelph Chemical laboratories LTD.

The following work between $/ *$ and $* \backslash$ was done by Peter H.M. Budzelaar and Femke F.B.J. Janssen
/* 2,6-( $\left.\mathbf{C F}_{3} \mathbf{C O}\right)_{2} \boldsymbol{C}_{5} \boldsymbol{H}_{3} \mathbf{N}$. In a 250 mL three-necked flask with Ar connection, dropping funnel, and septum equipped with an internal temperature sensor, was placed 5 g (21.1 mmol) 2,6-dibromopyridine in 56 mL diethyl ether and 44 mL THF. The magnetically stirred mixture was cooled in a methanol/liquid nitrogen cooling bath to an internal temperature of $-95^{\circ} \mathrm{C}$ (dibromopyridine starts to precipitate). 13.6 mL of 1.6 M n - BuLi in hexanes ( 21.6 mmol ) was added in about 10 minutes, keeping the temperature of the mixture below $-90^{\circ} \mathrm{C} .3 \mathrm{~mL}$ of diethyl ether was used to rinse the wall of the dropping funnel and this was added to the mixture. Warming of the mixture to $-90^{\circ} \mathrm{C}$ resulted in dissolution of the precipitated dibromopyridine, giving a clear yellow solution. After 5 more minutes stirring at $-90^{\circ} \mathrm{C}$, the mixture was cooled to $-100^{\circ} \mathrm{C}$ and $2.74 \mathrm{~g}(21.4 \mathrm{mmol})$ methyl trifluoroacetate was added over 10 minutes, keeping the temperature below $-90^{\circ} \mathrm{C}$. Some ether was used to rinse the funnel. The mixture was stirred for 20 minutes at $-90^{\circ} \mathrm{C}$, then cooled to $-113^{\circ} \mathrm{C}$, and 13.6 mL of $1.6 \mathrm{M} n$ - BuLi was added while the
temperature was kept below $-100^{\circ} \mathrm{C}$. After 5 minutes of stirring, $2.8 \mathrm{~g}(21.8 \mathrm{mmol})$ methyl trifluoroacetate was added while keeping the temperature below $-100^{\circ} \mathrm{C}$.

The mixture was allowed to warm, and when it reached $-60^{\circ} \mathrm{C}$, a mixture of 7 mL 12 M HCl and 5 mL water was added. The reaction mixture was then poured into a mixture of 25 mL 12 M HCl and 150 mL water. The organic layer was separated, dried with magnesium sulphate, and the solvent was evaporated in vacuo. The crude product was refluxed in rotary vane pump vacuum for 1 h (bath $120^{\circ} \mathrm{C}$, small flask, short condensor) and then solidified on cooling. Short-path distillation (the product solidifies in the receiver) gave $4.47 \mathrm{~g}(82 \%)$ of the colorless product, which according to NMR still contained ca $14 \%$ of the monohydrate. This mixture was used without further purification for the synthesis of $\mathbf{5}$.
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\left.\mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}\right): \delta 8.43\left(2 \mathrm{H}, \mathrm{d},{ }^{3} J 7.9 \mathrm{~Hz}, \operatorname{Py} H 3\right), 8.27\left(1 \mathrm{H}, \mathrm{t},{ }^{3} J\right.$ 7.9 Hz, Py $H 4$ ). ${ }^{13} \mathrm{C}$ NMR ( $75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$ ): $\delta 179.7$ (q, ${ }^{2} J_{\mathrm{CF}} 35 \mathrm{~Hz}, C=\mathrm{O}$ ), 147.9 (Py C2), 139.2 (Py C4), 129.1 (Py C3), 116.4 ( $\mathrm{q},{ }^{1} \mathrm{~J}_{\mathrm{CF}} 290 \mathrm{~Hz}, C \mathrm{~F}_{3}$ ). ${ }^{19} \mathrm{~F}$ NMR (282.4 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}\right): \delta-73.1$.

Before refluxing and distillation, the crude mixture contained only a small amount of 2,6-( $\left.\mathrm{CF}_{3} \mathrm{CO}\right)_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$; the main components were its bis(hemiketal) (a mixture of 2 diastereomers), hemiketal/hydrate, bis(hydrate), mono-hemiketal and mono-hydrate, causing the NMR spectra to look messy. Crystals of the bis(hydrate), suitable for X-ray diffraction, crystallized spontaneously from the THF solution of an NMR sample (for Xray structure, see Figure C. 2 in the Appendix C).

2,6-[2,4,6-Me $\left.3_{3} C_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{C}\left(\mathrm{CF}_{3}\right)\right]_{2} \mathrm{C}_{5} \mathrm{H}_{3} N$ (5). (This synthesis does not require an inert atmosphere) The crude bis(trifluoroacetyl)pyridine mixture described above was dissolved in 50 mL toluene, 4.3 g 2,4,6-trimethylaniline and a small quantity of $p$ toluenesulphonic acid were added, and the orange mixture was refluxed in a Dean-Stark apparatus for 72 h . The toluene was removed using a rotary evaporator. The residue was crystallized from hexane/toluene ( 50 mL , ca $2: 1,85^{\circ} \mathrm{C} / \mathrm{RT}$ ) to give $6.23 \mathrm{~g}(78 \%)$ of yellow crystals. A crystal from this batch was used for X-ray structure determination.
${ }^{1} \mathrm{H}$ NMR (300.1 MHz, $\left.\mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}\right): \delta 7.42\left(1 \mathrm{H}, \mathrm{t},{ }^{3} \mathrm{~J} 7.9 \mathrm{~Hz}\right.$, Py $\left.H 4\right), 6.93\left(2 \mathrm{H}, \mathrm{d},{ }^{3} J\right.$ $7.9 \mathrm{~Hz}, \operatorname{Py} H 3), 6.75(4 \mathrm{H}, \mathrm{s}, \mathrm{Ar} m), 2.22(6 \mathrm{H}, \mathrm{s}, \operatorname{Ar} p-\mathrm{Me}), 1.90(12 \mathrm{H}, \mathrm{s}, \operatorname{Ar} o-M e)$.
${ }^{13} \mathrm{C}$ NMR ( $75.5 \mathrm{MHz}, \mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}$ ): $\delta 154.6\left(\mathrm{q},{ }^{2} J_{\mathrm{CF}} 33 \mathrm{~Hz}, C=\mathrm{N}\right), 149.1$ (Py C2), $142.3(\operatorname{Ar} i), 136.6(\operatorname{Py} C 4), 134.1(\operatorname{Ar} p), 128.8(\operatorname{Ar} m), 124.8(\operatorname{Ar} o), 124.2(\operatorname{Py} C 3)$, $119.2\left(\mathrm{q},{ }^{1} J_{\mathrm{CF}} 280 \mathrm{~Hz}, \mathrm{CF}_{3}\right)$, 20.6 ( $\mathrm{Ar} p-\mathrm{Me}$ ), $17.5(\mathrm{Ar} o-\mathrm{Me}) .{ }^{19} \mathrm{~F}$ NMR ( 282.4 MHz , $\left.\mathrm{CDCl}_{3}, 25^{\circ} \mathrm{C}\right): ~ \delta-68.6$.

Anal. Calcd for $\mathrm{C}_{27} \mathrm{H}_{25} \mathrm{~F}_{6} \mathrm{~N}_{3}$ (505.50): C, 64.15; H, 4.98; N, 8.31. Found: C, 64.34; H, 5.30; N 8.40. *

## Synthesis of [2,6-bis(2,6-Me $\left.e_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{CMe}\right)-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N} / \mathrm{CoR}$ ((1)CoR) from (Py) $\mathrm{CoR}_{2}$.

 $(\mathrm{Py})_{2} \mathrm{CoR}_{2}\left(1.14 \mathrm{mmol}\right.$ assuming $75 \%$ yield from $(\mathrm{Py})_{4} \mathrm{CoCl}_{2}$; see experimental section of Chapter 5) was dissolved in 8 mL diethyl ether and the green solution was cooled to $-30^{\circ} \mathrm{C}$. Ligand $1(0.39 \mathrm{~g}, 1.06 \mathrm{mmol})$ was dissolved in 20 mL diethyl ether and the clear yellow solution was slowly added to the above $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ solution at $-30^{\circ} \mathrm{C}$. After the addition, the solution (which had turned red) was allowed to warm to room temperature (around $0^{\circ} \mathrm{C}$ the color changed to purple). After stirring for another hour, the deep purplesolution was filtered and the solvent was evaporated in vacuo. The residue was dissolved in 4 mL diethyl ether/pentane (1:1), the solution was concentrated to 2 mL , and 1 mL of hexane was added and the mixture was cooled to $-35^{\circ} \mathrm{C}$ overnight. The purple mother liquor was decanted and the residue was recrystallized from toluene ( 6 drops)/hexane (5 $\mathrm{mL})$ to give shiny dark crystalline (1)CoR $(0.23 \mathrm{~g}, 42 \%)$ suitable for X-ray diffraction.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene $\left.-d_{6}, 300 \mathrm{MHz}\right): \delta 10.08(\mathrm{t}, 1 \mathrm{H}, J 7.7 \mathrm{~Hz}, \operatorname{Py} H 4), 7.74(\mathrm{~d}, 2 \mathrm{H}, J$ $7.7 \mathrm{~Hz}, \operatorname{Py} H 3), 7.36(\mathrm{t}, 2 \mathrm{H}, J 7.4 \mathrm{~Hz}, \operatorname{Ar} p), 7.27(\mathrm{~d}, 4 \mathrm{H}, J 7.4 \mathrm{~Hz}, \operatorname{Ar} m), 2.12(\mathrm{~s}, 12 \mathrm{H}, \mathrm{Ar}$ $M e), 0.81\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CoCH}_{2}\right),-0.62\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si} M e_{3}\right),-1.26(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe})$.
${ }^{13} \mathrm{C}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 75 \mathrm{MHz}\right) \delta 165.6(\mathrm{ArN}=C \mathrm{Me}), 158.4$ (o-C, Py), $156.0(i-$ $C, \operatorname{Ar}), 130.2$ (o-C, Ar), 129.1(m-C, Ar), 125.9 ( $p-C, \operatorname{Ar),~} 123.3$ (m-C, Py), 116.7 ( $p-C$, Py), $23.8(\mathrm{~N}=\mathrm{CMe}), 19.5\left(\mathrm{o}-\mathrm{CH}_{3}, \mathrm{Ar}\right), 3.8(\mathrm{SiMe} 3),-10.7\left(\mathrm{br}, \mathrm{CoCH}_{2}\right)$.

Anal. Calcd for $\mathrm{C}_{29} \mathrm{H}_{38} \mathrm{CoN}_{3} \mathrm{Si}$ (515.65): C, 67.55; H, 7.43; N, 8.15. Found: C, 67.32; H, 7.14; N, 7.70.

Synthesis of $\quad\left[2,6-b i s\left(2,6-\mathrm{Me}_{2} \mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}=\mathrm{CMe}\right)-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right] \mathrm{CoR} \quad$ ((1)CoR) from (TMEDA)Co( $\left.\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. (A verbatim copy from the published: Zhu, D.; Budzelaar, P.H.M. Organometallics 2010, 29, 5759) In a dry-box, (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}(0.31$ $\mathrm{g}, 0.89 \mathrm{mmol})$ was weighed and dissolved in 10 mL hexane. The mixture was transferred to a Schlenk line and cooled to $-20^{\circ} \mathrm{C}$. At this temperature, ligand $\mathbf{1}(0.32 \mathrm{~g}, 0.87 \mathrm{mmol})$ in 10 mL diethyl ether was added dropwisely. The resulting mixture was allowed to warm to room temperature over 30 mins and stirred for another 4 h . All solvents were evaporated, 10 mL fresh diethyl ether was added and the mixture was stirred for another hour. The resulting purple solution was filtered over a glass frit, the filtrate was
evaporated to dryness and the residue was crystallized from diethyl ether (0.5 $\mathrm{mL})$ /hexane ( 3 mL ) at $-35^{\circ} \mathrm{C}$ over two days. The mother liquor was pipetted off and the residue was dried in vacuo, leaving dark purple solid (1)CoR (0.20 g, 44\%).

Low-temperature NMR study: in a dry-box, (TMEDA)CoR $2(0.017 \mathrm{~g}, 0.049 \mathrm{mmol})$ and ligand $1(0.030 \mathrm{~g}, 0.081 \mathrm{mmol})$ was weighed into an NMR tube and cooled to $-80{ }^{\circ} \mathrm{C}$, followed by adding 2 mL of toluene- $d 8$ which is precooled to $-70^{\circ} \mathrm{C}$ to dissolve all the solids. The resulting mixture was slowly warmed to room temperature, during which ${ }^{1} \mathrm{H}$ NMR spectra were taken at $-35{ }^{\circ} \mathrm{C},-20{ }^{\circ} \mathrm{C}$ (Figure 9.7A), $0{ }^{\circ} \mathrm{C}$ (Figure 9.7B) and 25 ${ }^{\circ} \mathrm{C}($ Figure 9.7 C$)$. Below $0{ }^{\circ} \mathrm{C}$, peaks of paramagnetic compounds are too broad to be interpretable. At $0{ }^{\circ} \mathrm{C}$, only (TMEDA) $\mathrm{CoR}_{2}$, ligand $\mathbf{1},(\mathbf{1}) \mathrm{CoR}_{2}$ were observed. No other paramagnetic intermediate could be detected. The low-temperature reaction of ligand $\mathbf{1}$ with $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ gave too broad peaks which cannot be interpreted.



Figure 9.7. (TMEDA)CoR + Ligand (1) at: A) $-20^{\circ} \mathrm{C}$; B) $0{ }^{\circ} \mathrm{C}$; C) $25^{\circ} \mathrm{C}$

Synthesis of [2,6-bis(2,4,6-Me $\left.\mathbf{3}_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{CMe}\right)-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N} / \mathrm{CoR}$ ((2)CoR). This reaction was done as described for $\mathbf{1}$, using 0.9 mmol of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ and $0.35 \mathrm{~g}(0.88 \mathrm{mmol})$ of $\mathbf{2}$. After evaporation of the solvents, the resulting thick purple oil was dissolved in pentane and filtered through glass wool. Slow evaporation produced a sticky product ( 0.26 g , crude yield: $56 \%$ ). All attempts to further purify it failed.
${ }^{1} \mathrm{H}$ NMR ( $25^{\circ} \mathrm{C}$, benzene- $d_{6}, 300 \mathrm{MHz}$ ): $\delta 10.13(\mathrm{t}, 1 \mathrm{H}, J 7.0 \mathrm{~Hz}, \operatorname{Py} H 4), 7.79(\mathrm{~d}, 2 \mathrm{H}, J$ $7.0 \mathrm{~Hz}, \operatorname{Py} H 3$ ), 7.11 ( $\mathrm{s}, 4 \mathrm{H}, \operatorname{Ar} m$ ), 2.37 (s, 6H, Ar $p-\mathrm{Me}$ ), 2.16 ( $\mathrm{s}, 12 \mathrm{H}, \operatorname{Ar} o-\mathrm{Me}$ ), -0.60 (s, $9 \mathrm{H}, \mathrm{Si} \mathrm{Se}_{3}$ ), $-1.14(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe})$. The $\mathrm{CoCH}_{2}$ signal could not be unambiguously assigned.

Reaction of (TMEDA)CoR $2_{2}$ with 2,6-bis $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~N}=\mathrm{CMe}\right)-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ (3). In a dry-box, 0.0052 g ( 0.0166 mmol ) of $\mathbf{3}$ was dissolved in benzene- $d_{6}$ and transferred into an NMR tube, and a solution of 0.0062 g of (TMEDA) $\mathrm{CoR}_{2}(0.0177 \mathrm{mmol}, 1.1$ equiv) in benzene$d_{6}$ was added. For the ${ }^{1} \mathrm{H}$ NMR spectrum, see Figure 6.3 A .
${ }^{1} \mathrm{H}$ NMR ( $25^{\circ} \mathrm{C}$, benzene-d6, 300 MHz ; tentative assignments): $\delta 9.79(\mathrm{t}, 1 \mathrm{H}, J 7.4 \mathrm{~Hz}$, Py H4), 8.17 (d, 4H, J 6.6 Hz, Ar o), 7.76 (d, 2H, J7.2 Hz, Py H3), 7.35-7.43 (m, 6H, Ar $m$ and $\operatorname{Ar} p), 0.35\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CoCH}_{2}\right),-0.64(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiMe} 3),-1.10(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe})$.

The part between following $/ *$ and $*$ was not reported in the published paper in reference 217.
/* $1.3 \mu \mathrm{~L}$ Pyridine was injected into this NMR sample and the immediate ${ }^{1} \mathrm{H}$ NMR spectrum showed that there were obvious changes in shifts of the ${ }^{1} \mathrm{H}$ NMR signals attributed to the $\mathrm{Co}^{\mathrm{I}}$ alkyl in Figure 6.3C.*

Reaction of $(\mathbf{P y})_{2}$ CoR $_{2}$ with 3. In a dry-box, about 0.059 mmol of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ was dissolved in benzene- $d_{6}$ and $0.15 \mathrm{~g}\left(0.048 \mathrm{mmol} ; 0.81\right.$ equiv) of $\mathbf{3}$ was added. $\mathrm{A}^{1} \mathrm{H}$ NMR spectrum recorded immediately afterwards (Figure $6.3 \mathrm{~B}, \mathrm{C}$ ) showed peaks that we tentatively assign in terms of formation of 1 equiv of $\mathrm{Me}_{4} \mathrm{Si}$ and 1 equiv of (3)CoR or (3)(Py)CoR.
${ }^{1} \mathrm{H}$ NMR ( $25^{\circ} \mathrm{C}$, benzene- $d_{6}, 300 \mathrm{MHz}$; tentative assignments): $\delta 8.71$ (br, 1 H , Py H 4 ), 8.37 (br, Py H3), $7.00(4 \mathrm{H}, \mathrm{Ph} o), 6.91(4 \mathrm{H}, \mathrm{Ph} m), 6.82(2 \mathrm{H}, \mathrm{Ph} p), 0.85(\mathrm{~s}, 6 \mathrm{H}$, $M e \mathrm{C}=\mathrm{N}), 0.45\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CoCH}_{2}\right), 0.05\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{Me}_{4} \mathrm{Si}\right),-0.50\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si} M e_{3}\right)$.

Reaction of (TMEDA)CoR ${ }_{2}$ with $2,6-b i s\left(C_{6} H_{5} \mathrm{CH}_{2} \mathrm{~N}=\mathrm{CMe}\right)-\mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ (4). In a dry-box, $0.0068 \mathrm{~g} 4(0.020 \mathrm{mmol})$ was weighed and dissolved in benzene- $d 6$, followed by addition of around 0.0092 g (TMEDA) $\mathrm{CoR}_{2}$ ( $0.026 \mathrm{mmol}, 1.3$ equiv) in benzene $-d_{6} . \mathrm{A}{ }^{1} \mathrm{H}$ NMR spectrum recorded immediately (Figure 6.4 A ) showed peaks that could be tentatively assigned to (4)CoR.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $d_{6}, 300 \mathrm{MHz}$; tentative partial assignments): $\delta 9.74(\mathrm{t}, 1 \mathrm{H}, J$ 7.4 Hz, Py H4), 7.40 (d, 2H, J 7.4 Hz, Py H3), 6.61 (s, 4H, PhCH2), -0.16 (s, 9H, SiMe $)_{3}$ ), -0.64 (s, 6H, N=CMe).

Pyridine was added to this sample in small increments $(1 \mu \mathrm{~L}, 2.0 \mu \mathrm{~L})$; this resulted in changes in shifts of the ${ }^{1} \mathrm{H}$ NMR signals attributed to the $\mathrm{Co}^{\mathrm{I}}$ alkyl. Figure 6.4D shows the spectrum after addition of $3 \mu \mathrm{LPy}$.

Reaction of $(\mathbf{P y})_{2}$ CoR $_{2}$ with 4 . In a dry-box, into about $0.0068 \mathrm{~g}(0.02 \mathrm{mmol})$ of $\mathbf{4}$ was added to a solution of about 0.04 mmol of $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ in benzene- $d_{6} . \mathrm{A}{ }^{1} \mathrm{H}$ NMR spectrum
recorded immediately afterward (Figure 6.4C) showed peaks that could be interpreted in terms of formation of 1 equiv of $\mathrm{Me}_{4} \mathrm{Si}$ and 1 equiv of (4)CoR or its Py.
${ }^{1} \mathrm{H}$ NMR ( $25^{\circ} \mathrm{C}$, benzene-d6, 300 MHz ; tentative assignments): $\delta 9.32(\mathrm{t}, 1 \mathrm{H}, J 6.6 \mathrm{~Hz}$, Py H4), $7.54(\mathrm{~d}, 2 \mathrm{H}, J 6.6 \mathrm{~Hz}$, Py $H 3$ ), 7.05-7.08 (br, Ar o), 6.90-6.93 (m, Ar p and Ar $\mathrm{m}), 6.32(\mathrm{~s}, 4 \mathrm{H}, \mathrm{PhCH} 2),-0.15(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe}),-0.24\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si} M e_{3}\right) . \mathrm{CoCH} 2$ cannot be unambiguously assigned.

Figure 6.4B shows the results of a similar experiment using different concentrations of 4 and $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $d_{6}, 300 \mathrm{MHz}$; tentative assignments): $\delta 8.94$ (br, $1 \mathrm{H}, \mathrm{Py} H 4$ ), 7.63 (br, Py H3), 6.95, 6.89 (br, 10H, Ph), $6.08\left(4 \mathrm{H}, \mathrm{NCH}_{2}\right), 0.25(\mathrm{~s}, 6 \mathrm{H}, \mathrm{MeC}=\mathrm{N}), 0.12$ ( $\mathrm{s}, 2 \mathrm{H}, \mathrm{CoCH}_{2}$ ), $0.02\left(\mathrm{~s}, 12 \mathrm{H}, \mathrm{Me}_{4} \mathrm{Si}\right),-0.32\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si}_{\mathrm{Me}}^{3}\right.$ ).

Reaction of $(\mathbf{P y})_{2}$ CoR $_{2}$ with 5 . In a dry-box, $0.0069 \mathrm{~g}(0.0174 \mathrm{mmol}) \mathbf{5}$ was weighed and dissolved in benzene- $d_{6}$, followed by addition about $0.028 \mathrm{mmol}(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ in benzene$d_{6} \cdot{ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ NMR spectra were recorded immediately (Figure 6.6B, Figure 6.7B) and showed the formation of $\mathrm{Me}_{4} \mathrm{Si}$ and a small amount of a new diamagnetic compound, possibly (5)CoR or its Py adduct, as well as a large amount of both starting materials.
${ }^{1} \mathrm{H}$ NMR ( $25^{\circ} \mathrm{C}$, benzene- $d_{6}, 300 \mathrm{MHz}$; tentative assignments): $\delta 8.56$ (d, $2 \mathrm{H}, J 7.9$, Py $H 3), 2.36(\mathrm{~s}, 6 \mathrm{H}), 0.34\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CoCH}_{2}\right),-0.35\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{Si} M e_{3}\right) .{ }^{19} \mathrm{~F}$ NMR (282.4 MHz, benzene $\left.-d_{6}, 25^{\circ} \mathrm{C}\right): \delta-54.1$.

On standing, black solid precipitated from the sample. A spectrum recorded after 2 h still showed the presence of unreacted starting materials, although the amount of free 5
had decreased. 0.5 mL water was injected, and after separation of layers spectra taken of the benzene- $d 6$ layer showed mainly free 5 (Figure 6.7C).

Reaction of $(\mathbf{T M E D A})_{2}$ CoR $_{2}$ with 5 . (This paragraph was not reported in the published paper in reference 217) In a dry-box, (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}(0.0150 \mathrm{~g}, 0.043 \mathrm{mmol})$ was weighed into a small vial, followed by adding ligand 5 ( $0.0217 \mathrm{~g}, 0.043 \mathrm{mmol})$. After adding 0.4 mL benzene- $d_{6}$ and dissolving all solid, the immediate NMR showed that there was no reaction and longer standing just deposited black solid.

Formation of (6)CoR 2 (6: 2,6-bis(4',4'-dimethyloxazolin-2-yl)pyridine). (TMEDA)CoR 2 $(0.082 \mathrm{~g}, 0.23 \mathrm{mmol})$ was dissolved in 2 mL benzene and cooled to $-35^{\circ} \mathrm{C}$, and 0.06 g ( 0.23 mmol ) of $\mathbf{6}$ in 2 mL benzene was added. After warming to room temperature, the resulting blue solution was stirred for 10 min and filtered through glass wool, solvents were evaporated, 2 mL of pentane was added and the solution was again filtered through glass wool. Cooling failed to produce crystals, so the solvents were evaporated and the crude product (a mixture of (6) $\mathrm{CoR}_{2}$ and (TMEDA) $\mathrm{CoR}_{2}$, see Figure 6.8) was characterized by ${ }^{1} \mathrm{H}$ NMR.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 44.4\left(2 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 80 \mathrm{~Hz}\right.$, Py $\left.H 3\right), 21.8(18 \mathrm{H}$, $\left.\mathrm{br}, \Delta v_{1 / 2} 120 \mathrm{~Hz}, \mathrm{Si}_{1} \mathrm{Me}_{3}\right),-5.6\left(4 \mathrm{H}, \mathrm{br}, \mathrm{CH}_{2} \mathrm{O}\right),-16.9\left(12 \mathrm{H}, \mathrm{br}, \Delta \mathrm{v}_{1 / 2} 110 \mathrm{~Hz}, \mathrm{CMe} 2\right),-66.5$ (1H, br, Py H4).

Synthesis of (6)CoCl $2_{2}$ (6: 2,6-bis(4',4'-dimethyloxazolin-2-yl)pyridine) ${ }^{159 b-\mathrm{c}}$.(not published) Anhydrous $\mathrm{CoCl}_{2}(0.45 \mathrm{~g}, 3.5 \mathrm{mmol})$ was dissolved in 40 mL THF at refluxing temperature. At around $70{ }^{\circ} \mathrm{C}$, ligand $\mathbf{6}(0.95 \mathrm{~g}, 3.5 \mathrm{mmol})$ was dissolved in hot THF.

After the heater was turned off, the $\mathrm{CoCl}_{2}$ solution in THF was added dropwise to the solution of ligand $\mathbf{6}$. The resulting blue suspension was stirred for 1 h . after the stirrer was turned off, the suspension was allowed to settle down. The top light-green liquid was removed by syringe and the bottom solid was washed with dry THF for 3 times and dried in high vacuum. Around 1.0 g light-blue powder was obtained (yield: $71 \%$ ).
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{MHz}\right.$, all peaks are broad): $\delta 78.4(2 \mathrm{H}, \mathrm{Py} \mathrm{H3}), 11.7(1 \mathrm{H}$, Py H4), $-35.6\left(12 \mathrm{H}, \mathrm{CMe}_{2}\right)$. The peak at -12.4 ppm was tentatively assigned to be $\mathrm{CH}_{2} \mathrm{O}$.

Synthesis of (6) $\mathrm{FeCl}_{2}$ (6: 2,6-bis(4',4'-dimethyloxazolin-2-yl)pyridine). ${ }^{159 b-\mathrm{c}}$ (not published) Anhydrous $\mathrm{FeCl}_{2}(0.38 \mathrm{~g}, 3.0 \mathrm{mmol})$ was suspended in 10 mL THF, followed by adding a THF solution of ligand $\mathbf{6}(0.84 \mathrm{~g}, 3.0 \mathrm{mmol})$. The resulting blue suspension was stirred at room temperature overnight. After filtered over frit filter, the resulting blue solid was dissolved in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and layered with dry hexane at room temperature overnight. The top clear liquid was removed by syringe and the blue solid was washed with dry THF ( 15 mL ) twice and dried in high vacuum. Around 1.0 g blue solid was obtained (yield: around 83\%) .
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 300 \mathrm{MHz}\right.$, all peaks are broad): $\delta 61.5(2 \mathrm{H}, \mathrm{Py} \mathrm{H3}), 4.2(12 \mathrm{H}$, $\left.\mathrm{CMe}_{2}\right),-7.6(1 \mathrm{H}, \mathrm{Py} \mathrm{H} 4)$. The peak at 16.7 ppm was tentatively assigned to be $\mathrm{CH}_{2} \mathrm{O}$.

Reaction of (TMEDA)CoR 2 with 8 (8: 2,6-bis(2,4,6-Me $\left.3_{3} C_{6} H_{2} N=P_{6} H_{5}\right)-C_{5} H_{3} N$ ). (not published). In a dry-box, ligand $8(0.0847 \mathrm{~g}, 0.14 \mathrm{mmol})$ was weighed into 2 mL vial, followed by adding (TMEDA) $\mathrm{CoR}_{2}(0.0495 \mathrm{~g}, 0.14 \mathrm{mmol})$. The resulting mixture was
dissolved in 2 mL benzene-d6 at room temperature. The immediate ${ }^{1} \mathrm{H}$ NMR spectrum of this solution indicated that there was no reaction happening.

Reaction of (TMEDA)CoR 2 with 9. (this paragraph is not reported in the published paper in reference 217). Procedure is the same as the reaction with ligand $\mathbf{8}$. Ligand $9(0.0977 \mathrm{~g}$, $0.136 \mathrm{mmol})$ and (TMEDA) $\mathrm{CoR}_{2}(0.0478 \mathrm{~g}, 0.136 \mathrm{mmol})$. The immediate ${ }^{1} \mathrm{H}$ NMR spectrum of this solution showed only a mixture of the two products.

Reaction of (TMEDA)CoR 2 with 10 (10: 2,6-Bis[3'-(2,4,6-trimethylphenyl)-imidazol-2ylideneIpyridine): (this paragraph is not reported in the published paper in reference 217) In a dry-box, ligand $10(0.0113 \mathrm{~g}, 0.136 \mathrm{mmol})$ and $(\mathrm{TMEDA}) \mathrm{CoR}_{2}(0.0090 \mathrm{~g}, 0.026$ mmol ) was weighed into a small vial and the resulting mixture was dissolved in around 1 mL benzene- $d 6$. The color turned darker and the ${ }^{1} \mathrm{H}$ NMR spectrum was messy and a lot of black solid precipitated out. The reaction with $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ gives similar results.

## X-ray structure determinations (see Table 9.4)

General procedure refers to single-crystal X-ray diffraction in Chapter 2
2,6-[CF $\left.\mathbf{F}_{3} \mathrm{C}(\mathrm{OH})_{2}\right]_{2} \mathrm{C}_{5} \boldsymbol{H}_{3} \mathbf{N}$. (this work was done by Peter H.M Budzelaar and Femke F.B.J. Janssen) A transparent regular platelet (approximately $0.3 \times 0.2 \times 0.1 \mathrm{~mm}$ ) was glued on a thin glass fiber. Data were collected at 208K on a Nonius KappaCCD diffractometer with area detector $\varphi$ and $\omega$ scans. The structure was solved using CRUNCH. ${ }^{241}$ There is some minor rotational disorder in the $\mathrm{CF}_{3}$ groups, resulting in somewhat larger anisotropic thermal-displacement parameters. A co-crystallized THF solvent molecule is
situated on a mirror plane, implying the presence of some disorder, which is reflected in large thermal parameters perpendicular to the plane of the molecule. This disorder could not be described adequately, and attempts to do so resulted in physically unacceptable geometrical parameters. A thermal ellipsoid plot is provided in the appendix (Figure C. 2 in the Appendix C)

2,6-[2,4,6-Me $\left.3_{3} C_{6} H_{2} N=C\left(C_{3}\right)\right]_{2} C_{5} H_{3} N$ (5). (this work was done by Peter H.M Budzelaar and Femke F.B.J. Janssen) A transparent light yellow crystal fragment (approximately 0.2 mm in all directions) was glued on a thin glass fiber. Data were collected at room temperature on a Nonius KappaCCD diffractometer with area detector $\varphi$ and $\omega$ scans. The structure was solved using CRUNCH. ${ }^{241}$
(1)CoR. A deep purple crystal fragment (approx $0.6 \times 0.2 \times 0.1 \mathrm{~mm}$ ) was mounted in a thinwalled glass capillary. Data were collected at 293 K on a Bruker 4-circle diffractometer with APEX detector. The crystal system and space group were determined from the cell metric and systematic absences. Data integration was done using SAINT. ${ }^{101}$ The structure was solved by the Patterson method with SHELXS97. ${ }^{104}$

Table 9.4. Details of crystal-structure determinations

|  | $\begin{aligned} & \text { 2,6-[(HO) } \left.\mathbf{2}_{2} \mathrm{C}\left(\mathrm{CF}_{3}\right)\right]_{2} \\ & \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N} \cdot \mathrm{THF} \end{aligned}$ | $\begin{aligned} & \text { 2,6-[(2,4,6-Me } \left.\mathrm{C}_{3} \mathrm{C}_{6} \mathrm{H}_{2} \mathrm{~N}=\mathrm{C}\left(\mathrm{CF}_{3}\right)\right]_{2} \\ & \mathbf{C}_{5} \mathrm{H}_{3} \mathrm{~N} \end{aligned}$ | (1)CoR |
| :---: | :---: | :---: | :---: |
| Formula | $\mathrm{C}_{9} \mathrm{H}_{7} \mathrm{NO}_{4} \mathrm{~F}_{6} \cdot \mathrm{C}_{4} \mathrm{H}_{8} \mathrm{O}$ | $\mathrm{C}_{27} \mathrm{H}_{25} \mathrm{~F}_{6} \mathrm{~N}_{3}$ | $\mathrm{C}_{29} \mathrm{H}_{38} \mathrm{CoN}_{3} \mathrm{Si}$ |
| Mol wt | 375.23 | 505.50 | 515.65 |
| Cryst system | orthorhombic | tetragonal | monoclinic |
| Space group | Pcmn | I4 ${ }_{1}$ | $\mathrm{P} 21 / \mathrm{m}$ (No.11) |
| $a / \AA$ | 6.6689(3) | 14.9916(10) | 7.6802(3) |
| b/Å | 14.6578(8) | 14.9916(10) | 21.2770(10) |
| $c / \AA$ ¢ | 17.1651(12) | 11.1077(5) | 8.5207(4) |
| $\alpha / \mathrm{deg}$ | 90 | 90 | 90 |
| $\beta /$ deg | 90 | 90 | 99.1876(11) |
| $\gamma / \mathrm{deg}$ | 90 | 90 | 90 |
| $V / \AA^{3}$ | 1677.91(17) | 2496.4(3) | 1374.52(11) |
| Z | 4 | 4 | 2 |
| $D_{\mathrm{c}} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.485 | 1.345 | 1.246 |


|  | $\begin{aligned} & 2,6-\left[(\mathrm{HO})_{2} \mathrm{C}\left(\mathrm{CF}_{3}\right)\right]_{2} \\ & \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N} \cdot \mathrm{THF} \end{aligned}$ | $\begin{aligned} & \text { 2,6-[(2,4,6-Me } \left.\mathrm{C}_{3} \mathrm{H}_{2} \mathrm{~N}=\mathrm{C}\left(\mathrm{CF}_{3}\right)\right]_{2} \\ & \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N} \end{aligned}$ | (1)CoR |
| :---: | :---: | :---: | :---: |
| abs coef $/ \mathrm{mm}^{-1}$ | 0.154 | 0.111 | 0.689 |
| $\mathrm{F}_{000}$ | 760 | 1048 | 548 |
| index ranges | $\begin{aligned} & -7 \leq h \leq 7 \\ & -17 \leq k \leq 17 \\ & -20 \leq l \leq 16 \end{aligned}$ | $\begin{aligned} & -17 \leq h \leq 17 \\ & -17 \leq k \leq 17 \\ & -13 \leq l \leq 13 \end{aligned}$ | $\begin{aligned} & -9 \leq h \leq 9 \\ & -25 \leq k \leq 25 \\ & -10 \leq l \leq 10 \end{aligned}$ |
| $2 \theta_{\text {max }} /$ deg | 50 | 50 | 51 |
| \# rflctns | 21981 | 14675 | 9173 |
| \# unique | 1531 | 2193 | 2634 |
| $\#>2 \sigma$ | 1116 | 1925 | 2459 |
| GOF | 1.107 | 1.074 | 1.075 |
| \# parameters | 126 | 167 | 174 |
| $R(F \mathrm{O}>4 \sigma(F \mathrm{o})$ ) | 0.0649 | 0.0455 | 0.0379 |
| $R$ (all data) | 0.0935 | 0.0358 | 0.0398 |
| $w R 2$ (all data) | 0.1666 | 0.0853 | 0.1008 |
| largest peak, | 0.489, | 0.111, | 0.393, |


| $\left.\mathbf{2 , 6 - [ ( H O})_{2} \mathbf{C}\left(\mathbf{C F}_{3}\right)\right]_{2}$ <br> $\mathbf{C}_{5} \mathbf{H}_{3} \mathbf{N} \cdot \mathbf{T H F}$ | $\mathbf{2 , 6 - [ ( 2 , 4 , 6 - \mathbf { M e } _ { 3 } \mathbf { C } _ { 6 } \mathbf { H } _ { \mathbf { 2 } } \mathbf { N } = \mathbf { C } ( \mathbf { C F } _ { 3 } ) ] _ { 2 }}$ <br> $\mathbf{C}_{5} \mathbf{H}_{3} \mathbf{N}$ | $(\mathbf{1}) \mathbf{C o R}$ |  |
| :--- | :--- | :--- | :--- |
| hole $/ e \AA^{-3}$ | -0.344 | -0.157 | -0.174 |

## Computational methods

All geometry optimizations were done with Turbomole ${ }^{231}$ using the $\mathrm{SVP}^{230}$ and TZVP ${ }^{234}$ basis sets and the functionals b3-lyp ${ }^{229}$ and $b-p^{110,111}$ (the latter with the RI approximation) in combination with an external optimizer (PQS OPTIMIZE ${ }^{232}$ for minima, BOptimize ${ }^{147}$ for MECP $^{198}$ ). All calculations used the spin-unrestricted formalism, with $S_{\mathrm{z}}=3 / 2\left(\mathrm{Co}^{\mathrm{II}} \mathrm{HS}\right),{ }^{1 / 2}\left(\mathrm{Co}^{\mathrm{II}} \mathrm{LS}\right)$ or $0\left(\mathrm{Co}^{(0)} \mathrm{LS}\right)$. Vibrational analyses were done for all stationary points to confirm their nature, and also to calculate thermal corrections (enthalpy and entropy, gas phase, $298 \mathrm{~K}, 1 \mathrm{bar}$ ) and obtain free energies using the standard formulas of statistical thermodynamics. ${ }^{235}$ For the TZVP/b3-lyp calculations, calculation of analytical Hessians proved to be prohibitively expensive, so we here combine the TZVP optimized electronic energy with SV(P)-level thermal corrections (evaluated at the $\mathrm{SV}(\mathrm{P})$ optimized geometries).

The $\sigma$ and $\pi$ parameters of ligand $\mathbf{6}$ were generated according to the procedure in Chapter 4 and also in our previous paper. ${ }^{144}$

### 9.5 Experimental section for Chapter 7:

Experimental sections: (the work between $/ *$ and $* \backslash$ is a verbatim copy from the experimental parts of the published papers and reproduced in part with permissions from [Zhu, D.; Budzelaar, P.H.M. Organometallic 2010, 29, 5759.] Copyright [2010] American Chemical Society and from [Zhu, D.; Thapa, I.; Korobkov, I.; Gambarotta, S.;

Budzelaar, P.H.M. Inorg. Chem. 2011, ASAP] Copyright [2011] American Chemical Society)

General Considerations All experiments were done under argon atmosphere using standard Schlenk techniques, or in a nitrogen-filled dry-box. Pentane, hexane, toluene, diethyl ether, tetrahydrofuran, THF- $d_{8}$, benzene, and benzene- $d_{6}$ were distilled from sodium/benzophenone. Phenyl lithium solution (1.8 M in di-n-butyl ether) were purchased from Aldrich and used as received. 2,6-Bis[1-(2,6dimethylphenylimino)ethyl]pyridine (1) and 2,6-Bis[1-(2,6diisopropylphenylimino)ethyl]pyridine (4) were prepared according to published procedures. ${ }^{238}(\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ was prepared according to the literature procedure in Chapter 7 using (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$. Anhydrous chlorobenzene and anhydrous benzotrifluoride were purchased form Aldrich and used as received. Other aryl halides and alkyl halides were purchased from Aldrich or Acros, degassed and dried over 4 A molecular sieves in dry-box before use. The alkyl halide used in CC coupling reaction is used as received.
${ }^{1} \mathrm{H}$ NMR, ${ }^{13} \mathrm{C}\{\mathrm{H}\}$ NMR and ${ }^{19} \mathrm{~F}$ NMR spectra were recorded on a Bruker Avance 300 MHz or Bruker Avance 500 MHz spectrometer. All NMR shifts ( $\delta, \mathrm{ppm}$ ) of ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra were referenced to the solvent (benzene- $d_{6},{ }^{1} \mathrm{H}$ NMR: $\mathrm{C}_{6} \mathrm{D}_{5} \mathrm{H} \delta 7.16$ ppm; ${ }^{13} \mathrm{C}$ NMR: $\mathrm{C}_{6} \mathrm{D}_{6} \delta 128.0 \mathrm{ppm} ; \mathrm{CDCl}_{3},{ }^{1} \mathrm{H}$ NMR: $\mathrm{CHCl}_{3} \delta 7.26 \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR: $C \mathrm{HCl}_{3} \delta 77.0 \mathrm{ppm} ; \mathrm{THF}-d 8,{ }^{1} \mathrm{H}$ NMR: $\mathrm{CH}_{2}(2,5) ; \delta 3.62 \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR: $\mathrm{CH}_{2}(2,5) ; \delta$ $68.03 \mathrm{ppm}) .{ }^{19} \mathrm{~F}\{\mathrm{H}\}$ NMR spectra were referenced to the internal benzotrifluoride in
benzene- $d 6$ at $\delta-62.4 \mathrm{ppm}$. When necessary, COSY or HSQC NMR spectrum was also acquired in certain cases to assist the peak assignment in ${ }^{13} \mathrm{C}$ NMR or ${ }^{1} \mathrm{H}$ NMR spectrum. Data were collected at room temperature unless otherwise noted. GC/MS instrument: Varian 3800 gas-chromatograph with a 30 meter VF-5ms column coupled to a Varian 320-MS operated in single quadrupole mode. The KBr pellet was prepared in a $\mathrm{N}_{2}$-filled dry box and measured in Bruker Tensor27 IR instrument prepurged with ultrapure dinitrogen gas. The IR data was collected using OPUS6.5 software. Elemental analysis was done in Guelph Chemical laboratories LTD.
/* Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). The spectra were simulated by iteration of the anisotropic $g$ values, (super)hyperfine coupling constants, and line widths using the EPR simulation program W95EPR developed by Prof. Frank Neese (University of Bonn). $* \backslash$ (this work is done by Bas der Bruin in University of Amsterdam, the Netherland)

## /*Synthesis of 4-methylphenyl lithium:

$\mathbf{L i C}_{\mathbf{6}} \mathbf{H}_{\mathbf{4}} \mathbf{- 4} \mathbf{- M e} .^{\mathbf{2 4 2}} \mathrm{BrC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}(1.40 \mathrm{~g}, 8.02 \mathrm{mmol})$ was dissolved in 16 mL diethyl ether and cooled to $-70^{\circ} \mathrm{C}$. At this temperature, $n$-butyl lithium ( $5.1 \mathrm{~mL}, 1.6 \mathrm{M}$ in hexane, 8.16 mmol ) was added dropwise to the stirred solution. The resulting clear solution was stirred for 4 h at $-65^{\circ} \mathrm{C}$. The solvent was removed in vacuo below $-20^{\circ} \mathrm{C}$ to produce a white solid. 2 mL dry toluene was added. After standing for 1 day, the top layer was pipetted off and the remaining solid was washed with 3 mL toluene, followed by 6 mL dry
pentane. The white solid was dried in vacuo, giving 0.72 g of a white powder (yield $89 \%$ ). This crude product was used without further purification.

## Synthesis of (1) $\mathrm{CoCl}_{\mathbf{2}}$ complex ${ }^{16}$

Under argon atmosphere, anhydrous $\mathrm{CoCl}_{2}(0.10 \mathrm{~g}, 0.77 \mathrm{mmol})$ was weighed into a 50 mL Schlenk tube and 10 mL dry THF was added into it. The resulting blue suspension was stirred for 20 min at room temperature. Ligand $\mathbf{1}(0.28 \mathrm{~g}, 0.76 \mathrm{mmol})$ in 15 mL THF was dropped into above mixture. The green suspension was stirred overnight, filtered through a frit filter, washed with THF and dried in high vacuum. The green powder $(0.38 \mathrm{~g}, 100 \%)$ was used in the following synthesis of its cobalt(I) aryl complex without further purification.

## Synthesis of (1)Co(I)(Ph-4-Me) complex:

(1) $\mathbf{C o C}_{6} \mathbf{H}_{\mathbf{4}} \mathbf{- 4}-\mathrm{Me}$. (1) $\mathrm{CoCl}_{2}(0.36 \mathrm{~g}, 0.72 \mathrm{mmol})$ was weighed and suspended in 12 mL dry toluene. At room temperature and high stirring speed, $\mathrm{LiC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}(0.1480 \mathrm{~g}$; assuming $95 \%$ purity: $1.44 \mathrm{mmol}, 2.0$ eq.) in 4 mL dry diethyl ether was slowly dropped into the suspension over a period of 3 h . Near the end of the addition, the mixture turned purple. The mixture was stirred overnight. All solvents were evaporated. 14 mL toluene was used to extract the purple residue, the solution was filtered, and the filtrate was concentrated and centrifuged. The liquid was collected and evaporated to dryness. The resulting purple residue was dissolved in dry THF, layered with pentane and cooled to $35^{\circ} \mathrm{C}$ overnight. The mother liquid was pipetted off, leaving deep purple crystalline
(1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}(0.12 \mathrm{~g}, 32 \%$ yield). The crystal suitable for X-ray diffraction was obtained by layering a toluene solution with pentane at $-35^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}, 300 \mathrm{MHz}$ ): $\delta 10.36(\mathrm{t}, 1 \mathrm{H}, J 7.4 \mathrm{~Hz}, \operatorname{Py} H 4), 7.57(\mathrm{~d}, 2 \mathrm{H}, J 7.4 \mathrm{~Hz}$, Py H3), 7.11 (t, 2H, J 7.0 Hz, NAr $H p$ ), 7.02 (d, 4H, $J 7.0 \mathrm{~Hz}, \mathrm{NAr} H m), 6.38$ (d, 2H, $J$ 6.9 Hz, CoAr Hm), 4.68 (d, 2H, J $6.9 \mathrm{~Hz}, \mathrm{CoAr} H o$ ), 2.05 (s, 12H, NAr o-CH3), 2.00 (s, $\left.3 \mathrm{H}, \mathrm{CoAr} p-\mathrm{CH}_{3}\right),-1.12\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CCH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR (THF- $\left.d_{8}, 75 \mathrm{MHz}\right): \delta 168.8\left(\mathrm{~N}=\mathrm{CCH}_{3}\right), 159.5(\operatorname{Py} C 2), 157.9(\mathrm{NAr} C-i), 132.9$ (CoAr C-o), 130.7 (NAr C-m), 129.7 (NAr C-o), 129.3 (NAr C-p), 126.0 (Py C3), 124.6 $(\mathrm{CoAr} C-m), 123.8(\mathrm{CoAr} C-p), 119.7(\mathrm{Py} C 4), 24.8\left(\mathrm{~N}=\mathrm{CCH}_{3}\right), 21.4\left(\mathrm{CoAr} p-\mathrm{CH}_{3}\right), 20.1$ (NAr o-CH3 $)$. CoAr C-i was not observed, probably due to a large linewidth.

Anal. Calcd for $\mathrm{C}_{32} \mathrm{H}_{34} \mathrm{CoN}_{3}$ (519.57): C, 73.97; H, 6.60; N, 8.09. Found: C, 73.07; H, 6.96; N, 7.90.

## Synthesis of (1)Co(I)Ph complex:

(1) $\mathrm{CoCl}_{2}(0.40 \mathrm{~g}, 0.80 \mathrm{mmol})$ was weighed and suspended in 12 mL toluene. At room temperature and at high stirring speed, $\mathrm{LiC}_{6} \mathrm{H}_{5}(0.90 \mathrm{~mL}, 1.8 \mathrm{M}$ in diethyl ether, 1.62 mmol ) was slowly added to the suspension over a period of 3 h , producing a deep purple suspension. The mixture was stirred overnight. All solvents are evaporated in vacuo. 10 mL toluene was used to extract the purple residue, and filtered. The resulting filtrate was centrifuged. The solution was collected and evaporated to dryness. The resulting purple residue was dissolved in around 1 mL toluene layered with pentane and cooled to $-35^{\circ} \mathrm{C}$
overnight. The deep purple precipitate was re-dissolved in THF and layered with pentane at $-35^{\circ} \mathrm{C}$ overnight, the mother liquor was pipetted away and the residue dried in vacuo, leaving deep purple crystalline $(\mathbf{1}) \mathrm{CoC}_{6} \mathrm{H}_{5}(0.075 \mathrm{~g}, 19 \%)$. For unknown reasons, we were not able to obtain satisfactory elemental analysis for this compound.
${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}, 300 \mathrm{MHz}$ ): $\delta 10.36(\mathrm{t}, 1 \mathrm{H}, J 7.6 \mathrm{~Hz}$, Py $H 4), 7.56(\mathrm{~d}, 2 \mathrm{H}, J 7.6 \mathrm{~Hz}$, Py H3), 7.09 (t, 2H, J 7.5 Hz, NAr Hp), 7.01 (d, 4H, J 7.5 Hz, NAr Hm), 6.48-6.50 (m, 3H, CoPh Hm and Hp), 4.72-4.76 (m, 2H, CoPh Ho), 2.05 (s, 12H, NAr Me), -1.07 (s, $\left.6 \mathrm{H}, \mathrm{N}=\mathrm{CCH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR (benzene- $d_{6}, 75 \mathrm{MHz}$ ): $\delta 167.5\left(\mathrm{~N}=\mathrm{CCH}_{3}\right), 158.1(\mathrm{Py} C-2), 156.4(\mathrm{NAr} C-i)$, 137.7 (br, CoPh C-i), 131.9 ( $\mathrm{CoPh} C-o$ ), 129.4 (NAr $C-o$ ), 128.5 (NAr $C-m$ ), 125.4 (NAr $C-p), 123.2(\operatorname{Py} C 3), 122.3,121.5(\mathrm{CoPh} C-m$ and $C-p), 118.2(\operatorname{Py} C 4), 23.8\left(\mathrm{~N}=\mathrm{CH}_{3}\right)$, $19.4\left(\mathrm{NAr} o-\mathrm{CH}_{3}\right) .{ }^{*}$

## Synthesis of (1)CoCl complex ${ }^{215,243}$

0.23 mL mercury ( 3.12 g ) was injected into a 100 mL Schlenk flask, and sodium (15.6 $\mathrm{mg}, 0.68 \mathrm{mmol}$ ) was added; after addition of 20 mL dry toluene and violent stirring, all sodium dissolved into mercury within 30 min . (1) $\mathrm{CoCl}_{2}(0.34 \mathrm{~g}, 0.68 \mathrm{mmol})$ was weighed and suspended in 20 mL toluene; the resulting suspension was added dropwise to the above sodium amalgam in portions. After stirring violently for around 20 min , the mixture turned pink. The reaction mixture was stirred overnight (around 24 h ). The deep purple mixture was removed from the remaining mercury using pipet in dry box, and filtered over Celite. The resulting filtrate was evaporated concentrated slightly and cooled
to $-35{ }^{\circ} \mathrm{C}$ overnight. A lot of dark color powder precipitated and filtered over frit filter and washed with pentane. 0.12 g of product ( $37 \%$ yield) was obtained.
$/{ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 9.49(\mathrm{t}, 1 \mathrm{H}, J 7.7 \mathrm{~Hz}$, Py $H 4), 7.23(\mathrm{t}, 2 \mathrm{H}, J$ $7.3 \mathrm{~Hz}, \operatorname{Ar} H p), 7.12(\mathrm{~d}, 4 \mathrm{H}, J 7.3 \mathrm{~Hz}, \mathrm{Ar} H m), 6.90(\mathrm{~d}, 2 \mathrm{H}, J 7.7 \mathrm{~Hz}$, Py $H 3), 2.15(\mathrm{~s}$, 12H, $\operatorname{Ar} M e$ ), $-0.09(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe})$.
${ }^{13} \mathrm{C}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 75 \mathrm{MHz}\right) \delta 166.9\left(\mathrm{~N}=\mathrm{CCH}_{3}\right), 154.3(\operatorname{Py} C 2), 152.9(\mathrm{Ar} C$ $i), 130.2(\operatorname{Ar} C-o), 128.5(\operatorname{Ar} C-m), 126.1$ ( $\operatorname{Ar} C-p), 125.3$ (Py C3), 115.1 (Py C4), 20.2 $\left(\mathrm{N}=\mathrm{CCH}_{3}\right), 19.4\left(\mathrm{Ar} o-\mathrm{CH}_{3}\right)$.

## Reaction of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with $\mathrm{H}_{2}$ under nitrogen.

In a dry-box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(14 \mathrm{mg}, 27 \mu \mathrm{~mol})$ was weighed and dissolved in around 0.4 mL benzene- $d 6$ in an NMR tube. Outside of the dry-box, $2 \mathrm{~mL} \mathrm{H}_{2}$ was injected into the tube; the solution turned green within one minute. The ${ }^{1} \mathrm{H}$ NMR taken is shown in Figure 7.2. After all solvents were evaporated, the resulting solid was characterized by IR (the sample was prepared as KBr pellet) (Figure D. 3 in the Appendix D). A sharp and strong peak at $2084 \mathrm{~cm}^{-1}$ indicated the coordination of dinitrogen to the cobalt center.

## Reaction of (1) $\mathbf{C o C H}_{2} \mathrm{SiMe}_{3}$ with $\mathbf{H}_{\mathbf{2}}$ under nitrogen in the presence of $\mathbf{P h}_{2} \mathbf{C}_{\mathbf{2}}$.

In a dry-box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(28 \mathrm{mg}, 55 \mu \mathrm{~mol})$ was weighed and dissolved in around 0.4 mL benzene- $d 6$ in an NMR tube, and diphenylacetylene ( $10 \mathrm{mg}, 55 \mu \mathrm{~mol}$ ) was added. A ${ }^{1} \mathrm{H}$ NMR recorded after one day indicated that no reaction had taken place. 1.5 mL hydrogen gas was injected into the tube, the NMR tube was shaken and one ${ }^{1} \mathrm{H}$ NMR
spectrum was taken immediately. This (Figure 7.4a) showed partial conversion of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ to one new $\mathrm{Co}(\mathrm{I})$ complex, tentatively identified as $(\mathbf{1}) \mathrm{CoC}(\mathrm{Ph})=\mathrm{CHPh}$. After injection of another 2 mL hydrogen gas, the ${ }^{1} \mathrm{H}$ NMR spectrum (Figure 7.4b) showed mainly $(\mathbf{1}) \mathrm{CoC}(\mathrm{Ph})=\mathrm{CHPh}$ together with a small amount of another new $\mathrm{Co}(\mathrm{I})$ complex which could not be identified. After adding around 4 mL hydrogen gas, the sample turned blue. An ${ }^{1} \mathrm{H}$ NMR spectrum recorded at that time showed (1) $\mathrm{CoC}(\mathrm{Ph})=\mathrm{CHPh}$ and the unidentified $\mathrm{Co}(\mathrm{I})$ complex as the main components. After hydrolysis of the mixture, $\mathrm{GC} / \mathrm{MS}$ showed $\mathrm{PhCH}=\mathrm{CHPh}$ and $\mathrm{PhCH}_{2} \mathrm{CH}_{2} \mathrm{Ph}$ but no unreacted diphenylacetylene.
(1) $\mathbf{C o C}(\mathbf{P h})=\mathbf{C H P h}$, tentative assignment:
${ }^{1} \mathrm{H}$ NMR (benzene- $d 6,300 \mathrm{MHz}$ ): $\delta 10.26(\mathrm{t}, 1 \mathrm{H}, J 7.6$, Py $H 4$ ), 7.46 (d, 2H, $J 7.6$, Py H3), 7.04-7.12 (br, 5H, $=\mathrm{CHPh} H o, m, p), 6.86(\mathrm{t}, 2 \mathrm{H}, 7.2,=\mathrm{CCoPh} H m), 6.78$ and $6.71(\mathrm{t}$, 2H, Ar Hp), 6.50-6.60 (m, 4H, Ar Hm), 5.49 (d, 2H, J 7.2, $=\mathrm{CCoPh} H o$ ), 3.06 (s, 1H, $=\mathrm{CHPh}), 2.21(\mathrm{~s}, 6 \mathrm{H}, \operatorname{Ar} M e), 1.88(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar} M e),-1.08(\mathrm{~s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe}) . \mathrm{The}=\mathrm{CCoPh}$ $H p$ resonance could not be unambiguously assigned and may overlap with the residual solvent peak. *\}

## Reaction of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with PhCCH

In a $\mathrm{N}_{2}$-filled dry box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(0.010 \mathrm{~g}, 0.019 \mathrm{mmol})$ was weighed into a small vial and dissolved in 0.4 mL benzene- $d 6$, followed by adding two drops of phenylacetylene (around $0.1 \mathrm{~mL}, 0.91 \mathrm{mmol}$ ), it turned purple immediately. After evaporating all solvent, the residue was dissolved in dry toluene and layered with pentane
at $-35^{\circ} \mathrm{C}$. After overnight, a dark snow-flake shaped solid precipitated out. The yield is not determined. The ${ }^{1} \mathrm{H}$ NMR spectrum is shown in Figure D. 4 in the Appendix D. (1) $\mathbf{C o C}(\mathbf{P h})=\mathbf{C H C C P h}$, tentative assignment:
${ }^{1} \mathrm{H}$ NMR (benzene- $d 6,300 \mathrm{MHz}$ ): $\delta 10.15(\mathrm{t}, 1 \mathrm{H}, J 7.5$, Py $H 4$ ), 7.36 (d, 2H, $J 7.5$, Py $H 3), 6.91(\mathrm{~d}, 2 \mathrm{H}, J 7.3), 6.70-6.78(\mathrm{~m}, 4 \mathrm{H}), 6.58(\mathrm{t}, 2 \mathrm{H}, J 7.3), 6.16(\mathrm{~m}, 2 \mathrm{H}), 5.47(\mathrm{~d}, 2 \mathrm{H}$, $J 7.4,=\mathrm{CCoPh} H o), 4.28(1 \mathrm{H}, \mathrm{s},=\mathrm{C}(H)), 2.85(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar} M e), 1.58(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar} M e),-0.76$ ( $\mathrm{s}, 6 \mathrm{H}, \mathrm{N}=\mathrm{CMe}$ ). The CCPh peaks might be overlapped with benzene residue peaks.

## Reaction of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with $\mathrm{H}_{2}$ under nitrogen in the presence of 4chlorophenylnitrile.

In a $\mathrm{N}_{2}$ filled dry-box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(0.1031 \mathrm{~g}, 0.20 \mathrm{mmol})$ was weighed in a small vial, followed by adding 4-chlorophenylnitrile $(0.0278 \mathrm{~g}, 0.20 \mathrm{mmol}) .3 \mathrm{~mL}$ of dry Toluene was added into it to dissolve the two reactants and the resulting solution was transferred into a 25 mL Schlenk tube. When stirring, $20 \mathrm{~mL} \mathrm{H}_{2}$ gas was injected into it. The resulting deep purple mixture continued to be stirred for 30 min at room temperature. All solvents were evaporated to dryness. 3 mL Hexane and $0.5 \mathrm{~mL} \mathrm{Et}_{2} \mathrm{O}$ was added to dissolve it and cooled to $-35{ }^{\circ} \mathrm{C}$ overnight. Dark-colored crystalline precipitate was isolated by pipetting off the mother liquid and washing with dry hexane. 0.096 g product ( $85 \%$ yield) was obtained. One fragment of this crystalline material was used for determination of the crystal structure by single-crystal X-ray diffraction.
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 9.62(\mathrm{~s}, 1 \mathrm{H}, \mathrm{N}=\mathrm{CH}), 7.92(\mathrm{t}, 1 \mathrm{H}, J 7.7$, Py H4), 7.63 (d, 2H, J7.7, Py H3), 7.01 (d, 2H, J 8.3, N=CAr H3), 6.78-6.84 (br, 6H, N-Ar $m, p), 6.77$ (d, 2H, J 8.3, N=CAr H2), 2.04 (s, 12H, NAr Me), 1.09 (s, 6H, N=CMe).
${ }^{13} \mathrm{C}$ NMR ( $25{ }^{\circ} \mathrm{C}$, benzene- $d 6,75 \mathrm{MHz}$ ): $\delta: 156.7$ (Py C-2), $152.0(\mathrm{NAr} C-i), 148.6$ (br, $\mathrm{CoN}=C), 147.5(\mathrm{~N}=\mathrm{CAr} \mathrm{C-o}), 138.7(\mathrm{NAr} C-o), 132.9(\mathrm{CoN}=\mathrm{CAr} \mathrm{C}-p), 130.0(\mathrm{~N}=\mathrm{CAr}$ C-m), 127.6 ( $\mathrm{N}=\mathrm{CAr} C-m$ or $C-p$ ), 126.3 (NAr $C-p$ or $C-m$ ), 124.9 (NAr C-p), 119.8 (Py $C-3), 115.6(\operatorname{Py} C 4), 18.7\left(\mathrm{~N}-\mathrm{Ar} o-\mathrm{CH}_{3}\right), 17.1\left(\mathrm{~N}=\mathrm{CCH}_{3}\right) . \mathrm{N}=\mathrm{CCH}_{3}$ was not observed, probably due to the low intensity.

## Reaction of (4)Co(N2) with $4-\mathrm{CF}_{3} \mathrm{C}_{6} \mathbf{H}_{4} \mathbf{C l}$.

In a $\mathrm{N}_{2}$-filled dry-box, $(4) \operatorname{Co}\left(\mathrm{N}_{2}\right)(11.8 \mathrm{mg}, 20 \mu \mathrm{~mol})$ was weighed and dissolved in about 0.4 mL dry benzene- $d 6$, and $4-\mathrm{CF}_{3} \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl}(2.45 \mu \mathrm{~L}, 19.6 \mu \mathrm{~mol})$ was added. The mixture turned gray-blue. The immediately recorded ${ }^{1} \mathrm{H}$ NMR spectrum showed that the reaction was not complete (still $(4) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ visible) and three diamagnetic cobalt(I) complexes could be clearly observed: (4) $\mathrm{CoH}:(4) \mathrm{CoAr}:(4) \mathrm{CoCl}=0.11: 0.14: 1.00$. After 4 h , the ${ }^{1} \mathrm{H}$ NMR spectrum showed that there was no $(4) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ left and the reaction was complete, with a product ratio (4) $\mathrm{CoH}:(\mathbf{4}) \mathrm{CoAr}:(4) \mathrm{CoCl}=0.045: 0.14: 1.00$. Assignments for (4) CoH and (4) CoCl are based on literature values, ${ }^{216}$ and for (4) CoAr on analogy with previously reported (1)CoAr. ${ }^{244}$

Tentative, partial assignments for (4)CoAr:
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 10.27(1 \mathrm{H}, \mathrm{t}, J 7.6 \mathrm{~Hz}$, Py $H 4), 5.14(2 \mathrm{H}, \mathrm{d}, J$ 7.1Hz, CoAr H2), $-0.65(6 \mathrm{H}, \mathrm{s}, \mathrm{CH} 3 \mathrm{C}=\mathrm{N})$.
${ }^{19} \mathrm{~F}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 282 \mathrm{MHz}\right): \delta-61.2$.

## Reaction of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with $\mathbf{C H}_{3} \mathrm{I}$.

In a dry-box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(37.5 \mathrm{mg}, 72 \mu \mathrm{~mol})$ was dissolved in benzene- $d 6$, followed by injecting $8 \mu \mathrm{LCH}_{3} \mathrm{I}$ ( $130 \mu \mathrm{~mol}, 1.8$ eq.). The mixture immediately turned pink. ${ }^{1} \mathrm{H}$ NMR showed only broad peaks. After 30 mins, a lot of solid had precipitated. In a drybox, this sample was filtered over glass wool and the filtrate was analyzed by ${ }^{1} \mathrm{H}$ NMR, but peaks were still too broad for useful interpretation. Around 0.5 mL air was injected into the NMR tube to quench any paramagnetic Co complexes and after shaking, the sample was quickly filtered over glass wool in air. The ${ }^{1} \mathrm{H}$ NMR spectrum obtained in this way (Figure 7.9) had reasonable linewidths and showed a new quartet at $\delta 0.45 \mathrm{ppm}$ $(J 8.0 \mathrm{~Hz}) . \mathrm{GC} / \mathrm{MS}$ analysis of this NMR sample clearly showed that $\mathrm{EtSiMe}_{3}$ was the main compound and the ${ }^{1} \mathrm{H}-{ }^{29} \mathrm{Si}$ COSY (Figure D. 1 in the Appendix D) also confirmed that the ethyl group and methyl groups were attached to the same silicon atom.

## /*Reaction of (1) $\mathbf{C o}\left(\mathbf{N}_{2}\right)$ with aryl halides.

Procedure A: In a dry-box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(14 \mathrm{mg}, 27 \mathrm{mmol})$ was weighed and dissolved in around 0.4 mL benzene- $d_{6}$ in an NMR tube. Outside of the dry-box, $2 \mathrm{~mL} \mathrm{H}_{2}$ was injected into the tube; the solution turned green within one minute. The NMR tube was transferred back into the dry-box and the excess hydrogen was removed by flushing; then 1.0 or 0.5 eq. of the organic halide was added. The NMR tube was immediately shaken to mix the reactants. The reaction was monitored by ${ }^{1} \mathrm{H}$ NMR (and ${ }^{19} \mathrm{~F}$ NMR
where possible). The products were not isolated; attempted separations of (1)CoAr and (1)CoX were never successful. All reactions in Table 7.2 were done according to this procedure. Because several aryl ${ }^{1} \mathrm{H}$ peaks overlap with the benzene- $d_{6}$ solvent signal, Table D. 1 in the Appendix D lists only those peaks which could be assigned unambiguously.

Procedure B: in a dry-box, (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(14 \mathrm{mg}, 27 \mathrm{mmol})$ was weighed and dissolved in around 0.4 mL benzene $-d_{6}$ in an NMR tube, and 1.0 eq. aryl halide was added. The tube was taken out of the dry-box, 1.5 mL hydrogen gas was injected into it and the tube was shaken immediately. More hydrogen was injected into it until all peaks belonging to (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ had disappeared according to the ${ }^{1} \mathrm{H}$ NMR. Entry 20 in Table 7.2 was also done using this procedure for comparison. ${ }^{*}$

## CC coupling reactions

General: the product mixture of (1)CoAr and (1)CoX generated according to procedure A in reaction of $(\mathbf{1}) \mathrm{CoN}_{2}$ with aryl halides was injected 0.5 eq. organic halides relative to ArX. For benzyl bromide and methyl iodide, the reaction was instant. For benzyl chloride and allyl chloride, it would take hours for the reaction to complete. After addition of activated alkyl halide, the mixture slowly turned to green and deposited black solid. After all the sample turned grey, 0.5 mL water was added. The organic layer was filtered over glass wool and examined by GC\MS. The results are shown in Table 7.3.

C-O bond cleavage (not reported in the published paper of reference 244)

## Reaction of (1)CoN 2 with PhOCOPh

In a dry box, (1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ was made by hydrogenation of $(\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(0.0140 \mathrm{~g}, 27$ $\mu \mathrm{mol})$ and diphenyl carbonate $(0.030,14 \mu \mathrm{~mol})$ was added. Immediate ${ }^{1} \mathrm{H}$ NMR showed that there is no reaction happening. After two weeks, it turned pink and the ${ }^{1} \mathrm{H}$ NMR showed that only (1)Co(OPh) was present; no other cobalt(I) alkyl complex was observed.
(1) $\mathrm{Co}(\mathrm{OPh})$, partial tentative assignment:
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 9.11(1 \mathrm{H}, \mathrm{t}, J 7.3, \operatorname{Py} H 4), 6.71(2 \mathrm{H}, \mathrm{t}, J$
$7.2 \mathrm{~Hz}, \mathrm{CoOPh} m), 6.47(1 \mathrm{H}, \mathrm{t}, J 7.2, \mathrm{CoOPh} p), 5.68(2 \mathrm{H}, \mathrm{d}, J 7.4, \mathrm{CoOPh} o), 2.13$
$(12 \mathrm{H}, \mathrm{s}, \mathrm{NAr} M e), 0.05\left(6 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right)$.

## Reaction of (1)CoN ${ }_{2}$ with PhCOOEt

The procedure is the same as that of the reaction with PhOCOPh except using ethyl benzoate $(2.0 \mu \mathrm{~L}, 14 \mu \mathrm{~mol})$. It takes three weeks for the sample to turn purple and only one complex ((1)CoOEt) can be identified from ${ }^{1} \mathrm{H}$ NMR.

## Reaction of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with PhOCOPh under $\mathrm{H}_{2}$ gas

In a dry box, $(\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}(0.0140 \mathrm{~g}, 27 \mu \mathrm{~mol})$ and diphenyl carbonate $(0.030,14$ $\mu \mathrm{mol})$ was dissolved in 0.4 benzene- $d_{6}$ and transferred into a NMR tube. After injection of $1.0 \mathrm{~mL} \mathrm{H}_{2}$ and violent shaking, ${ }^{1} \mathrm{H}$ NMR spectrum showed that there were two triplet
peaks ( 9.2 ppm and 8.8 ppm indicates cobalt(I) complexes) and some ( $\mathbf{1}) \mathrm{CoN}_{2}$. The further addition of $\mathrm{H}_{2}$ gas leads to near disappearance of the peak at 8.8 ppm .

Tentative assignment of the other complex at 8.8 ppm :
${ }^{1} \mathrm{H}$ NMR $\left(25^{\circ} \mathrm{C}\right.$, benzene- $\left.d_{6}, 300 \mathrm{MHz}\right): \delta 8.80(1 \mathrm{H}, \mathrm{t}, J 7.3$, Py $H 4), 7.41(2 \mathrm{H}, \mathrm{d}, J 7.4$, Py H3), $3.82(3 \mathrm{H}, \mathrm{s}), 2.12(12 \mathrm{H}, \mathrm{s}, \mathrm{NAr} M e), 0.16\left(6 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3} \mathrm{C}=\mathrm{N}\right)$.

## X-ray diffraction Determinants (see Table 9.5)

(1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}$. A deep-purple long needle fragment (approximately $0.25 * 0.10 * 0.05$ mm ) was mounted in a thin glass capillary. Closer inspection showed it to consist of one big block and a smaller fragment. Data were collected at 293 K on a Bruker 4-circle diffractometer with an APEX detector using Mo-K $\alpha$ radiation ( $0.71073 \AA$ ). The two data sets (for the big and small fragments) could be collected and processed separately, and these fragments were found to have the same unit cell. Only the set for the large fragment was used for solution and refinement. The crystal system and space group were determined from the cell metric and systematic absences. An absorption correction was done using SADABS,,${ }^{102}$ and the data were integrated using the SAINT program. ${ }^{101}$ The structure was solved by Patterson methods using SHELXS, ${ }^{104}$ and refined using SHELXL97 ${ }^{105}$ (full-matrix least-squares refinement on $\mathrm{F}^{2}$ ); hydrogen atoms were placed at calculated positions and refined in riding mode. The structure was checked for solventaccessible voids with PLATON. ${ }^{106}$
(1) $\mathrm{CoN}=\mathrm{C}(\mathrm{H}) \mathrm{C}_{6} \mathrm{H}_{4}-\mathrm{Cl}-4$. A deep purple fragment (approximately $0.20 * 0.20 * 0.25 \mathrm{~mm}$ ) broken from a large crystal cluster was mounted in a thin glass capillary. Data were
collected at 293 K in a Bruker 4-circle diffractometer with APEX detector using Mo-K $\alpha$ radiation ( $0.71073 \AA$ ). A sphere of data was collected with $0.2^{\circ}$ scan width and 45 s scan time. The crystal system and space group were determined from the cell metric and systematic absences. An absorption correction was done using SADABS, ${ }^{102}$ and the data were integrated using the SAINT program. ${ }^{101}$ The structure was solved by Patterson methods using SHELXS, ${ }^{104}$ and refined using SHELXL97 ${ }^{105}$ (full-matrix least-squares refinement on $\mathrm{F}^{2}$ ); hydrogen atoms were placed at calculated positions and refined in riding mode. The structure was checked for solvent-accessible voids with PLATON. ${ }^{106}$

Table 9.5. Details of crystal structure determination

|  | $(\mathbf{1}) \mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}$ | $(\mathbf{1}) \mathrm{CoNCHC}_{6} \mathrm{H}_{4}-4-\mathrm{Cl}$ |
| :--- | :--- | :--- |
| Formula | $\mathrm{C}_{32} \mathrm{H}_{34} \mathrm{CoN}_{3}$ | $\mathrm{C}_{32} \mathrm{H}_{32} \mathrm{ClCoN}_{4}$ |
| Mol wt | 519.55 | 5677.00 |
| Crystal system | Triclinic | Orthorhombic |
| Space group | $\mathrm{P}-1$ | P 212121 |
| $a / \AA$ | $8.3015(4)$ | $10.9905(8)$ |
| $b / \AA$ | $10.6604(6)$ | $14.5602(11)$ |
| $c / \AA$ | $15.9805(9)$ | $18.7056(15)$ |
| $\alpha /$ deg | $91.7982(10)$ | 90 |
| $\beta /$ deg | $93.3207(14)$ | 90 |
| $\gamma /$ deg | $103.7817(14)$ | 90 |


|  | $(\mathbf{1}) \mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}$ | $(\mathbf{1}) \mathrm{CoNCHC}_{6} \mathrm{H}_{4}-4-\mathrm{Cl}$ |
| :--- | :--- | :--- |
| $V / \AA^{3}$ | $1369.72(13)$ | $2993.3(4)$ |
| $Z$ | 2 | 4 |
| $D_{\mathrm{c}} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.260 | 1.258 |
| abs coef $/ \mathrm{mm}^{-1}$ | 0.651 | 0.689 |
| $\mathrm{~F}_{000}$ | 548 | 1184 |
| index ranges | $-10 \leq \mathrm{h} \leq 10$ | $-13 \leq \mathrm{h} \leq 13$ |
| $2 \theta_{\text {max }} /$ deg | $-12 \leq \mathrm{k} \leq 12$ | $-17 \leq \mathrm{k} \leq 17$ |
| \# rflctns | 10154 | 51 |
| \# unique | 5096 | 19632 |
| \# $2 \sigma$ | 3961 | 5568 |
| GOF | 0.948 | 3614 |
| \# parameters | 345 | 0.923 |
| $R(F$ o $>4 \sigma(F))$ | 0.0556 | 0.0523 |
| $R($ all data $)$ | 0.0738 | 0.0784 |
| $w R 2($ all data $)$ | 0.1456 | 0.1443 |
| largest peak, hole $/ e \AA \AA^{-3}$ | $0.472,-0.201$ | $0.421,-0.350$ |

## Computational details

All geometries were optimized with Turbomole ${ }^{231}$ using the TZVP basis set, the b3-lyp ${ }^{229}$ functional and the unrestricted DFT formalism in combination with an external optimizer
(PQS OPTIMIZE). ${ }^{232}$ The low-spin state was found to be the lowest in energy for most species studied; square-planar $\mathrm{Co}(\mathrm{I})$ complexes preferred a broken-symmetry $\mathrm{Sz}=0$ solution. Vibrational analyses were done to confirm the nature of all stationary points and to calculate thermal corrections (enthalpy and entropy, gas phase, $298 \mathrm{~K}, 1$ bar) using the standard formulae of statistical thermodynamics. Improved single-point energies were obtained using the TZVPP ${ }^{234}$ basis set at TZVP geometries, and combined with TZVPlevel thermal corrections to generate the final free energies.

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## Appendix

## Appendix A: For Chapter 3

Table A.1. CSD refcodes and references for structures used in this work

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| Small, B.L.; Carney, M.J.; Holman, D.M.; O'Rourke, C.E.; Halfen, | JAPLUI |
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LOSBIF

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|  | QETSUE |

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EKINER
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EMEJAH
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FEQLUJ
FEQLET
FEQLOD
FEQMAQ
FEQLIX
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PUGWIX02
GUCXIL GUCXUX

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Hao, P.; Zhang, S.; Sun, W.-H.; Shi, Q.; Adewuyi, S.; Lu, X.; Li, P.
GIFGIM Organometallics 2007, 26, 2439

GIFGEI

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Table A.2. Bond angles for DIP complexes


$$
\theta 12=\text { angle } 1-\mathrm{M}-2
$$

| Refcode | $\vartheta 12$ | $\vartheta 13$ | $\vartheta 14$ | $\vartheta 15$ | $\vartheta 23$ | $\vartheta 24$ | $\vartheta 25$ | $\vartheta 34$ | $\vartheta 35$ | $\vartheta 45$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |



| PIKGUM | 75.4 | 98.1 | 101.8 | 146.5 | 93.1 | 161.0 | 76.3 | 105.9 | 100.9 | 99.2 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |


| (DIP)MnCl ${ }_{2}$ complexes |  |  |  |  |  |  |  |  |  |  |
| :--- | :---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| ADOROA | 69.7 | 103.2 | 100.5 | 135.4 | 98.9 | 141.4 | 70.4 | 119.7 | 101.7 | 98.4 |
| AHUPOI | 71.3 | 98.9 | 101.1 | 143.0 | 120.7 | 122.3 | 71.7 | 117.0 | 98.1 | 100.0 |
| HURHOR | 70.6 | 103.0 | 99.3 | 141.4 | 117.6 | 130.6 | 71.2 | 111.8 | 99.5 | 101.0 |
| HURHOR | 71.3 | 100.8 | 100.9 | 142.6 | 122.2 | 125.3 | 71.3 | 112.5 | 100.2 | 99.2 |
| HURHUX | 71.2 | 97.2 | 97.9 | 143.0 | 109.3 | 123.0 | 71.9 | 127.8 | 97.4 | 99.6 |
| JEXVAJ | 72.3 | 102.2 | 97.2 | 142.8 | 118.8 | 119.9 | 70.5 | 121.3 | 96.5 | 100.1 |
| LOSBIF | 71.0 | 98.5 | 103.7 | 140.9 | 106.5 | 143.1 | 70.7 | 110.4 | 99.8 | 101.8 |
| MIRBAR | 71.5 | 98.2 | 103.2 | 142.3 | 118.0 | 125.7 | 70.9 | 116.2 | 96.5 | 101.1 |
| MIRBAR | 71.4 | 98.8 | 100.4 | 142.8 | 118.4 | 123.3 | 71.4 | 118.3 | 100.0 | 98.5 |
| PIGKAR | 71.8 | 94.6 | 96.0 | 144.4 | 107.2 | 134.3 | 72.7 | 117.7 | 95.5 | 109.1 |
| REHDAK | 70.3 | 96.5 | 102.0 | 141.1 | 116.1 | 126.1 | 70.8 | 117.8 | 102.0 | 99.1 |
| VURZIR | 71.3 | 99.9 | 101.4 | 140.6 | 105.9 | 141.1 | 71.2 | 112.9 | 101.5 | 100.1 |
| (DIP)FeCl ${ }_{2}$ complexes |  |  |  |  |  |  |  |  |  |  |
| ACATEE | 73.1 | 101.1 | 92.4 | 147.7 | 111.7 | 124.8 | 74.8 | 123.4 | 93.3 | 103.6 |
| ACATII | 72.5 | 96.6 | 100.1 | 141.9 | 92.8 | 153.7 | 72.9 | 113.3 | 100.4 | 103.9 |
| COBHIL | 73.6 | 96.4 | 103.8 | 141.9 | 94.4 | 147.9 | 72.6 | 117.6 | 103.3 | 95.6 |
| EKINAN | 73.0 | 100.6 | 97.5 | 146.1 | 119.2 | 129.6 | 73.1 | 111.3 | 96.8 | 103.0 |
| EMEHOT | 73.8 | 95.8 | 103.3 | 147.7 | 113.8 | 127.9 | 73.9 | 118.3 | 97.3 | 96.2 |
| EMEJAH | 71.7 | 105.4 | 95.9 | 141.1 | 106.5 | 146.3 | 72.3 | 107.0 | 98.4 | 106.2 |


| Refcode | $\bigcirc 12$ | $\vartheta 13$ | $\bigcirc 14$ | $\vartheta 1$ | Э2 | Э2 | 92 | 93 | 93 | Э45 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| FEQLUJ | 73.0 | 98.0 | 105.5 | 141.0 | 91.6 | 159.7 | 72.6 | 108.6 | 100.8 | 100 |
| FEQMAQ | 73.0 | 96.5 | 03 | 14 | 98 | 155.9 | 71.8 | 105.6 | 102.3 | 102.9 |
| GATNOF | 72.7 | 99.6 | 98. | 145 | 124.3 | 124.4 | 73.2 | 111.3 | 100.2 | 99. |
| GEQYAD | 73.7 | 100.0 | 100.8 | 139.2 | 89.3 | 151.1 | 72.9 | 119.5 | 102.5 | 97.2 |
| GEQ | 73.2 | 102.0 | 102.2 | 142 | 95.1 | 155.4 | 72.9 | 109.5 | 95.9 | 102 |
| GEQ | 73.7 | 97.9 | 103.2 | 144 | 91.8 | 153.4 | 73.0 | 114.7 | 95.1 | 101.0 |
| GIGH | 72.2 | 101. | 99.6 | 145 | 115.7 | 133.0 | 74.0 | 111.3 | 100.3 | 97.6 |
| GIGH | 71 | 102 | 95.8 | 14 | 97 | 147.6 | 74 | 11 | 97.0 | 104.9 |
| GUC | 72 | 102 | 97 | 14 | 11 | 131.2 | 73 | 109.8 | 96 | 10 |
| GU | 72 | 10 | 98 | 14 | 11 | 13 | 72 | 10 | 97 | 102.0 |
| H | 72 | 10 | 10 | 14 | 12 | 12 | 72 | 112.6 | 97.8 | 97.1 |
| H | 72 | 103 | 10 | 14 | 11 | 13 | 73 | 109.4 | 93 | 100.0 |
| H | 73 | 10 | 100 | 14 | 10 | 135.5 | 73 | 9 | 90 | 99.5 |
| HOBPO | 73 | 98 | 103 | 146 | 11 | 127.9 | 73 | 116.1 | 95 | 97.6 |
| HOBQA | 73.7 | 94.3 | 102. | 147. | 12 | 12 | 73.7 | 117.8 | 102.4 | 94.3 |
| HOBQEV | 73.5 | 98.9 | 103 | 145 | 110.7 | 134.9 | 72.5 | 114 | 96.6 | 97.3 |
| HOBQIZ | 73.2 | 100. | 104.7 | 147 | 107.4 | 133.8 | 74.0 | 118.2 | 92.1 | 95.9 |
| H | 73.5 | 100. | 103. | 146 | 114.9 | 130.1 | 72.6 | 114.5 | 95.8 | 96.3 |
| H | 73 | 98.8 | 103 | 146 | 109.6 | 136.6 | 72.9 | 113.6 | 96.7 | 97.8 |
| JI | 72 | 96. | 102. | 145 | 120.5 | 126.1 | 73.0 | 113.4 | 98.3 | 100.4 |
| JI | 73 | 102. | 10 | 145 | 121.8 | 126.3 | 72 | 111.6 | 94. | 99. |
| JIYQOY | 73. | 100. | 100 | 145 | 121.8 | 126.5 | 72.5 | 111.6 | 99.3 | 97.9 |
| JIYQOY | 73.3 | 97.6 | 99.9 | 147 | 115.5 | 126.7 | 74.2 | 117.8 | 97.2 | 98. |
| JIYQUE | 73.4 | 101. | 102.5 | 146.0 | 117.6 | 132.0 | 72.7 | 110.1 | 96.0 | 98.7 |
| JIYRAL | 72.4 | 99.3 | 102. | 146.0 | 116.4 | 134.5 | 73.6 | 109.1 | 97.3 | 99.3 |
| JIZTIW | 73.0 | 99.9 | 96.9 | 146.4 | 121.2 | 126.4 | 73.4 | 112.4 | 97.8 | 102.4 |
| JIZTOC | 73.5 | 98.7 | 101.0 | 146.8 | 121.5 | 125.2 | 73.3 | 113.3 | 99.9 | 96.6 |
| KIZZID | 72.9 | 102.1 | 98.4 | 145.5 | 120.1 | 124.9 | 73.1 | 115.0 | 99.6 | 96.3 |
| KIZZID | 72.7 | 97.5 | 99.5 | 144.4 | 109.9 | 131.2 | 73.8 | 118.9 | 104.9 | 93.5 |
| LOPTAM | 73.1 | 102.2 | 99.7 | 143.5 | 96.8 | 143.5 | 73.7 | 119.6 | 96.4 | 97.9 |
| LOPTEQ | 73.2 | 101.1 | 98.1 | 146.1 | 98.7 | 141.1 | 74.2 | 120.2 | 92.7 | 101.4 |


| Refcode | $\vartheta 12$ | $\vartheta 13$ | $\vartheta 14$ | $\vartheta 15$ | 923 | 924 | 925 | 934 | 935 | 945 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| MAZWEP | 73.6 | 97.9 | 99.6 | 146.9 | 117.2 | 126.3 | 73.3 | 116.5 | 97.5 | 99.5 |
| MAZWIT | 73.4 | 98.4 | 99.0 | 146.5 | 119.4 | 124.0 | 73.2 | 116.5 | 100.3 | 97.2 |
| MAZWOZ | 73.3 | 98.2 | 98.4 | 146.4 | 117.3 | 125.5 | 73.3 | 117.2 | 100.4 | 97.7 |
| NIGHOB | 73.3 | 98.3 | 101.7 | 140.8 | 90.5 | 153.1 | 72.9 | 116.4 | 101.4 | 99.4 |
| OBIFOU | 73.7 | 99.5 | 94.6 | 145.7 | 95.7 | 127.8 | 74.1 | 136.4 | 95.1 | 96.0 |
| OBIFUA | 73.7 | 96.0 | 96.8 | 147.9 | 108.2 | 122.1 | 74.3 | 129.7 | 95.7 | 98.4 |
| OBIGAH | 73.8 | 96.7 | 96.9 | 147.7 | 111.3 | 118.7 | 74.1 | 129.9 | 97.5 | 95.8 |
| OGODIX | 73.5 | 98.6 | 99.5 | 143.1 | 96.7 | 138.7 | 72.9 | 124.6 | 100.1 | 95.7 |
| PAYTEP | 74.7 | 102.7 | 98.2 | 142. | 91.1 | 150.7 | 73.1 | 118.2 | 97.0 | 100.3 |
| PUGWIX | 73. | 100.6 | 98.2 | 140. | 94.5 | 147.9 | 72.6 | 117.5 | 102.5 | 99.3 |
| PUGWIX01 | 73.2 | 100.7 | 98.6 | 140. | 94.6 | 147.9 | 72.9 | 117.4 | 102.4 | 98.9 |
| QELJAT | 72.7 | 100.6 | 100.2 | 145.4 | 127.3 | 127.3 | 72.7 | 105.4 | 100.2 | 100.6 |
| QELJIB | 73.9 | 93.3 | 101.9 | 146.7 | 114.6 | 126.7 | 73.0 | 118.7 | 96.8 | 100.8 |
| QELJOH | 72.2 | 103.1 | 101.1 | 146.2 | 114.0 | 132.0 | 74.0 | 113.8 | 91.9 | 100.1 |
| QELJOH | 73.1 | 102.9 | 102.0 | 145.5 | 120.4 | 131.8 | 72.5 | 107.6 | 95.4 | 99.9 |
| QELJUN | 73.9 | 95.6 | 102.7 | 147.5 | 115.1 | 127.2 | 73.6 | 117.7 | 98.6 | 96.3 |
| VIBSOP | 73.3 | 100.3 | 99.3 | 144.1 | 99.4 | 143.9 | 73.2 | 116.7 | 97.6 | 100.1 |
| VIFMON | 72.7 | 98.4 | 101.2 | 145.5 | 120.1 | 128.9 | 72.8 | 110.9 | 100.3 | 98.8 |
| VIFMON | 74.0 | 96.8 | 101.8 | 146.4 | 119.0 | 129.0 | 72.5 | 112.0 | 100.6 | 98.0 |
| VIFMUT | 73.3 | 99.6 | 99.0 | 145.9 | 117.9 | 129.9 | 72.7 | 112.2 | 97.8 | 101.2 |
| VIFMUT | 73.7 | 99.8 | 99.1 | 144.0 | 108.2 | 139.4 | 72.9 | 112.4 | 102.9 | 97.5 |
| VIFNAA | 73.7 | 99.5 | 101.9 | 141.1 | 90.7 | 155.4 | 72.7 | 113.9 | 99.9 | 100.5 |
| VIFPIK | 73.0 | 99.5 | 101.3 | 145.9 | 123.0 | 127.3 | 72.9 | 109.7 | 99.5 | 98.5 |
| VIFPUW | 73.2 | 96.5 | 99.3 | 146.7 | 109.7 | 135.8 | 73.6 | 114.5 | 96.9 | 102.6 |
| VIFQAD | 73.9 | 101.1 | 104.5 | 146.2 | 113.6 | 131.3 | 72.5 | 114.4 | 94.9 | 95.5 |
| VIFQEH | 73.3 | 100.3 | 96.6 | 146.9 | 123.1 | 123.7 | 73.5 | 113.2 | 98.4 | 100.9 |
| XEBDIR | 79.3 | 88.9 | 93.9 | 161.6 | 115.0 | 115.4 | 82.4 | 129.2 | 96.8 | 96.0 |
| XEBDIR | 81.8 | 91.5 | 94.3 | 162.8 | 113.5 | 117.7 | 81.7 | 128.8 | 90.8 | 97.5 |
| (8) $\mathrm{FeCl}_{2}$ (a) | 71.8 | 94.8 | 96.8 | 146.6 | 88.4 | 157.1 | 79.7 | 112.8 | 101.6 | 103.1 |
| (8) $\mathrm{FeCl}_{2}$ (b) | 80.7 | 100.3 | 103.8 | 148.0 | 91.7 | 151.9 | 72.1 | 114.2 | 97.2 | 93.0 |
| (10) $\mathrm{FeCl}_{2}$ | 73.3 | 93.1 | 95.2 | 154.3 | 98.3 | 137.7 | 81.9 | 123.3 | 97.2 | 98.6 |


| Refcode | $\vartheta 12$ | $\vartheta 13$ | $\vartheta 14$ | $\vartheta 15$ | $\vartheta 23$ | 924 | 925 | 934 | $\vartheta 35$ | $\vartheta 4$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (9) $\mathrm{FeCl}_{2}$ | 73.9 | 93.5 | 95.7 | 149.1 | 94.9 | 154.2 | 81.4 | 109.4 | 107.1 | 98.7 |
| (7) $\mathrm{FeCl}_{2}$ | 72.8 | 101.7 | 100.2 | 145.2 | 116.4 | 136.0 | 72.9 | 107.6 | 98.4 | 100.4 |
| (DIP) $\mathrm{CoCl}_{2}$ complexes |  |  |  |  |  |  |  |  |  |  |
| BIZRAE | 75.4 | 96.1 | 96.2 | 150.7 | 119.1 | 123.8 | 75.4 | 117.1 | 98.4 | 99.6 |
| COBHOR | 73.8 | 103.7 | 96.2 | 142.8 | 94.7 | 148.6 | 74.2 | 116.7 | 97.2 | 101.4 |
| EKINER | 75.3 | 95.9 | 102.7 | 149.6 | 111.9 | 134.7 | 74.5 | 113.3 | 98.3 | 96.2 |
| EMEHUZ | 75.3 | 95.8 | 98.2 | 150.0 | 107.4 | 134.2 | 75.1 | 118.4 | 97.5 | 98.9 |
| EMEJEL | 75.1 | 94.9 | 97.8 | 149.6 | 106.6 | 132.9 | 74.6 | 120.5 | 96.6 | 100.3 |
| FEQLET | 73.9 | 98.8 | 104.3 | 141.3 | 90.2 | 162.9 | 73.6 | 106.9 | 101.8 | 100.7 |
| FEQLIX | 74.2 | 97.3 | 102.2 | 143.1 | 96.0 | 159.3 | 73.0 | 104.8 | 102.6 | 102.4 |
| FEQLOD | 73.9 | 101.3 | 101.3 | 139.0 | 89.9 | 158.6 | 73.4 | 111.4 | 102.6 | 100.2 |
| FERRIE | 73.5 | 101.9 | 101.9 | 138.8 | 91.3 | 159.1 | 73.5 | 109.7 | 102.8 | 100.2 |
| GIGHUA | 74.0 | 98.8 | 98.4 | 147.7 | 101.9 | 142.4 | 75.9 | 115.7 | 98.4 | 98.3 |
| GIGJAI | 75.3 | 97.5 | 98.2 | 146.2 | 98.4 | 145.8 | 74.1 | 115.9 | 100.8 | 99.1 |
| GIGJEM | 72.8 | 102.1 | 96.6 | 144.5 | 96.6 | 149.3 | 75.6 | 113.9 | 97.4 | 102.2 |
| GUCXUX | 74.0 | 100.6 | 98.3 | 141.3 | 92.9 | 150.6 | 74.0 | 116.5 | 102.3 | 98.8 |
| JADMEH | 76.7 | 99.8 | 99.9 | 149.3 | 107.6 | 131.9 | 73.4 | 120.1 | 95.7 | 94.9 |
| JIZTUI | 75.5 | 98.0 | 97.5 | 149.9 | 114.5 | 130.4 | 74.7 | 115.1 | 98.0 | 98.5 |
| KIZZOJ | 74.8 | 102.8 | 98.3 | 144.6 | 93.7 | 151.5 | 74.9 | 114.8 | 97.1 | 99.6 |
| KIZZUP | 73.3 | 96.0 | 97.5 | 147.2 | 108.2 | 132.3 | 75.9 | 119.4 | 104.1 | 94.8 |
| KIZZUP | 74.1 | 100.6 | 98.1 | 149.7 | 118.1 | 126.3 | 76.0 | 115.6 | 97.6 | 95.5 |
| LOPSEP | 74.2 | 102.0 | 98.3 | 143.6 | 93.4 | 147.3 | 74.8 | 119.3 | 98.4 | 97.6 |
| LOPSIT | 74.3 | 102.6 | 98.2 | 144.9 | 96.8 | 143.9 | 74.7 | 119.3 | 97.1 | 97.1 |
| LOPSOZ | 74.0 | 101.2 | 96.7 | 148.2 | 98.8 | 140.9 | 75.9 | 120.3 | 93.4 | 100.1 |
| LOPSUF | 74.1 | 101.4 | 96.7 | 143.9 | 94.5 | 146.6 | 75.1 | 118.9 | 99.3 | 98.7 |
| LUXGUG | 75.7 | 96.9 | 100.6 | 150.4 | 119.9 | 127.1 | 74.8 | 112.9 | 98.8 | 96.2 |
| MIFCOU | 75.2 | 91.2 | 98.4 | 151.8 | 111.3 | 120.5 | 76.6 | 128.1 | 99.5 | 95.3 |
| OBIGEL | 74.5 | 99.5 | 94.0 | 147.6 | 105.9 | 126.2 | 75.3 | 127.9 | 99.9 | 94.4 |
| PAYSOY | 75.1 | 97.5 | 97.4 | 145.6 | 92.7 | 145.4 | 74.6 | 121.8 | 99.8 | 98.3 |
| PELTUW | 74.7 | 97.9 | 97.9 | 148.5 | 121.1 | 121.1 | 73.8 | 117.7 | 98.2 | 98.2 |
| PUGWET | 72.3 | 97.3 | 104.4 | 141.6 | 93.7 | 161.5 | 74.0 | 104.8 | 102.9 | 101.6 |


| Refcode | $\vartheta 12$ | $\vartheta 13$ | $\vartheta 14$ | $\vartheta 15$ | 923 | 924 | Э25 | $\vartheta 34$ | 935 | $\vartheta 45$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| PUGWET | 73.7 | 105.1 | 100.0 | 142.1 | 90.9 | 165.3 | 74.7 | 103.7 | 95.8 | 105.4 |
| RESLAD | 74.8 | 95.6 | 98.0 | 149.8 | 113.4 | 130.3 | 75.2 | 116.2 | 99.2 | 98.8 |
| VIKWES | 75.1 | 100.3 | 100.0 | 143.6 | 91.0 | 150.8 | 73.5 | 118.1 | 98.2 | 98.4 |
| YAKRAE | 75.5 | 104.9 | 95.0 | 149.9 | 117.3 | 121.1 | 74.6 | 121.2 | 91.0 | 98.2 |
| YAKRAE | 73.2 | 100.1 | 92.2 | 149.9 | 119.4 | 121.9 | 76.7 | 118.5 | 95.3 | 102.9 |
| (3) $\mathrm{CoCl}_{2}$ | 76.4 | 95.2 | 97.4 | 151.5 | 120.5 | 124.4 | 75.1 | 115.0 | 99.6 | 98.2 |
| (7) $\mathrm{CoCl}_{2}$ | 74.8 | 97.5 | 98.5 | 149.2 | 109.4 | 136.5 | 75.3 | 114.0 | 99.2 | 98.0 |
| (10) $\mathrm{CoCl}_{2}$ | 84.9 | 99.2 | 98.0 | 157.1 | 101.0 | 135.0 | 73.4 | 122.5 | 92.3 | 92.3 |
| (DIP) $\mathrm{NiCl}_{2}$ complexes |  |  |  |  |  |  |  |  |  |  |
| AHUQAV | 77.4 | 95.3 | 96.2 | 154.5 | 108.1 | 121.7 | 77.2 | 130.2 | 95.0 | 94.8 |
| AHUQEZ | 78.0 | 94.9 | 93.7 | 154.9 | 111.4 | 114.9 | 77.0 | 133.7 | 96.7 | 94.2 |
| BOKZEH | 76.7 | 100.8 | 100.1 | 152.3 | 95.3 | 147.8 | 77.3 | 116.6 | 91.1 | 96.6 |
| BOKZIL | 77.8 | 91.4 | 100.5 | 152.3 | 92.2 | 159.3 | 76.7 | 108.5 | 100.1 | 99.6 |
| ECORIY | 76.8 | 99.7 | 99.4 | 148.4 | 92.3 | 153.2 | 75.2 | 114.5 | 95.9 | 98.9 |
| ECORIY | 75.9 | 97.6 | 100.0 | 149.8 | 90.2 | 155.0 | 78.0 | 114.8 | 97.4 | 97.3 |
| ECOROE | 76.8 | 95.3 | 98.0 | 153.2 | 107.3 | 132.1 | 76.7 | 120.6 | 96.0 | 97.0 |
| GIFGAE | 76.2 | 98.7 | 98.7 | 152.6 | 100.4 | 149.4 | 77.8 | 110.2 | 94.3 | 99.3 |
| GIFGEI | 77.7 | 95.0 | 98.5 | 152.2 | 96.0 | 150.0 | 76.4 | 114.0 | 97.6 | 98.9 |
| GIFGIM | 77.3 | 95.8 | 99.4 | 150.5 | 97.3 | 154.7 | 75.9 | 108.0 | 99.5 | 99.6 |
| KAVVEJ | 77.2 | 96.6 | 93.8 | 154.4 | 114.3 | 114.3 | 77.2 | 131.5 | 93.9 | 96.6 |
| KECFII | 76.7 | 97.1 | 100.2 | 150.3 | 90.7 | 155.6 | 76.8 | 113.7 | 96.3 | 98.5 |
| KECFOO | 76.8 | 98.6 | 99.5 | 149.7 | 92.4 | 156.1 | 76.9 | 111.5 | 97.1 | 98.6 |
| KOBBAF | 76.7 | 95.0 | 102.0 | 152.2 | 94.2 | 153.5 | 77.4 | 112.2 | 96.7 | 96.8 |
| KOBBEJ | 76.9 | 96.9 | 101.4 | 150.0 | 92.1 | 157.8 | 76.8 | 110.0 | 98.2 | 97.5 |
| PEDGOV | 77.2 | 92.1 | 93.8 | 154.8 | 101.2 | 115.8 | 77.6 | 142.9 | 94.5 | 95.5 |
| PEDGUB | 77.1 | 97.1 | 93.4 | 154.3 | 114.3 | 114.3 | 77.1 | 131.3 | 93.4 | 97.1 |
| SIGCOB | 76.2 | 95.7 | 99.0 | 151.3 | 99.1 | 147.7 | 76.7 | 113.2 | 97.7 | 98.9 |
| (DIP) $\mathrm{CuCl}_{2}$ complexes |  |  |  |  |  |  |  |  |  |  |
| BOBHAB | 77.5 | 100.5 | 93.9 | 152.0 | 98.4 | 159.2 | 77.6 | 101.7 | 95.6 | 105.1 |
| CELGUW | 76.7 | 98.3 | 93.7 | 153.5 | 119.4 | 121.8 | 76.8 | 118.8 | 95.1 | 99.7 |
| DIQJAO | 78.4 | 95.4 | 100.0 | 156.4 | 116.9 | 132.3 | 77.9 | 110.8 | 95.4 | 95.7 |


| Refcode | $\Im 12$ | $\Im 13$ | $\vartheta 14$ | $\vartheta 15$ | $\Im 23$ | $\vartheta 24$ | $\vartheta 25$ | 934 | 935 | $\vartheta 45$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| DIQJAO | 77.9 | 95.6 | 98.1 | 156.2 | 120.1 | 125.9 | 78.4 | 113.9 | 94.7 | 97.3 |
| FAGWEQ | 78.3 | 95.0 | 99.0 | 157.0 | 93.3 | 162.4 | 79.1 | 104.3 | 90.8 | 101.1 |
| FAGWEQ | 79.1 | 90.8 | 101.1 | 157.0 | 93.3 | 162.5 | 78.4 | 104.2 | 95.0 | 99.0 |
| IOHZCU | 77.0 | 95.0 | 102.4 | 155.2 | 92.1 | 168.8 | 79.3 | 99.0 | 93.0 | 99.5 |
| IOHZCU | 77.0 | 95.0 | 102.4 | 155.2 | 92.1 | 168.8 | 79.3 | 99.0 | 93.0 | 99.5 |
| LEKDOU | 77.4 | 94.0 | 106.3 | 152.1 | 98.8 | 158.2 | 77.2 | 102.3 | 101.2 | 93.3 |
| LEKDOU | 78.0 | 94.4 | 103.8 | 151.3 | 98.0 | 158.5 | 77.5 | 103.1 | 103.5 | 93.9 |
| LOCGAM | 78.8 | 94.2 | 100.5 | 156.5 | 98.4 | 158.2 | 78.0 | 103.4 | 92.2 | 99.9 |
| LOCGAM | 79.2 | 96.5 | 99.4 | 157.3 | 102.1 | 143.3 | 78.3 | 114.4 | 90.9 | 97.0 |
| MIFCIO | 78.1 | 94.9 | 98.4 | 155.5 | 98.7 | 145.8 | 78.0 | 115.5 | 94.0 | 98.2 |
| MOLVEO | 77.6 | 96.2 | 97.7 | 155.3 | 124.3 | 124.3 | 77.6 | 111.5 | 97.7 | 96.2 |
| MOLVIS | 77.3 | 95.5 | 97.9 | 155.3 | 117.3 | 130.4 | 78.1 | 112.3 | 97.1 | 96.9 |
| QEZJIP | 77.6 | 94.8 | 101.4 | 155.5 | 108.5 | 143.2 | 77.9 | 108.2 | 94.5 | 97.2 |
| QEZJIP | 77.9 | 93.2 | 102.0 | 154.8 | 102.5 | 151.9 | 77.7 | 105.5 | 98.2 | 96.5 |
| SICPUP | 78.3 | 99.3 | 99.8 | 153.8 | 90.3 | 166.1 | 78.6 | 103.5 | 93.1 | 99.6 |
| TEHZEM | 77.5 | 96.4 | 101.2 | 149.7 | 93.6 | 160.4 | 77.4 | 105.9 | 101.9 | 96.8 |
| BOBHAB | 77.5 | 100.5 | 93.9 | 152.0 | 98.4 | 159.2 | 77.6 | 101.7 | 95.6 | 105.1 |


| $($ DIP $) \mathrm{ZnCl}_{2}$ complexes |  |  |  |  |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| AHUPUO | 74.1 | 98.1 | 98.9 | 148.4 | 120.3 | 121.8 | 74.3 | 117.9 | 96.5 | 98.8 |
| BOBHEF | 73.2 | 95.9 | 96.7 | 147.3 | 116.6 | 122.1 | 74.1 | 121.2 | 98.7 | 100.4 |
| ECIJEF | 73.2 | 97.9 | 97.5 | 147.0 | 116.0 | 118.6 | 73.9 | 125.4 | 94.2 | 100.2 |
| ECIJEF | 73.0 | 98.6 | 99.2 | 146.4 | 115.5 | 121.7 | 73.6 | 122.8 | 99.0 | 95.0 |
| HAWDOZ | 74.4 | 98.0 | 96.5 | 148.9 | 117.0 | 121.0 | 74.5 | 122.0 | 95.7 | 99.6 |
| HEFQIS | 74.8 | 96.1 | 98.8 | 149.5 | 117.2 | 123.5 | 74.8 | 119.3 | 99.7 | 95.9 |
| IMTPZN10 | 73.6 | 105.5 | 98.9 | 139.9 | 96.3 | 152.3 | 71.8 | 111.4 | 98.0 | 102.2 |
| IMTPZN10 | 72.3 | 104.7 | 101.1 | 137.6 | 97.1 | 151.1 | 71.2 | 111.7 | 100.4 | 100.4 |
| JEXTUB | 73.9 | 97.6 | 99.1 | 147.0 | 116.1 | 124.8 | 73.2 | 119.1 | 98.2 | 98.1 |
| JEXTUB | 73.7 | 95.9 | 100.1 | 148.0 | 117.7 | 123.3 | 74.3 | 119.0 | 96.8 | 99.3 |
| KALLEP | 72.4 | 102.7 | 98.2 | 139.9 | 98.4 | 142.1 | 72.9 | 119.5 | 101.7 | 96.8 |
| KALLIT | 74.1 | 97.8 | 99.6 | 147.8 | 117.8 | 125.3 | 73.9 | 116.8 | 99.5 | 96.6 |
| MAHWIC | 73.0 | 101.3 | 97.9 | 144.4 | 106.2 | 139.6 | 73.6 | 114.2 | 99.3 | 99.7 |


| Refcode | $\vartheta 12$ | $\vartheta 13$ | $\vartheta 14$ | $\vartheta 15$ | $\vartheta 23$ | $\vartheta 24$ | $\vartheta 25$ | $\vartheta 34$ | $\vartheta 35$ | $\vartheta 45$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| MAHWIC01 | 73.1 | 101.2 | 98.1 | 144.3 | 106.1 | 139.8 | 73.4 | 114.1 | 99.6 | 99.5 |
| MIFCEK | 75.6 | 100.6 | 96.1 | 149.4 | 111.8 | 121.8 | 73.8 | 126.3 | 91.4 | 99.3 |
| OLOLEG | 74.9 | 99.4 | 98.5 | 147.6 | 114.0 | 124.6 | 72.7 | 121.3 | 94.3 | 99.1 |
| QETSUE | 72.5 | 95.4 | 98.8 | 146.8 | 111.8 | 127.7 | 74.4 | 120.4 | 99.2 | 99.2 |
| QUPVEC | 73.8 | 100.6 | 97.2 | 147.4 | 123.6 | 123.6 | 73.7 | 112.8 | 97.4 | 100.4 |
| FOPSEJ | 74.0 | 98.2 | 98.1 | 148.0 | 120.9 | 120.9 | 74.0 | 118.2 | 98.1 | 98.2 |
| (DIP)Fe(CH2SiMe $\left.)_{2}\right)_{2}$ | complexes |  |  |  |  |  |  |  |  |  |
| LAQJAP | 74.0 | 103.4 | 98.2 | 141.1 | 107.9 | 140.0 | 72.9 | 112.0 | 105.8 | 94.2 |
| DAWKES | 73.7 | 100.0 | 98.5 | 144.1 | 106.1 | 136.7 | 74.3 | 117.2 | 104.0 | 93.8 |
| HIYJUV | 73.6 | 102.9 | 96.9 | 142.3 | 108.5 | 137.7 | 73.8 | 113.8 | 105.1 | 94.4 |
| AFUTEB | 75.1 | 93.2 | 100.9 | 150.1 | 118.4 | 118.4 | 75.0 | 123.2 | 100.5 | 93.6 |
| FeSi0m | 75.1 | 97.0 | 97.5 | 149.9 | 118.5 | 120.5 | 74.8 | 121.0 | 97.2 | 97.7 |
| FeSi0m | 74.6 | 97.9 | 97.2 | 149.4 | 118.5 | 123.1 | 74.9 | 118.4 | 98.0 | 98.0 |

Table A.3. Geometry analyses for DIP complexes

| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |  |  |
| :--- | :---: | :---: | :--- | :--- | :--- | :--- | :---: | :---: |
|  | $\sigma(\mathrm{TBP})$ | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | M dev $(\AA)$ |  |  |
| (DIP)CrCl ${ }_{2}$ complexes |  |  |  |  |  |  |  |  |
| JAPLUI | 0.772 | 0.451 | SP | 0.57 | SP | 0.33 |  |  |
| PIKGUM | 0.891 | 0.393 | SP | 0.75 | SP | 0.42 |  |  |
| $\left(\right.$ DIP)MnCl ${ }_{2}$ complexes |  |  |  |  |  |  |  |  |
| ADOROA | 0.547 | 0.756 | TBP | 0.47 | TBP | 0.58 |  |  |
| AHUPOI | 0.114 | 1.013 | TBP | 0.02 | TBP | 0.06 |  |  |
| HURHOR | 0.271 | 0.875 | TBP | 0.14 | TBP | 0.17 |  |  |
| HURHOR | 0.195 | 0.969 | TBP | 0.03 | TBP | 0.04 |  |  |
| HURHUX | 0.245 | 1.029 | TBP | 0.15 | TBP | 0.08 |  |  |
| JEXVAJ | 0.116 | 1.060 | TBP | 0.01 | TBP | 0.03 |  |  |
| LOSBIF | 0.516 | 0.658 | TBP | 0.41 | TBP | 0.23 |  |  |
| MIRBAR | 0.180 | 0.953 | TBP | 0.09 | TBP | 0.09 |  |  |


| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ (TBP) | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | $\mathrm{M} \mathrm{dev}(\AA)$ |
| MIRBAR | 0.113 | 0.996 | TBP | 0.05 | TBP | 0.05 |
| PIGKAR | 0.400 | 0.827 | TBP | 0.30 | TBP | 0.01 |
| REHDAK | 0.189 | 0.952 | TBP | 0.11 | TBP | 0.06 |
| VURZIR | 0.474 | 0.698 | TBP | 0.39 | TBP | 0.33 |
| (DIP) $\mathrm{FeCl}_{2}$ complexes |  |  |  |  |  |  |
| ACATEE | 0.246 | 0.998 | TBP | 0.15 | TBP | 0.08 |
| ACATII | 0.773 | 0.542 | SP | 0.68 | SP | 0.41 |
| COBHIL | 0.678 | 0.660 | SP | 0.59 | SP | 0.47 |
| EKINAN | 0.248 | 0.894 | TBP | 0.12 | TBP | 0.03 |
| EMEHOT | 0.207 | 0.922 | TBP | 0.16 | TBP | 0.01 |
| EMEJAH | 0.595 | 0.622 | TBP | 0.44 | TBP | 0.40 |
| FEQLUJ | 0.885 | 0.437 | SP | 0.76 | SP | 0.48 |
| FEQMAQ | 0.786 | 0.448 | SP | 0.64 | SP | 0.38 |
| GATNOF | 0.195 | 0.990 | TBP | 0.00 | TBP | 0.03 |
| GEQYAD | 0.768 | 0.658 | SP | 0.69 | SP | 0.61 |
| GEQYEH | 0.786 | 0.482 | SP | 0.67 | SP | 0.43 |
| GEQYEH | 0.777 | 0.551 | SP | 0.68 | SP | 0.34 |
| GIGHIO | 0.293 | 0.832 | TBP | 0.19 | TBP | 0.21 |
| GIGHOU | 0.644 | 0.628 | SP | 0.55 | SP | 0.42 |
| GUCXIL | 0.287 | 0.868 | TBP | 0.14 | TBP | 0.09 |
| GUCXOR | 0.307 | 0.850 | TBP | 0.15 | TBP | 0.10 |
| HOBPEU | 0.204 | 0.937 | TBP | 0.08 | TBP | 0.08 |
| HOBPEU | 0.314 | 0.856 | TBP | 0.15 | TBP | 0.02 |
| HOBPIY | 0.404 | 0.812 | TBP | 0.33 | TBP | 0.10 |
| HOBPOE | 0.200 | 0.917 | TBP | 0.14 | TBP | 0.01 |
| HOBQAR | 0.149 | 1.047 | TBP | 0.00 | TBP | 0.00 |
| HOBQEV | 0.342 | 0.797 | TBP | 0.27 | TBP | 0.11 |
| HOBQIZ | 0.367 | 0.837 | TBP | 0.29 | TBP | 0.07 |
| HOBQOF | 0.251 | 0.882 | TBP | 0.17 | TBP | 0.06 |
| HOBQUL | 0.373 | 0.767 | TBP | 0.30 | TBP | 0.13 |


| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ (TBP) | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | $\mathrm{M} \mathrm{dev}(\AA)$ |
| JIYQEO | 0.181 | 0.949 | TBP | 0.06 | TBP | 0.09 |
| JIYQIS | 0.219 | 0.955 | TBP | 0.05 | TBP | 0.01 |
| JIYQOY | 0.199 | 0.949 | TBP | 0.05 | TBP | 0.07 |
| JIYQOY | 0.152 | 0.938 | TBP | 0.12 | TBP | 0.03 |
| JIYQUE | 0.293 | 0.851 | TBP | 0.16 | TBP | 0.05 |
| JIYRAL | 0.335 | 0.805 | TBP | 0.20 | TBP | 0.05 |
| JIZTIW | 0.194 | 0.950 | TBP | 0.06 | TBP | 0.02 |
| JIZTOC | 0.165 | 0.971 | TBP | 0.04 | TBP | 0.04 |
| KIZZID | 0.149 | 0.975 | TBP | 0.05 | TBP | 0.15 |
| KIZZID | 0.303 | 0.882 | TBP | 0.24 | TBP | 0.33 |
| LOPTAM | 0.581 | 0.715 | TBP | 0.52 | SP | 0.39 |
| LOPTEQ | 0.538 | 0.746 | TBP | 0.47 | TBP | 0.25 |
| MAZWEP | 0.141 | 0.944 | TBP | 0.10 | TBP | 0.01 |
| MAZWIT | 0.105 | 0.987 | TBP | 0.05 | TBP | 0.08 |
| MAZWOZ | 0.126 | 0.961 | TBP | 0.09 | TBP | 0.11 |
| NIGHOB | 0.780 | 0.589 | SP | 0.70 | SP | 0.52 |
| OBIFOU | 0.534 | 1.045 | TBP | 0.36 | TBP | 0.32 |
| OBIFUA | 0.273 | 1.039 | TBP | 0.15 | TBP | 0.05 |
| OBIGAH | 0.233 | 1.048 | TBP | 0.08 | TBP | 0.08 |
| OGODIX | 0.532 | 0.817 | TBP | 0.47 | TBP | 0.41 |
| PAYTEP | 0.741 | 0.635 | SP | 0.66 | SP | 0.51 |
| PUGWIX | 0.666 | 0.653 | SP | 0.59 | SP | 0.55 |
| PUGWIX01 | 0.665 | 0.651 | SP | 0.59 | SP | 0.56 |
| QELJAT | 0.322 | 0.963 | TBP | 0.00 | TBP | 0.00 |
| QELJIB | 0.195 | 0.936 | TBP | 0.13 | TBP | 0.11 |
| QELJOH | 0.301 | 0.855 | TBP | 0.20 | TBP | 0.04 |
| QELJOH | 0.323 | 0.866 | TBP | 0.13 | TBP | 0.03 |
| QELJUN | 0.185 | 0.933 | TBP | 0.13 | TBP | 0.02 |
| VIBSOP | 0.557 | 0.676 | TBP | 0.50 | TBP | 0.34 |
| VIFMON | 0.233 | 0.904 | TBP | 0.10 | TBP | 0.05 |


| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ (TBP) | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | $\mathrm{M} \mathrm{dev}(\AA)$ |
| VIFMON | 0.227 | 0.902 | TBP | 0.11 | TBP | 0.04 |
| VIFMUT | 0.232 | 0.883 | TBP | 0.13 | TBP | 0.05 |
| VIFMUT | 0.427 | 0.726 | TBP | 0.35 | TBP | 0.35 |
| VIFNAA | 0.813 | 0.534 | SP | 0.72 | SP | 0.52 |
| VIFPIK | 0.236 | 0.940 | TBP | 0.05 | TBP | 0.02 |
| VIFPUW | 0.354 | 0.780 | TBP | 0.29 | TBP | 0.07 |
| VIFQAD | 0.286 | 0.867 | TBP | 0.20 | TBP | 0.08 |
| VIFQEH | 0.160 | 0.999 | TBP | 0.01 | TBP | 0.02 |
| XEBDIR | 0.317 | 1.062 | TBP | 0.00 | TBP | 0.05 |
| XEBDIR | 0.326 | 1.047 | TBP | 0.05 | TBP | 0.11 |
| (8) $\mathrm{FeCl}_{2}$ (a) | 0.873 | 0.541 | SP | 0.76 | SP | 0.42 |
| (8) $\mathrm{FeCl}_{2}$ (b) | 0.771 | 0.616 | SP | 0.67 | SP | 0.41 |
| $(\mathbf{1 0}) \mathrm{FeCl}_{2}$ | 0.521 | 0.847 | TBP | 0.44 | TBP | 0.17 |
| $\text { (9) } \mathrm{FeCl}_{2}$ | 0.792 | 0.565 | SP | 0.66 | SP | 0.44 |
| (7) $\mathrm{FeCl}_{2}$ | 0.367 | 0.782 | TBP | 0.22 | TBP | 0.16 |
| (DIP) $\mathrm{CoCl}_{2}$ complexes |  |  |  |  |  |  |
| BIZRAE | 0.105 | 0.997 | TBP | 0.05 | TBP | 0.01 |
| COBHOR | 0.678 | 0.640 | SP | 0.60 | SP | 0.49 |
| EKINER | 0.330 | 0.806 | TBP | 0.25 | TBP | 0.09 |
| EMEHUZ | 0.337 | 0.826 | TBP | 0.30 | TBP | 0.13 |
| EMEJEL | 0.333 | 0.853 | TBP | 0.29 | TBP | 0.08 |
| FEQLET | 0.917 | 0.390 | SP | 0.81 | SP | 0.53 |
| FEQLIX | 0.853 | 0.398 | SP | 0.70 | SP | 0.43 |
| FEQLOD | 0.871 | 0.491 | SP | 0.76 | SP | 0.61 |
| FERRIE | 0.860 | 0.466 | SP | 0.75 | SP | 0.62 |
| GIGHUA | 0.510 | 0.694 | TBP | 0.45 | TBP | 0.29 |
| GIGJAI | 0.593 | 0.653 | TBP | 0.53 | SP | 0.36 |
| GIGJEM | 0.671 | 0.600 | SP | 0.59 | SP | 0.42 |
| GUCXUX | 0.719 | 0.616 | SP | 0.64 | SP | 0.56 |
| JADMEH | 0.314 | 0.875 | TBP | 0.27 | TBP | 0.19 |
| - 360 |  |  |  |  |  |  |


| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ (TBP) | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | $\mathrm{M} \mathrm{dev}(\AA)$ |
| JIZTUI | 0.224 | 0.881 | TBP | 0.18 | TBP | 0.11 |
| KIZZOJ | 0.725 | 0.587 | SP | 0.64 | SP | 0.45 |
| KIZZUP | 0.324 | 0.871 | TBP | 0.27 | TBP | 0.30 |
| KIZZUP | 0.154 | 0.957 | TBP | 0.09 | TBP | 0.13 |
| LOPSEP | 0.668 | 0.677 | TBP | 0.60 | SP | 0.48 |
| LOPSIT | 0.586 | 0.712 | TBP | 0.52 | SP | 0.42 |
| LOPSOZ | 0.531 | 0.756 | TBP | 0.47 | TBP | 0.27 |
| LOPSUF | 0.646 | 0.679 | TBP | 0.58 | SP | 0.48 |
| LUXGUG | 0.187 | 0.942 | TBP | 0.08 | TBP | 0.03 |
| MIFCOU | 0.249 | 1.065 | TBP | 0.10 | TBP | 0.02 |
| OBIGEL | 0.320 | 1.003 | TBP | 0.23 | TBP | 0.31 |
| PAYSOY | 0.653 | 0.722 | TBP | 0.59 | SP | 0.43 |
| PELTUW | 0.050 | 1.038 | TBP | 0.00 | TBP | 0.00 |
| PUGWET | 0.908 | 0.379 | SP | 0.75 | SP | 0.49 |
| PUGWET | 0.878 | 0.352 | SP | 0.83 | SP | 0.54 |
| RESLAD | 0.229 | 0.883 | TBP | 0.19 | TBP | 0.09 |
| VIKWES | 0.741 | 0.628 | SP | 0.67 | SP | 0.48 |
| YAKRAE | 0.189 | 1.060 | TBP | 0.04 | TBP | 0.07 |
| YAKRAE | 0.160 | 1.039 | TBP | 0.03 | TBP | 0.03 |
| (3) $\mathrm{CoCl}_{2}$ | 0.137 | 0.991 | TBP | 0.04 | TBP | 0.01 |
| (7) $\mathrm{CoCl}_{2}$ | 0.359 | 0.777 | TBP | 0.30 | TBP | 0.20 |
| (10) $\mathrm{CoCl}_{2}$ | 0.487 | 0.907 | TBP | 0.38 | TBP | 0.18 |
| (DIP) $\mathrm{NiCl}_{2}$ complexes |  |  |  |  |  |  |
| AHUQAV | 0.300 | 1.050 | TBP | 0.15 | TBP | 0.06 |
| AHUQEZ | 0.327 | 1.009 | TBP | 0.04 | TBP | 0.07 |
| BOKZEH | 0.670 | 0.665 | SP | 0.58 | SP | 0.23 |
| BOKZIL | 0.876 | 0.462 | SP | 0.75 | SP | 0.25 |
| ECORIY | 0.763 | 0.567 | SP | 0.68 | SP | 0.37 |
| ECORIY | 0.810 | 0.564 | SP | 0.72 | SP | 0.36 |
| ECOROE | 0.320 | 0.879 | TBP | 0.28 | TBP | 0.09 |
|  |  |  |  |  |  | 36 |


| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ (TBP) | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | $\mathrm{M} \mathrm{dev}(\AA)$ |
| GIFGAE | 0.648 | 0.582 | SP | 0.55 | SP | 0.20 |
| GIFGEI | 0.685 | 0.602 | SP | 0.60 | SP | 0.24 |
| GIFGIM | 0.756 | 0.492 | SP | 0.64 | SP | 0.30 |
| KAVVEJ | 0.276 | 1.022 | TBP | 0.00 | TBP | 0.00 |
| KECFII | 0.816 | 0.539 | SP | 0.72 | SP | 0.32 |
| KECFOO | 0.809 | 0.510 | SP | 0.71 | SP | 0.36 |
| KOBBAF | 0.758 | 0.550 | SP | 0.66 | SP | 0.24 |
| KOBBEJ | 0.842 | 0.479 | SP | 0.73 | SP | 0.34 |
| PEDGOV | 0.544 | 0.868 | TBP | 0.16 | TBP | 0.04 |
| PEDGUB | 0.276 | 1.024 | TBP | 0.00 | TBP | 0.00 |
| SIGCOB | 0.622 | 0.616 | SP | 0.54 | SP | 0.23 |
| (DIP) $\mathrm{CuCl}_{2}$ complexes |  |  |  |  |  |  |
| BOBHAB | 0.859 | 0.438 | SP | 0.68 | SP | 0.29 |
| CELGUW | 0.122 | 1.046 | TBP | 0.03 | TBP | 0.01 |
| DIQJAO | 0.302 | 0.878 | TBP | 0.17 | TBP | 0.00 |
| DIQJAO | 0.192 | 0.982 | TBP | 0.06 | TBP | 0.04 |
| FAGWEQ | 0.936 | 0.418 | SP | 0.77 | SP | 0.10 |
| FAGWEQ | 0.936 | 0.418 | SP | 0.77 | SP | 0.10 |
| IOHZCU | 1.059 | 0.300 | SP | 0.85 | SP | 0.16 |
| IOHZCU | 1.059 | 0.300 | SP | 0.85 | SP | 0.16 |
| LEKDOU | 0.846 | 0.461 | SP | 0.66 | SP | 0.26 |
| LEKDOU | 0.847 | 0.460 | SP | 0.67 | SP | 0.33 |
| LOCGAM | 0.836 | 0.451 | SP | 0.66 | SP | 0.07 |
| LOCGAM | 0.550 | 0.716 | TBP | 0.46 | TBP | 0.06 |
| MIFCIO | 0.603 | 0.678 | TBP | 0.52 | SP | 0.13 |
| MOLVEO | 0.206 | 1.018 | TBP | 0.00 | TBP | 0.00 |
| MOLVIS | 0.252 | 0.904 | TBP | 0.15 | TBP | 0.03 |
| QEZJIP | 0.515 | 0.682 | TBP | 0.39 | TBP | 0.04 |
| QEZJIP | 0.698 | 0.546 | SP | 0.55 | SP | 0.15 |
| SICPUP | 1.008 | 0.370 | SP | 0.84 | SP | 0.27 |


| Refcode | FAA analysis |  |  | $\omega$ analysis |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\sigma$ (TBP) | $\sigma(\mathrm{SP})$ | assign | $\omega$ | assign | $\mathrm{M} \mathrm{dev}(\AA)$ |
| TEHZEM | 0.884 | 0.425 | SP | 0.74 | SP | 0.40 |
| (DIP) $\mathrm{ZnCl}_{2}$ complexes |  |  |  |  |  |  |
| AHUPUO | 0.058 | 1.025 | TBP | 0.02 | TBP | 0.04 |
| BOBHEF | 0.096 | 1.021 | TBP | 0.06 | TBP | 0.01 |
| ECIJEF | 0.141 | 1.083 | TBP | 0.03 | TBP | 0.07 |
| ECIJEF | 0.114 | 1.033 | TBP | 0.07 | TBP | 0.11 |
| HAWDOZ | 0.085 | 1.043 | TBP | 0.04 | TBP | 0.01 |
| HEFQIS | 0.100 | 1.003 | TBP | 0.07 | TBP | 0.07 |
| IMTPZN10 | 0.729 | 0.552 | SP | 0.62 | SP | 0.55 |
| IMTPZN10 | 0.703 | 0.571 | SP | 0.60 | SP | 0.60 |
| JEXTUB | 0.112 | 0.972 | TBP | 0.10 | TBP | 0.05 |
| JEXTUB | 0.094 | 0.996 | TBP | 0.06 | TBP | 0.06 |
| KALLEP | 0.550 | 0.735 | TBP | 0.49 | TBP | 0.56 |
| KALLIT | 0.123 | 0.965 | TBP | 0.08 | TBP | 0.08 |
| MAHWIC | 0.436 | 0.724 | TBP | 0.37 | TBP | 0.31 |
| MAHWIC01 | 0.438 | 0.721 | TBP | 0.37 | TBP | 0.32 |
| MIFCEK | 0.224 | 1.051 | TBP | 0.11 | TBP | 0.02 |
| OLOLEG | 0.154 | 0.981 | TBP | 0.12 | TBP | 0.02 |
| QETSUE | 0.205 | 0.928 | TBP | 0.18 | TBP | 0.08 |
| QUPVEC | 0.167 | 1.002 | TBP | 0.00 | TBP | 0.01 |
| FOPSEJ | 0.039 | 1.041 | TBP | 0.00 | TBP | 0.00 |
| (DIP)Fe( $\left.\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ |  |  |  |  |  |  |
| LAQJAP | 0.464 | 0.730 | TBP | 0.36 | TBP | 0.54 |
| DAWKES | 0.404 | 0.794 | TBP | 0.34 | TBP | 0.43 |
| HIYJUV | 0.415 | 0.770 | TBP | 0.32 | TBP | 0.50 |
| AFUTEB | 0.149 | 1.097 | TBP | 0.00 | TBP | 0.01 |
| (15) $\mathrm{FeR}_{2}$ | 0.046 | 1.052 | TBP | 0.02 | TBP | 0.00 |
| (15) $\mathrm{FeR}_{2}$ | 0.070 | 1.006 | TBP | 0.05 | TBP | 0.05 |



Figure A.1. Correlation between $\omega$ and out-of-plane deviation of the metal center for Xray structure of (DIP)MX ${ }_{2}$ complexes (M: first-row transition metals; X : halogens). (correlation coefficient $\rho=0.8112$ ).



Figure A.2. Plot of metal out-of-plane deviation as a function of $\omega$ computed by DFT

## Python Code

\#Codes for program "calcGeom" part

## Codes for file (calcGeom.Py):

\#Author: Andrew Chalaturnyk and Di Zhu
\#Year: 2009
\#Coded to work with python version 2.6.2
\#to assign a geometry type to one complex and the other angle parameters around metal centers

```
import sys
import pdbReader
import molecule
import spaceMatching
import itertools
from spaceMatching import angle,length,dot,vector,cross,mdis
from math import radians,acos,degrees
```

\# Only want atom lists from molecule that satisfy criteria given
def filter_lists_iter( m, e1, n1, e2, n2):
for atom in m.element_iterator(e1):
$\mathrm{c}=$ atom.connections
if len(c) $==\mathrm{n} 1$ and c. element_count(e2) $=\mathrm{n} 2$ :
yield atom, c
\# Given preordered metal center and its five connected atoms
\# the smallest distortion vector from ideal TBP was caclulated by pertuting the labelling
of the atoms
def best_TBP(a0, atoms):
\#chemically reasonable numbering was calculated
$\mathrm{p} 0=$ [a0.coord] + [i.coord for i in atoms]
$\mathrm{t} 0=$ spaceMatching.displacementVectorTBP(p0)
change = 'no' \#use to check whether the origonal order was changed
best $=(\mathrm{t} 0$, atoms, change $)$

```
    #Permute the atom list and calulate the distortion vector and the smallest one will be
chosen
    pIndex = [[0,1,2,4,3], [0,1,3,4,2], [0,2,3,4,1],[1,0,3,4,2],
[1,0,2,4,3],[1,0,2,3,4],[2,0,1,4,3], [2,0,1,3,4], [3,0,1,2,4]]
for permute in pIndex:
        a = [atoms[i] for i in permute]
        p = [a0.coord] + [j.coord for j in a]
        t = spaceMatching.displacementVectorTBP(p)
        if t < best[0]:
            change = 'yes'
            best = (t,a,change)
    return best
```

\#calculate the SP displacement vector and the permutation that gives the lowest distorsion vector will be recorded

```
def best_SP(a0, atoms):
    #calculate chemically reasonable numbering and use it as the criterion
    p0 = [a0.coord] + [i.coord for i in atoms]
    s0 = spaceMatching.displacementVectorSP(p0)
    change = 'no' #check the changing of the numbering
    best = (s0,atoms,change)
    #permute the atom list and find the lowest distortion vector
    pIndex
,[0,3,4,2,1],[0,3,4,1,2],[0,2,3,1,4],[0,4,1,2,3],[0,4,3,1,2],[0,1,4,2,3]]
    for permute in pIndex:
        a = [atoms[i] for i in permute]
        p=[a0.coord] + [j.coord for j in a]
        s = spaceMatching.displacementVectorSP(p)
        if s < best[0]:
            change = 'yes'
            best = ( }\textrm{s},\textrm{a},\mathrm{ change }
    return best
```

$=[[1,2,0,3,4],[1,2,0,4,3],[1,3,0,4,2],[0,1,2,4,3],[0,4,2,3,1],[0,2,1,3,4],[0,2,3,4,1],[0,3,1,4,2]$
files $=$ sys.argv[1:]
metals = [ 'Fe','Co','Sc','Ti','V','Cr','Mn','Ni','Cu','Zn']
for $m$ in pdbReader.pdbMoleculesIter(files):
for metal, atoms in filter_lists_iter(m, metals, $5, ~ ' \mathrm{~N} ', 3$ ):
mlist $=[] \quad$ \#create $\overline{\text { a }}$ list that store chemically reasonable numbering
mlistN $=[] \quad$ \#to store three nitrogen
mlistX $=[] \quad$ \#to store two halogen atoms or two carbon atoms
\#to put three nitrogen atoms in one list and the other two halogen or carbon atoms in another list
for i in atoms:
if i.element in ["Cl","Br","I","C"]:
mlistX.append(i)
elif i.element in ["N"]:
mlistN.append(i)
angleX $=$ angle(metal.coord,mlistX[0].coord, mlistX[1].coord) \#to calculate the angle betwee two metal halogen bonds or metal carbon bonds
\#to calculate three NMN angles and assign the trans nitrogen in positions 1 and 5 in the atoms list and put halgon atomd of smaller NMX in position 3
angle12 $=$ angle(metal.coord, mlistN[0].coord, mlistN[1].coord)
angle13 $=$ angle(metal.coord, mlistN[0].coord, mlistN[2].coord)
angle23 $=$ angle(metal.coord, mlistN[1].coord, mlistN[2].coord)
angleMax $=\max ($ angle12, angle13, angle23 $)$
if angleMax $==$ angle12:
if angle(metal.coord, mlistX[0].coord, mlistN[2].coord) $<$ angle(metal.coord, mlistX[1].coord, mlistN[2].coord):
$\operatorname{mlist}=[\operatorname{mlistN}[0], \mathrm{mlistN}[2]]+[\operatorname{mlistX}[0]]+[\operatorname{mlistX}[1]]+[\mathrm{mlistN}[1]]$
else:
$\operatorname{mlist}=[\operatorname{mlistN}[0], \operatorname{mlistN}[2]]+[\operatorname{mlistX}[1]]+[\operatorname{mlistX}[0]]+[\operatorname{mlistN}[1]]$
elif angleMax $==$ angle 13:
if angle(metal.coord, mlistX[0].coord, mlistN[1].coord) < angle(metal.coord, mlistX[1].coord, mlistN[1].coord):
$\operatorname{mlist}=[\operatorname{mlistN}[0], \operatorname{mlistN}[1]]+[\operatorname{mlistX}[0]]+[m \operatorname{listX}[1]]+[m \operatorname{listN}[2]]$
else:
$\operatorname{mlist}=[\operatorname{mlistN}[0], \operatorname{mlistN}[1]]+[\operatorname{mlistX}[1]]+[\operatorname{mlistX}[0]]+[\operatorname{mlistN}[2]]$
else:
if angle(metal.coord, mlistX[0].coord, mlistN[0].coord) < angle(metal.coord, mlistX[1].coord, mlistN[0].coord):
$\operatorname{mlist}=[\operatorname{mlistN}[1], \operatorname{mlistN}[0]]+[\operatorname{mlistX}[0]]+[\operatorname{mlistX}[1]]+[\operatorname{mlistN}[2]]$
else:

$$
\operatorname{mlist}=[\operatorname{mlistN}[1], \operatorname{mlistN}[0]]+[\operatorname{mlistX}[1]]+[\operatorname{mlistX}[0]]+[\operatorname{mlistN}[2]]
$$

\#calculate angle difference between two N(py)MX angles and genetatet the two angle criterion parameter of the complex
angle_difference $=($ angle $($ metal.coord, mlist[3].coord, mlist[1].coord $)-$ angle(metal.coord, mlist[2].coord,mlist[1].coord)) / radians(90)
\#assign the name to the complex
if angle_difference $<0.5$ :
angle_geom = "distorted TBP"
else:
angle_geom = "distorted SP"
\#calculate the vector that is perpendicular to the N3 plane defined by three nitrogens

\#calculate all the angles around metal centers
angle_12 $=$ degrees(angle(metal.coord, mlist[0].coord, mlist[1].coord) $)$
angle_13 $=\operatorname{degrees}($ angle(metal.coord, mlist[0].coord, mlist[2].coord) $)$
angle_14 $=$ degrees(angle(metal.coord, mlist[0].coord, mlist[3].coord))
angle_15 $=$ degrees(angle(metal.coord, mlist[0].coord, mlist[4].coord))
angle_23 $=$ degrees(angle(metal.coord, mlist[1].coord, mlist[2].coord) $)$
angle_24 $=$ degrees(angle(metal.coord, mlist[1].coord, mlist[3].coord))
angle_25 $=$ degrees(angle(metal.coord, mlist[1].coord, mlist[4].coord))
angle_34 $=$ degrees(angle(metal.coord, mlist[2].coord, mlist[3].coord))
angle_35 = degrees(angle(metal.coord, mlist[2].coord, mlist[4].coord))
angle_45 $=$ degrees(angle(metal.coord, mlist[3].coord, mlist[4].coord))
\#calculate the distance between metal and N3 plane
metal_dev $=$ mdis(vector(metal.coord,mlist[1].coord),norm_N)
atoms $=$ mlist
length_TBP, order_TBP, change_TBP = best_TBP(metal,atoms)
length_SP, order_SP, change_SP = best_SP(metal,atoms)
if length_TBP < length_SP:
final_geom = "distorted TBP"
final_permut $=$ order_TBP
final_length $=$ length_TBP
final_change $=$ change_TBP
elif length_TBP > length_SP:
final_geom = "distorted SP"
final_permut $=$ order_SP
final_length $=$ length_SP
final_change $=$ change_SP
else:
final_geom = "both are right"
final_permut $=$ TBP
final_length $=$ length_TBP
final_change $=$ change_TBP
print m.name, angle_12, angle_13, angle_14, angle_15, angle_23, angle_24, angle_25, angle_34, angle_35, angle_45, length_TBP, length_SP, final_geom, angle_difference, angle_geom, metal_dev
\#if angle XMX is larger than trans NMN, then two X atoms will be put in positions
1 and 5 in the atoms list if angleMax < angleX:
mlist2 $=[\mathrm{mlistX}[0]]+\operatorname{mlistN}+[\mathrm{mlistX}[1]]$
atoms $=$ mlist 2
print "two possible assignments",
lengthTBP, orderTBP, changeTBP $=$ best_TBP(metal, atoms)
lengthSP, orderSP, changeSP = best_SP(metal, atoms)
print "TBP:",lengthTBP,orderTBP,changeTBP
print "SP:",lengthSP,orderSP,changeSP

## Codes for file (molecule.Py):

```
# Author: Andrew Chalaturnyk
# Coded to work with python version 2.6.2
# molecule + atom classes + methods
import collections
coordT = collections.namedtuple('coordT','x y z')
class atomlist(list):
    def element_count(self, elements):
        if isinstance( elements, str):
            elements = [elements]
        return len([ i for i in self if i.element in elements ])
```

class atom(object):
def __init__( self,
a_id $=-1$,
label $=$ None,
element = 'H', $\operatorname{coord}=\operatorname{coordT}(0.0,0.0,0.0))$ :
self.a_id = a_id
self.coord = coord
self.element $=$ element
self.label = label
def __str__(self):
return '<<A' + self.a_id + ':' + self.element +'>>'
def __repr__(self):
return ( self.__str__() )
def __hash_(self):
return self.a_id
class molecule(dict):
def __init__(self, name = "unknown" ):

$$
\begin{aligned}
& \text { self.name }=\text { name } \\
& \text { self.connections }=\{ \}
\end{aligned}
$$

def __setitem__(self, key, value):
$\mathrm{al}=\operatorname{atomlist}()$
self.connections[key] = al
value.connections = al dict.__setitem_(self,key,value)
def element_iterator( self, elements ):
if isinstance( elements, str): elements $=$ [elements]
for e in self.itervalues():
if e.element in elements:
yield e

## Codes for file (pdbReader.Py):

```
import os
import os.path
from molecule import atom, molecule, coordT
# Author: Andrew Chalaturnyk
# Year: 2009
# Coded to work with python version 2.6.2
# Simple PDB file parser
SLICE_RNAME = slice(0,6)
SLICE_HEADER_CLASSIFICATION = slice(10,50)
SLICE_ATOM_SERRIAL = slice(6,11)
SLICE_ATOM_NAME = slice(12,16)
SLICE_ATOM_ALTLOC = slice(16,17)
SLICE_ATOM_RESNAME = slice(17,20)
SLICE_ATOM_CHAINID = slice (21,22)
SLICE_ATOM_RESSEQ = slice (22,26)
SLICE_ATOM_ICODE = slice (26,27)
SLICE_ATOM_X = slice(30,38)
SLICE_ATOM_Y = slice (38,46)
SLICE_ATOM_Z = slice (46,54)
SLICE_ATOM_OCC = slice(54,60)
SLICE_ATOM_TEMPF = slice(60,66)
```

```
SLICE_ATOM_ELEMENT= slice(76,78)
SLICE_ATOM_CHARGE = slice(78,80)
SLICE_CONNECT_ATOM = slice(6,11)
SLICE_CONNECT_A1 = slice(11,16)
SLICE_CONNECT_A2 = slice(16,21)
SLICE_CONNECT_A3 = slice(21,26)
SLICE_CONNECT_A4 = slice(26,31)
RNAME HEADER = 'HEADER'
RNAME_ATOM = ('ATOM','HETATM')
RNAME_CONNECT= 'CONECT'
RNAME_END = 'END'
```

def get_field( field, record, default = None ):
if field.start $>=$ len(record): return default
value $=$ record[field].strip()
if len(value) $==0$ : return default
return value
def connectAtoms(a1, a2):
if a2 not in a1.connections: a1.connections.append(a2)
if a1 not in a2.connections: a2.connections.append(a1)
class moleculeStateParser(object):
def __init__(self):
self.done $=$ False
self.molecule $=$ None
def processATOM(self, record):
aid $=$ get_field (SLICE_ATOM_SERIAL, record $)$
1 = get_field( SLICE_ATOM_NAME, record )
x = get_field(SLICE_ATOM_X, record)
y = get_field( SLICE_ATOM_Y, record )
$\mathrm{z}=$ get_field(SLICE_ATOM_Z, record)
e = get_field( SLICE_ATOM_ELEMENT, record )
$\mathrm{c}=\operatorname{coordT}($ float $(\mathrm{x})$, float( y$)$, float( z$)$ )
if $\mathrm{e}==$ None :
$\mathrm{i}=0$
while $\mathrm{i}<\operatorname{len}(\mathrm{l})$ and $1[\mathrm{i}]$. isalpha(): $\mathrm{i}+=1$
$\mathrm{e}=1[0: \mathrm{i}]$
$\mathrm{a}=\operatorname{atom}\left(\mathrm{a} \_\right.$id $=$aid,
label $=1$,
coord $=\mathrm{c}$,
element $=\mathrm{e}$

```
                )
        self.molecule[ aid ] = a
    def processCONNECTS(self, record):
        a0 = get_field( SLICE_CONNECT_ATOM, record )
        a1 = get_field( SLICE_CONNECT_A1, record )
        a2 = get_field( SLICE_CONNECT_A2, record )
        a3 = get_field( SLICE_CONNECT_A3, record )
    a4 = get_field( SLICE_CONNECT_A4, record )
    m = self.molecule
    a0 = m[a0]
    if a1!= None and a1 != '0' : connectAtoms(a0, m[a1])
    if a2!= None and a2 != '0' : connectAtoms(a0, m[a2])
    if a3!= None and a3!= '0' : connectAtoms(a0, m[a3])
    if a4!= None and a4!= '0' : connectAtoms(a0, m[a4])
    def processRECORD(self, record):
    h = get_field(SLICE_RNAME, record, None)
    h.upper()
    self.done = False
    if h == RNAME_HEADER:
        self.molecule = molecule(get_field(
                        SLICE_HEADER_CLASSIFICATION,
                record))
    elif h in RNAME_ATOM: self.processATOM(record)
    elif h == RNAME_CONNECT: self.processCONNECTS(record)
    elif h == RNAME_END: self.done = True
def pdf_from_file_gen( file, state ):
    with open(file) as f:
        for line in f:
            state.processRECORD(line)
            if state.done:
                yield state.molecule
def pdbMoleculesIter( files ):
    state = moleculeStateParser()
    if isinstance(files,str):
        files = [files]
    for f in files:
        m = pdf_from_file_gen(f, state)
        for molecule in m:
```

yield molecule

## Codes for file (spaceMatching.Py):

\#Codes for "spaceMatching" part
\#Author: Andrew Chalaturnyk and Di Zhu
\#Year: 2009
\#Coded to work with python version 2.6.2
\#Calculate the distortion vectors and the metal deviation fron N3 plane
from math import sqrt, acos, radians, sin, asin, degrees from itertools import imap
from operator import mul, sub, neg
def angle( $\mathrm{p} 0, \mathrm{p} 1, \mathrm{p} 2$ ):
""" Angle between vectors p0 -> p1 and p0 -> p2 """
$\mathrm{u}=\operatorname{vector}(\mathrm{p} 0, \mathrm{p} 1)$
$\mathrm{v}=\mathrm{vector}(\mathrm{p} 0, \mathrm{p} 2)$
return $\operatorname{acos}(\operatorname{dot}(u, v) /($ length(u)*length(v)))
def length(v):
""" Length of vector """
return $\operatorname{sqrt}(\operatorname{dot}(\mathrm{v}, \mathrm{v}))$
$\operatorname{def} \operatorname{dot}(\mathrm{v} 0, \mathrm{v} 1)$ :
""" dot product of two vectors """
return sum(imap(mul,v0,v1))
def vector(p0, p1):
""" Create vector from two points, represented as a tuple"""
return tuple([i for i in imap(sub,p1,p0)])
def $\operatorname{cross}(\mathrm{p} 0, \mathrm{p} 1, \mathrm{p} 2)$ :
"""generate the vectors"""
$\mathrm{u}=\operatorname{vector}(\mathrm{p} 0, \mathrm{p} 1)$
$\mathrm{v}=\mathrm{vector}(\mathrm{p} 0, \mathrm{p} 2)$
matrix $=()$
for i in range(len(u)): tList $=[]$
for j in range(len(v)):
tList.append(u[i] * v[j])
matrix $+=($ tList $)$,
product $=(($ matrix $[1][2]-$ matrix[2][1] $)$, (matrix[2][0] - matrix[0][2]), (matrix[0][1] - matrix[1][0]))
return product
def mdis(v1,v2):
$\mathrm{a} 1=\operatorname{dot}(\mathrm{v} 1, \mathrm{v} 2)$
$\mathrm{a} 2=$ length $(\mathrm{v} 2)$
if a2 ! $=0$ :
$\mathrm{p}=\mathrm{a} 1 / \mathrm{a} 2$
else:
$p=1000$
return $\operatorname{sqrt}(\mathrm{p} * \mathrm{p})$
def displacementVectorTBP ( p ):
""" Define the angles for ideal TBP"""
A_ideal $=74.0$
B_ideal $=97.9$
"""calculate the angle deviation of your molecule"""
$\mathrm{d} 12=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[2])-\operatorname{radians}(\mathrm{A}$ ideal)
$\mathrm{d} 13=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[3])-\operatorname{radians}(\mathrm{B}$ _ideal)
$\mathrm{d} 14=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[4])-\operatorname{radians}(\mathrm{B}$ _ideal)
$\mathrm{d} 15=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[5])-\operatorname{radians}(2 *$ A_ideal $)$
$\mathrm{d} 23=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[2], \mathrm{p}[3])-\operatorname{radians}(120)$
$\mathrm{d} 24=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[2], \mathrm{p}[4])-\operatorname{radians}(120)$
$\mathrm{d} 25=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[2], \mathrm{p}[5])-$ radians(A_ideal)
$\mathrm{d} 34=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[3], \mathrm{p}[4])-\operatorname{radians}(120)$
$\mathrm{d} 35=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[3], \mathrm{p}[5])-\operatorname{radians}(\mathrm{B}$ _ideal $)$
$\mathrm{d} 45=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[4], \mathrm{p}[5])-\operatorname{radians}\left(\mathrm{B}_{-}\right.$ideal $)$
"""Get trigonal bipyramidal displacement vector given 7 co-ordinates"""
s4 $=\operatorname{sub}(\operatorname{sum}([d 12, d 13, d 14])$,sum([d25,d35,d45])) $/ \operatorname{sqrt}(6)$
$\mathrm{s} 6 \mathrm{a}=(2 * \mathrm{~d} 24-\mathrm{d} 34-\mathrm{d} 23) / \operatorname{sqrt}(6)$
$\mathrm{s} 6 \mathrm{~b}=(\mathrm{d} 34-\mathrm{d} 23) / \operatorname{sqrt}(2)$
$\mathrm{s} 7 \mathrm{a}=(2 * \mathrm{~d} 13-\mathrm{d} 12-\mathrm{d} 14+2 * \mathrm{~d} 35-\mathrm{d} 25-\mathrm{d} 45) / \operatorname{sqrt}(12)$
$\mathrm{s} 7 \mathrm{~b}=(\mathrm{d} 12-\mathrm{d} 14+\mathrm{d} 25-\mathrm{d} 45) / 2$

```
    \(\mathrm{s} 8 \mathrm{a}=(2 * \mathrm{~d} 13-\mathrm{d} 12-\mathrm{d} 14-2 * \mathrm{~d} 35+\mathrm{d} 25+\mathrm{d} 45) / \operatorname{sqrt}(12)\)
    \(\mathrm{s} 8 \mathrm{~b}=(\mathrm{d} 12-\mathrm{d} 14-\mathrm{d} 25+\mathrm{d} 45) / 2\)
```

    """calculate the distorsion vector"""
    return length((s4,s6a,s6b,s7a,s7b,s8a,s8b))
    def displacementVectorSP(p):
"""define the angles for ideal square pyramid"""
A_ideal $=74.0$
B_ideal $=90$
C_ideal $=180$
"""calculate the angle deviation of your molecule"""
$\mathrm{d} 12=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[2])-\operatorname{radians}(\mathrm{A}$ ideal)
$\mathrm{d} 13=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[3])-\operatorname{radians}(\mathrm{B}$ _ideal)
$\mathrm{d} 14=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[4])-\operatorname{radians}(180-\mathrm{A}$ ideal $)$
$\mathrm{d} 15=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[1], \mathrm{p}[5])-\operatorname{radians}(2 *$ A_ideal $)$
$\mathrm{d} 23=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[2], \mathrm{p}[3])-\operatorname{radians}(\mathrm{B}$ ideal $)$
$\mathrm{d} 24=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[2], \mathrm{p}[4])-\operatorname{radians}(\mathrm{C}$ ideal $)$
$\mathrm{d} 25=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[2], \mathrm{p}[5])-\operatorname{radians}(\mathrm{A}$ _ideal)
$\mathrm{d} 34=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[3], \mathrm{p}[4])-\operatorname{radians}(\mathrm{B}$ _ideal)
$\mathrm{d} 35=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[3], \mathrm{p}[5])-\operatorname{radians}\left(\mathrm{B}_{-}\right.$ideal $)$
$\mathrm{d} 45=\operatorname{angle}(\mathrm{p}[0], \mathrm{p}[4], \mathrm{p}[5])-\operatorname{radians}\left(180-\right.$ A_ideal $\left.^{2}\right)$
"""calculate the displacement value in each coordinate" ""
$\mathrm{s} 3=(\mathrm{d} 15+\mathrm{d} 24) / \operatorname{sqrt}(2)$
$\mathrm{s} 5=(\mathrm{d} 15-\mathrm{d} 24) / \operatorname{sqrt}(2)$
$\mathrm{s} 6=(\mathrm{d} 12+\mathrm{d} 45-\mathrm{d} 14-\mathrm{d} 25) / 2$
$\mathrm{s} 8 \mathrm{a}=(\mathrm{d} 13-\mathrm{d} 35) / \operatorname{sqrt}(2)$
$\mathrm{s} 8 \mathrm{~b}=(\mathrm{d} 34-\mathrm{d} 23) / \operatorname{sqrt}(2)$
s9a $=(\mathrm{d} 12-\mathrm{d} 45) / \operatorname{sqrt}(2)$
$\mathrm{s} 9 \mathrm{~b}=(\mathrm{d} 14-\mathrm{d} 25) / \operatorname{sqrt}(2)$
"""calculate the distorsion vector from ideal SP"""
return length((s3,s5,s6,s8a,s8b,s9a,s9b))

## Appendix B: for Chapter 5

Table B.1. Calculated-free energy differences for exchange of pyridine by TMEDA $(\mathrm{kcal} / \mathrm{mol})^{\mathrm{a}}$

| R: | Me | $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ |
| ---: | ---: | ---: |
| $(\mathrm{Py})_{2} \mathrm{CoR}_{2}+$ TMEDA $\rightarrow$ | -3.5 | -1.4 |
|  |  |  |
| (TMEDA)CoR $2+2$ Py |  |  |

${ }^{\text {a }}$ Electronic energies calculated using b3-lyp/TZVP; ZPE, enthalpy and entropy corrections for $298 \mathrm{~K}, 1 \mathrm{bar}$, gas phase, taken from $\mathrm{SV}(\mathrm{P})$ calculations.

Table B.2. Observed (X-ray) and calculated average bond lengths ( $\AA$ ) for (TMEDA) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$

|  | $\mathbf{C o}-\mathbf{N}$ | $\mathbf{C o}-\mathbf{C H}_{\mathbf{2}}$ | $\mathbf{C H}_{2}$-Si | $\mathbf{S i - M e}$ | $\mathbf{N}-\mathbf{M e}$ | $\mathbf{N - C H}$ | $\mathbf{C H}_{\mathbf{2}}-\mathbf{C H}_{\mathbf{2}}$ |
| :---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| X-ray | 2.1827 | 2.0339 | 1.8326 | 1.8699 | 1.4717 | 1.4782 | 1.4833 |
| bp86/SV(P) | 2.2180 | 2.0254 | 1.8827 | 1.9142 | 1.4730 | 1.4800 | 1.5317 |
| bp86/TZVP | 2.2119 | 2.0337 | 1.8844 | 1.9137 | 1.4782 | 1.4850 | 1.5263 |
| b3-lyp/SV(P) | 2.2664 | 2.0576 | 1.8747 | 1.9092 | 1.4698 | 1.4756 | 1.5302 |
| b3-lyp/TZVP | 2.2687 | 2.0632 | 1.8766 | 1.9091 | 1.4744 | 1.4796 | 1.5253 |

Table B.3. Observed (X-ray) and calculated average bond lengths ( $\AA$ ) and angles (deg) for $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}\left(\mathrm{R}^{\prime}=\mathrm{CH}_{2} \mathrm{CMe}_{2} \mathrm{Ph}\right)$.

|  | Co-N |  | Co-C |  | N-Co-N | C-Co-C |
| :---: | :---: | :---: | :---: | :---: | ---: | ---: |
| X-ray | 2.108 | 2.118 | 2.076 | 2.067 | 96.21 | 127.32 |
| bp86/SV(P) | 2.020 | 2.032 | 2.020 | 2.021 | 99.73 | 120.27 |
| bp86/TZVP | 2.032 | 2.040 | 2.034 | 2.035 | 99.99 | 121.13 |
| b3-lyp/SV(P) | 2.163 | 2.161 | 2.060 | 2.062 | 97.12 | 125.32 |
| b3-lyp/TZVP | 2.177 | 2.169 | 2.072 | 2.073 | 97.58 | 126.48 |

Table B.4. Paramagnetic ${ }^{1} \mathrm{H}$ NMR shifts for Co complexes calculated at BP86 ${ }^{\text {a }}$

| System | H | Aiso (MHz) | $\delta_{\text {orb }}(\mathrm{ppm})^{\text {a }}$ | $\delta_{\text {pred }}(\mathrm{ppm})$ | $\delta_{\text {obs }}(\mathrm{ppm})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $(\mathrm{Py})_{2} \mathrm{CoR}_{2}$ | Py H2 | 1.198 | 8.379 | 166.1 | 114 |
|  | Py H3 | 0.477 | 7.023 | 69.9 | 38.4 |
|  | Py H4 | -0.422 | 7.173 | -48.3 | -8.5 |
|  | $\mathrm{CoCH}_{2}$ | 3.940 | 1.212 | 520.0 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.085 | -0.293 | 10.9 | 10.3 |
| (TMEDA) $\mathrm{CoR}_{2}$ | $\mathrm{NCH}_{2}$ | 0.710 | 2.624 | 96.1 | 80 |
|  | $\mathrm{NMe}_{2}$ | 0.888 | 2.365 | 119.3 | 78 |
|  | $\mathrm{CoCH}_{2}$ | 3.423 | 1.177 | 451.9 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.100 | -0.109 | 13.0 | 9.6 |
| $(\mathrm{Py})_{2} \mathrm{CoR}^{\prime}{ }_{2}$ | Py H2 | 1.136 | 7.951 | 157.6 | 108 |
|  | Py H3 | 0.473 | 11.673 | 73.9 | 32.7 |
|  | Py H4 | -0.507 | 6.931 | -59.8 | -8.3 |
|  | $\mathrm{CoCH}_{2}$ | 4.665 | 2.982 | 617.3 | n.o. |
|  | $\mathrm{CMe}_{2}$ | 0.002 | 1.113 | 1.3 | 21.6 |
|  | Ph Ho | -0.037 | 7.455 | 2.6 | 10.2 |


| System | $\mathbf{H}$ | Aiso $(\mathbf{M H z})$ | $\boldsymbol{\delta}_{\text {orb }}(\mathbf{p p m})^{\mathbf{a}}$ | $\boldsymbol{\delta}_{\text {pred }}(\mathbf{p p m})$ | $\boldsymbol{\delta}_{\text {obs }}(\mathbf{p p m})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Ph Hm | 0.034 | 7.111 | 11.6 | 7.4 |
|  |  |  |  |  |  |
|  | Ph Hp | -0.085 | 6.981 | 138.7 | 3.9 |

${ }^{\text {a }}$ Geometry was optimized at b-p86/TZVP. R: $-\mathrm{CH}_{2} \mathrm{SiMe}_{3} ; \mathrm{R}$ ':- $\mathrm{CH}_{2} \mathrm{C}\left(\mathrm{Me}_{2}\right) \mathrm{Ph}$


Figure B.1. Comparison of calculated (BP86: $\delta^{\text {orb }}+\delta^{\mathrm{FC}}$ only) and observed ${ }^{1} \mathrm{H}$ chemical shifts (correlation coefficient: 0.818). (The solid line represents the ideal $\delta_{\text {obs }}=\delta_{\text {calc }}$ relation).

## Appendix C: for Chapter 6

## Spin-cross reactions using DFT computation

Spin-cross reactions refer to the reaction where the reactant and the product have different spin states. It normally involves at least two potential-energy surfaces. Take conversion of a singlet reactant to a triplet product as an example (Figure C.1). The singlet potential-energy surface will cross with triplet-energy surface. At the crossing point, the spin flips.


Figure C.1. Potential-energy surfaces of singlet state (red line) and triplet state (blue line).* denotes the crossing point of these two potential-energy surfaces.

## Locating the spin-cross points

Considering the three-dimension potential-energy surface, the cross points can be the joint line between two surfaces. Thus the cross point must be the lowest point in this line.

There are several ways to locate this point. One is partial optimization. In this approach, one geometrical coordinate will be followed to build the potential-energy surface and at each point, the coordinate will be fixed and the geometry will be partially optimized at both spin states separately to generate two potential-energy profiles. If the coordinate chosen is good enough, the two profiles will cross. However, this approach requires a lot of geometry optimization on both PES. Thus it can be quite expensive.

Another quite accurate way is called minimum-energy crossing point (MECP) which performs in quite a similar way to the geometry minimization by minimizing the gradient. However, the gradient to be minimized depends on two potential-energy surfaces rather than single potential-energy surface. The generation of gradient can be computed according to following equation: ${ }^{198}$

$$
\mathrm{g}=\alpha\left(\mathrm{V}_{1}-\mathrm{V}_{2}\right)\left(\mathrm{g}_{1}-\mathrm{g}_{2}\right)+\mathrm{g}_{1}-\mathrm{h}\left(\mathrm{~g}_{1} \cdot \mathrm{~h}\right)
$$

where,

- $\alpha$ is an arbitrary constant
- $\mathrm{V}_{1}$ and $\mathrm{V}_{2}$ are potentials on the two PES
- $g_{1}$ and $g_{2}$ are corresponding gradients on the two PES
- $h$ is a unit vector parallel to $\left(g_{1}-g_{2}\right)$

The cross point located by MECP is considered to be more accurate than other approaches and at less calculation cost. Thus this method is done in current research in this thesis.


Figure C.2. Thermal ellipsoid plot for 2,6-[(HO) $\left.)_{2} \mathrm{C}\left(\mathrm{CF}_{3}\right)\right]_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}$ (30\% probability, hydrogens and THF of crystallization omitted for clarity) (this work was done by Peter Budzelaar)

Table C.1. Equilibrium between (TMEDA) $\mathrm{CoR}_{2}$ and (6) $\mathrm{CoR}_{2}\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$ as determined by ${ }^{1} \mathrm{H}^{\mathrm{NMR}}{ }^{\mathrm{a}}$

| [TMEDA] | [(TMEDA)CoR $\mathbf{2}$ ] | [6] | [(6)CoR $\mathbf{2}$ ] | $\boldsymbol{K}$ |
| ---: | ---: | ---: | ---: | ---: |
| 0.27 | 0.18 | 0.34 | 0.21 | 0.91 |
| 0.08 | 0.21 | 0.19 | 0.51 | 1.00 |
| 0.10 | 0.12 | 0.35 | 0.43 | 1.01 |
| 0.08 | 0.06 | 0.52 | 0.33 | 0.81 |
|  |  |  | average: | 0.93 |
|  |  |  | error (1 $\sigma$ ): | 0.09 |

${ }^{\mathrm{a}}$ Relative concentrations from integrals.

Table C.2. Free energies ( $\mathrm{kcal} / \mathrm{mol}$ ) of equilibrium between (TMEDA) $\mathrm{CoR}_{2}$ and (6) $\mathrm{CoR}_{2}$ or (1)CoR ${ }_{2}$ predicted by DFT using b3-lyp and $b-p^{a}$

| Reactions | b3-lyp | b-p86 |
| :---: | :---: | :---: |
| (TMEDA) $\mathrm{CoMe}_{2}+\mathbf{6} \rightarrow$ <br> (6) $\mathrm{CoMe}_{2}+$ TMEDA | -1.4 | -18.6 |
| (TMEDA)Co $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}+\mathbf{6} \rightarrow$ <br> (6) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}+$ <br> TMEDA | +2.8 | -13.0 |
| (TMEDA) $\mathrm{CoMe}_{2}+\mathbf{1} \rightarrow$ <br> (1) $\mathrm{CoMe}_{2}+$ TMEDA | +7.0 | -29.5 |
| (TMEDA)Co $\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}+\mathbf{1} \rightarrow$ <br> (1) $\mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}+$ <br> TMEDA | +12.7 | -14.6 |

[^25]Table C.3. Paramagnetic ${ }^{1} \mathrm{H}$ NMR shifts for Co complexes $\left(\mathrm{R}=\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)$ calculated at BP86

| System | H | Aiso (MHz) | $\delta_{\text {orb }}(\mathrm{ppm})^{\text {a }}$ | $\delta_{\text {pred }}(\mathrm{ppm})$ | $\delta_{\text {obs }}(\mathrm{ppm})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (6) $\mathrm{CoR}_{2}$ | Py H3 | 0.223 | 8.423 | 37.83 | 44.4 |
| $\left(\mathrm{HS}^{\kappa^{2 *}}\right)$ | Py H4 | -2.633 | 7.580 | -339.13 | -66.5 |
|  | OCH2 | 0.380 | 4.242 | 54.34 | -5.6 |
|  | $\mathrm{NCMe}_{2}$ | 0.083 | 1.317 | 12.29 | -16.9 |
|  | $\mathrm{CoCH}_{2}$ | 4.146 | 1.177 | 547.13 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.044 | -0.109 | 5.72 | 21.8 |
| (6) $\mathrm{CoR}_{2}$ | Py H3 | 3.047 | 8.423 | 409.67 | 44.4 |
| $\left(\mathrm{LS}^{3}\right)$ | Py H4 | 1.438 | 7.580 | 196.87 | -66.5 |
|  | OCH2 | -0.250 | 4.242 | -28.66 | -5.6 |
|  | $\mathrm{NCMe}_{2}$ | -0.015 | 1.317 | -0.72 | -16.9 |
|  | $\mathrm{CoCH}_{2}$ | 8.614 | 1.177 | 1135.41 | n.o. |
|  | $\mathrm{SiMe}_{3}$ | 0.030 | -0.109 | 3.78 | 21.8 |

[^26]Table C.4. Relative electronic and free energies for all cobalt complexes in Figure $6.12(\mathrm{kcal} / \mathrm{mol} ; 298 \mathrm{~K}, 1 \mathrm{bar}$, gas phase) $(\mathrm{R}=$ $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ )

| Species |  | Sz | b3-lyp |  |  |  | ri-b-p |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\Delta E_{\text {rel }}(\mathrm{SVP})$ | $\Delta G_{\text {rel }}(\mathrm{SVP})$ | $\Delta E_{\text {rel }}(\mathbf{T Z V P})$ | $\Delta G_{\text {est }}(\text { TZVP })^{\text {d }}$ | $\Delta E_{\text {rel }}(\mathrm{SVP})$ | $\Delta G_{\text {rel }}(\mathbf{S V P})$ | $\Delta E_{\text {rel }}(\mathrm{TZVP})$ | $\Delta G_{\text {rel }}(\mathbf{T Z V P})$ |
| (1) $\mathrm{CoMe}_{2}$ | $\kappa^{2}$ | $3 / 2$ | 4.53 | 1.59 | 3.08 | 0.15 | 25.17 | 22.33 | 23.95 | 22.40 |
|  | $\kappa^{2}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 5.08 | a | 4.26 | a | 25.13 | a | 24.06 | a |
|  | $\kappa^{2}$ | $1 / 2$ | 4.04 | 1.64 | 3.47 | 1.08 | b | b | b | b |
|  | $\kappa^{3}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 6.17 | a | 5.79 | a | c | c | c | c |
|  | $\kappa^{3}$ | $1 / 2$ | (0) | (0) | (0) | (0) | (0) | (0) | (0) | (0) |
| (1) CoMe | $\kappa^{3}$ | 0 | 25.58 | 10.64 | 22.03 | 7.09 | 34.31 | 19.25 | 30.66 | 17.23 |
| (1) $\mathrm{CoR}_{2}$ | $\kappa^{2}$ | $3 / 2$ | (0) | (0) | (0) | (0) | 16.16 | 13.35 | 15.46 | 12.86 |
|  | $\kappa^{2}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 1.32 | a | 2.32 | a | 16.29 | a | 15.78 | a |
|  | $\kappa^{2}$ | $1 / 2$ | 1.09 | 3.92 | 2.18 | 5.02 | b | b | b | b |
|  | $\kappa^{3}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 5.91 | a | 6.95 | a | c | c | c | c |
|  | $\kappa^{3}$ | $1 / 2$ | 3.81 | 9.24 | 5.07 | 10.51 | (0) | (0) | (0) | (0) |
| (1) CoR | $\kappa^{3}$ | 0 | 17.43 | 5.43 | 14.38 | 2.38 | 22.17 | 7.69 | 17.75 | 4.27 |
| (6) $\mathrm{CoMe}_{2}$ | $\kappa^{2}$ | 3/2 | (0) | 0.45 | 0.23 | 0.89 | 10.79 | 7.79 | 10.10 | 7.02 |
|  | $\kappa^{2^{*}}$ | $3 / 2$ | 0.20 | (0) | (0) | (0) | 11.19 | 8.15 | 10.29 | 7.05 |
|  | $\kappa^{2^{*}}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 2.50 | a | 3.35 | a | 11.80 | a | 11.23 | a |
|  | $\kappa^{2 *}$ | $1 / 2$ | 2.31 | 4.60 | 3.09 | 5.58 | 7.10 | 5.12 | 5.57 | 4.02 |
|  | $\kappa^{2}$ | $3 / 2 \leftrightarrow 41 / 2$ | 1.76 | a | 2.86 | a | c | c | c | c |


| Species |  | Sz | b3-lyp |  |  |  | ri-b-p |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\Delta E_{\text {rel }}(\mathbf{S V P})$ | $\Delta G_{\text {rel }}(\mathbf{S V P})$ | $\Delta E_{\text {rel }}(\mathbf{T Z V P})$ | $\Delta G_{\text {est }}(\mathbf{T Z V P})^{\text {d }}$ | $\Delta E_{\text {rel }}(\mathrm{SVP})$ | $\Delta G_{\text {rel }}(\mathrm{SVP})$ | $\Delta E_{\text {rel }}($ TZVP $)$ | $\Delta G_{\text {rel }}(\mathrm{TZVP})$ |
|  | $\kappa^{2}$ | 1/2 | 1.37 | 3.41 | 2.52 | 4.76 | b | b | b | b |
|  | $\kappa^{3}$ | $3 / 2 \leftrightarrow^{1 / 2}$ | 4.15 | a | 5.72 | a | 11.30 | a | 10.96 | a |
|  | $\kappa^{3}$ | $1 / 2$ | 6.32 | 10.54 | 7.43 | 11.85 | (0) | (0) | (0) | (0) |
| (6) CoMe | $\kappa^{3}$ | 0 | 28.83 | 20.98 | 26.92 | 19.27 | 28.15 | 15.34 | 24.59 | 12.38 |
| (6) $\mathrm{CoR}_{2}$ | $\kappa^{2}$ | $3 / 2$ | 2.28 | 1.34 | 2.06 | 1.12 | 8.39 | 5.85 | 7.26 | 4.17 |
|  | $\kappa^{2 *}$ | $3 / 2$ | (0) | (0) | (0) | (0) | 7.09 | 4.05 | 6.21 | 2.39 |
|  | $\kappa^{2 *}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 7.70 | a | 8.98 | a | 9.89 | a | 9.22 | a |
|  | $\kappa^{2^{*}}$ | 1/2 | 7.09 | 5.62 | 8.18 | 6.71 | 4.68 | 1.99 | 2.99 | 0.08 |
|  | $\kappa^{2}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 7.66 | a | 8.84 | a | c | c | c | c |
|  | $\kappa^{2}$ | $1 / 2$ | 7.65 | 5.96 | 8.74 | 7.04 | 7.57 | 3.75 | b | b |
|  | $\kappa^{3}$ | $3 / 2 \leftrightarrow{ }^{1 / 2}$ | 14.97 | a | 15.96 | a | 10.24 | a | 9.54 | a |
|  | $\kappa^{3}$ | 1/2 | 11.42 | 14.77 | 13.16 | 16.50 | (0) | (0) | (0) | (0) |
| (6) CoR | $\kappa^{3}$ | 0 | 32.34 | 16.15 | 29.24 | 13.04 | 25.10 | 9.94 | 20.65 | 5.63 |

${ }^{a}$ Free energy not evaluated at minimum-energy crossing points. ${ }^{b}$ Not a local minimum. ${ }^{\text {c }}$ No crossing point located. ${ }^{\text {d }} G_{\text {est }}(\mathrm{TZVP})=$ $E(\mathrm{TZVP})+G(\mathrm{SV}(\mathrm{P}))-E(\mathrm{SV}(\mathrm{P}))$.

(1) $\mathrm{CoR}_{2} \mathrm{HS} \mathrm{K}^{2}$

(1) $\mathrm{CoR}_{2}$ MECP $\kappa^{2}$

(1) $\mathrm{CoR}_{2} \mathrm{LS} \mathrm{K}^{2}$

(1) CoR, $\mathrm{LS} \mathrm{K}^{3}$

(1) CoR LS $\kappa^{3}$

Figure C.3. Structures along the profile for $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ loss from $(\mathbf{1}) \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in Figure 6.12

(6) $\mathrm{CoR}_{2} \mathrm{HS}^{2}{ }^{2+}$

(6) $\mathrm{CoR}_{2} \mathrm{LS} \mathrm{K}^{2}$

(6) $\mathrm{CoR}_{2}$ cross $\kappa^{2}$

(6) $\mathrm{CoR}_{2} \mathrm{LS}^{3}$

(6) $\mathrm{CoR}_{2} \mathrm{LS}^{\kappa^{2 *}}$

(6) CoR LS $\kappa^{3}$

Figure C.4. Structures along the profile for R loss from $(\mathbf{6}) \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in Figure 6.12

## Appendix D: for Chapter 7



Figure D.1. Si-H HMBC for the hydrolysis of the mixture from the reaction of (1) $\mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$ with MeI


Figure D.2. ${ }^{1} \mathrm{H}$ NMR spectrum of the reaction between (1) $\mathrm{Co}\left(\mathrm{N}_{2}\right)$ and $\mathrm{C}_{6} \mathrm{~F}_{13} \mathrm{CH}=\mathrm{CH}_{2}$


Figure D.3. IR spectrum of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ prepared by hydrogenolysis of $(\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{SiMe}_{3}$


Figure D.4. ${ }^{1} \mathrm{H}$ NMR spectrum of $(\mathbf{1}) \mathrm{CoC}(\mathrm{Ph})=\mathrm{C}(\mathrm{H}) \mathrm{CCPh}$


Figure D.5. ${ }^{1} \mathrm{H}$ NMR spectrum for the reaction of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with 0.5 eq . allyl chloride


Figure D.6. ${ }^{1} \mathrm{H}$ NMR spectrum for the reaction of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ with 0.5 eq. cyclopropylmethyl chloride

Table D.1. ${ }^{1} \mathrm{H}$ NMR assignments for all (1)Co complexes relevant to Table 7.2. ( $\delta$ in ppm, J in Hz)

| Complex | $\begin{gathered} \hline \text { Py } H 4 \\ (\mathbf{t}, 1 H) \\ \delta, J \end{gathered}$ | Py, H3 <br> (d, 2H) <br> $\delta, J$ | $\begin{gathered} \mathrm{Ar} \mathrm{o-} \\ \mathrm{CH} \\ (\mathrm{~s}, 12 \mathrm{H}) \\ \delta \end{gathered}$ | $\begin{gathered} \mathrm{N}=\mathrm{CCH}_{3} \\ (\mathrm{~s}, 6 \mathrm{H}) \\ \delta \end{gathered}$ | $\begin{gathered} \text { CoAr o-H } \\ (\approx \mathrm{d}, 2 \mathrm{H}) \\ \delta, J \end{gathered}$ | Additional assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{5}$ | 10.36, 7.6 | 7.56, 7.6 | 2.05 | -1.07 | 4.74 |  |
| $\begin{aligned} & (\mathbf{1}) \mathrm{CoCH}_{2} \mathrm{CMe}_{2}\left(\mathrm{C}_{6} \mathrm{H}_{3}-3,5-\right. \\ & \left.t \mathrm{Bu}_{2}\right)^{\mathrm{b}} \end{aligned}$ | 10.83, 7.5 | 7.83, 7.5 | 1.96 | -1.93 |  | 0.53 (s, 6H, CMe2) |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{COMe}$ | 10.26, 7.4 | a | 2.00 | -0.95 | 4.92, 7.3 |  |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4$-COOMe | 10.26, 7.4 | a | 1.98 | -0.96 | 4.91, 7.5 | 3.34 (s, 3H, $\mathrm{COOCH}_{3}$ ) |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{CF}_{3}$ | 10.26, 7.4 | 7.36, 7.4 | 1.95 | -0.95 | 4.83, 7.3 | $\begin{aligned} & { }^{19} \text { F NMR: } \\ & -61.3(\mathrm{~s}) \end{aligned}$ |
| $\overline{(1)} \mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{F}$ | 10.32, 7.5 | 7.46, 7.5 | 1.97 | -1.05 | $\begin{gathered} 4.62(t) \\ J_{\mathrm{HF}} \approx J_{\mathrm{HH}} \approx 6.8 \end{gathered}$ | $\begin{aligned} & { }^{19} \text { F NMR: } \\ & -124.9(\mathrm{~s}) \end{aligned}$ |
| $\overline{(1) \mathrm{CoC}_{6} \mathrm{H}_{3}-3,5-(\mathrm{OMe})_{2}}$ | 10.32, 7.4 | 7.52, 7.4 | 2.05 | -1.05 | 3.90 | $\begin{gathered} 5.80(\mathrm{~s}, 1 \mathrm{H}, \operatorname{CoAr} H p) \\ 3.25\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{OCH}_{3}\right) \end{gathered}$ |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{Cl}$ | 10.29, 7.3 | 7.42, 7.3 | 1.96 | -1.01 | 4.65, 7.3 |  |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{Me}$ | 10.36, 7.4 | 7.57, 7.4 | 2.05 | -1.12 | 4.68, 6.9 |  |
| (1) $\mathrm{CoC}_{6} \mathrm{H}_{4}-4-\mathrm{OMe}$ | 10.35, 7.4 | 7.56, 7.4 | 2.02 | -1.12 | 4.69, 7.3 | $\begin{gathered} 3.20\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right) \\ 6.28(\mathrm{~d}, J 7.3,2 \mathrm{H}, \mathrm{CoAr} H m) \end{gathered}$ |
| (1)CoMe | 10.1 (br) | 7.88 (br) | 1.95 | -1.27 |  | 0.51 (s, 3H, $\mathrm{CoCH}_{3}$ ) |


| Complex | $\begin{gathered} \text { Py } H 4 \\ (t, 1 H) \\ \delta, J \end{gathered}$ | $\begin{gathered} \hline \text { Py, H3 } \\ (\mathrm{d}, 2 \mathrm{H}) \\ \delta, J \end{gathered}$ | $\begin{gathered} \mathrm{Aro-} \\ \mathrm{CH} \\ (\mathrm{~s}, 12 \mathrm{H}) \\ \delta \end{gathered}$ | $\begin{gathered} \mathrm{N}=\mathrm{CCH}_{3} \\ (\mathrm{~s}, \mathbf{6 H}) \\ \delta \end{gathered}$ | $\begin{gathered} \text { CoAr } o-\mathrm{H} \\ (\approx \mathrm{~d}, 2 \mathrm{H}) \\ \delta, J \end{gathered}$ | Additional assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (1) $\mathrm{Co}-n-\mathrm{C}_{4} \mathrm{H}_{9}$ | 10.23 (br) | 8.04 (br) | 2.01 | -1.60 |  |  |
| (1)Co-n-C6 $\mathrm{H}_{13}$ | 10.23 (br d) | $\begin{aligned} & \text { 8.05, (br } \\ & \text { d) } \end{aligned}$ | 2.01 | -1.60 |  |  |
| (1) $\mathrm{CoCH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}$ | 10.40, 7.4 | 7.72, 7.4 | 1.91 | -1.53 |  | $\begin{aligned} & 5.81(\mathrm{~d}, J 7.3,2 \mathrm{H}, \mathrm{Bz} H o) \\ & 6.56(\mathrm{t}, J 7.0,2 \mathrm{H}, \mathrm{Bz} \mathrm{Hm}) \end{aligned}$ |
| 2-(1)Co-6-Cl-C5 $\mathrm{H}_{3} \mathrm{~N}$ | 10.11, 7.5 | 7.45, 7.5 | 2.06 | -0.85 | $\begin{gathered} 5.55,6.9(\mathrm{CoPy} \\ H 3) \end{gathered}$ | $\begin{aligned} & 5.98(\mathrm{t}, J 7.3,1 \mathrm{H}, \text { CoPy } H 4) \\ & 6.09(\mathrm{~d}, J 7.5,1 \mathrm{H}, \text { CoPy } H 5) \end{aligned}$ |
| (1) $\mathrm{CoCH}_{2} \mathrm{CH}=\mathrm{CF}-n-\mathrm{C}_{5} \mathrm{~F}_{11}$ | 10.17, 7.5 | 7.39, 7.5 | 2.03 | -1.12 |  | $\begin{gathered} 4.66\left(\mathrm{dt}, J_{\mathrm{HF}} 35.7, J_{\mathrm{HH}} 10.0,1 \mathrm{H},\right. \\ \mathrm{CH}=\mathrm{CF}) \\ 1.55\left(\mathrm{~d}, J 10.0,2 \mathrm{H}, \mathrm{CoCH}_{2}\right) \\ { }^{19} \mathrm{~F} \text { NMR: }-148.6(1 \mathrm{~F}),-115.1(2 \mathrm{~F}) \end{gathered}$ |
| (1) $\mathrm{Co}\left(\eta^{3}\right.$-allyl) | 7.41, 7.7 | 7.84, 7.7 | 1.76 | 1.55 |  | $\begin{gathered} 5.15(\text { quintet, } J 10.2,1 \mathrm{H}, \\ \left.\mathrm{CH}_{2} \mathrm{CHCH}_{2}\right), \\ 2.43\left(\mathrm{br}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CHCH}_{2}\right. \end{gathered}$ |
| (1) $\operatorname{Co}\left(\eta^{3}\right.$-crotyl) | 7.40, 7.5 | 7.89, 7.5 | 1.82 | 1.57 |  | $5.18\left(\mathrm{tt}, J_{1} 11.2, J_{2} 9.2,1 \mathrm{H}\right.$, $\left.\left.\mathrm{CH}_{2} \mathrm{C} H\right)\right), 2.48\left(\mathrm{qq}, J_{1} 11.2, J_{2} 6.5\right.$, $1 \mathrm{H}, \mathrm{CH} 3 \mathrm{CH}), 1.82\left(2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}\right)$, $1.24\left(\mathrm{~d}, J 6.5,3 \mathrm{H}, \mathrm{CH} \mathrm{H}_{3} \mathrm{CH}\right)$ |
| (1) CoF | 9.18, 7.4 | 7.05, 7.4 | 2.14 | 0.04 |  | ${ }^{19}$ F NMR: -256 (br) |
| (1) CoCl | 9.49, 7.7 | 6.90, 7.7 | 2.15 | -0.09 |  |  |


| Complex | $\begin{gathered} \text { Py } H 4 \\ (\mathbf{t}, 1 \mathrm{H}) \\ \delta, J \end{gathered}$ | $\begin{gathered} \hline \mathbf{P y}, H 3 \\ (\mathbf{d}, 2 \mathrm{H}) \\ \delta, J \end{gathered}$ | $\begin{gathered} \mathrm{Aro-} \\ \mathrm{CH} \\ (\mathrm{~s}, 12 \mathrm{H}) \\ \delta \end{gathered}$ | $\begin{gathered} \mathrm{N}=\mathrm{CCH}_{3} \\ (\mathrm{~s}, 6 \mathrm{H}) \\ \delta \end{gathered}$ | $\begin{gathered} \text { CoAr } o-\mathrm{H} \\ (\approx \mathrm{~d}, 2 \mathrm{H}) \\ \delta, J \end{gathered}$ | Additional assignments |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (1) CoBr | 9.72 (br t) | $6.86 \text { (br }$ <br> d) | 2.17 | -0.27 |  |  |
| (1) CoI | 10.06 (br t) | a | 2.18 | -0.58 |  |  |

${ }^{\text {a }}$ Resonance could not be assigned. ${ }^{\text {b }}$ the correction to the original published results


Figure D.7. ${ }^{1} \mathrm{H}$ NMR spectrum of liquid part from reaction of (1) $\mathrm{Co}(\mathrm{Py}-6-\mathrm{Cl})$ and (1) CoCl with 0.5 eq. BzBr


Figure D.8. ${ }^{1} \mathrm{H}$ NMR spectrum of solid part in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ from reaction of $(\mathbf{1}) \mathrm{Co}(\mathrm{Py}-6-\mathrm{Cl})$ and (1) CoCl with 0.5 eq. BzBr

## Supporting Information

| Name of compound | Name of the CIF file |
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| CIF files for X-ray structures in Section 9.1 |  |
| Ligand 8 in Chapter 3 | zd03 |
| (3) $\mathrm{CoCl}_{2}$ in Chapter 3 | zd01 |
| (7) $\mathrm{CoCl}_{2}$ in Chapter 3 | budz06 |
| (10) $\mathrm{CoCl}_{2}$ in Chapter 3 | phc0m |
| (7) $\mathrm{FeCl}_{2}$ in Chapter 3 | budz05 |
| (10) $\mathrm{FeCl}_{2}$ in Chapter 3 | zd05 |
| (8) $\mathrm{FeCl}_{2}$ in Chapter 3 | ddi60 |
| (9) $\mathrm{FeCl}_{2}$ in Chapter 3 | fesi0m |
| (Pybox) $\mathrm{Fe}^{2}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ in Chapter 3 | zd10 |
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Crystals suitable for X-ray structure determination
were obtained from toluene.
A crystal of approximate dimensions 0.3 x 0.3 x 0.2 mm was
mounted on top of a thin glass fiber using epoxy glue.
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Data were collected on a Bruker four-circle diffractometer
with APEX detector, and were corrected for absorption using
SADABS (Sheldrick, 1996). The structure was solved using
direct methods with the SHELXS package (Sheldrick, 1997),
and refined using SHELXL (Sheldrick, 1997).
One molecule of toluene was found
to be disordered over an inversion center. It was
refined as a rigid hexagon with the methyl carbon
placed at a fixed distance of 1.50 A. Analysis
using PLATON (Spek, 2003) indicated there were no further
solvent-accessible voids.
One of the phenyl rings bound to phosphorus was also
found to be ca 50:50 disordered, its two orientations
differing only by a twist around the P-phenyl bond.
Since this aryl ring is fairly close to the
disordered toluene solvent molecule, the supercell
indications noted above might be a sign of partial order
in the arrangements of phenyl rings and toluene
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using the supercell in either P1 or P-1.
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Vol. IV, Birmingham, England: Kynoch Press.
Sheldrick, G.M. (1996).
SADABS. Program for Emperical Absorption Correction.
University of G\"ottingen, Germany.
Sheldrick, G. M. (1997).
SHELXL-97, Program for the refinement of
crystal structures. University of G\"ottingen, Germany.
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Sheldrick, G. M. (1997).
SHELXS-97, Program for crystal structure solution.
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Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands.
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This work was supported by a Canada Research Chair
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by Natural Sciences and Engineering Research Council
of Canada Discovery, Research Tools and Infrastructure
and Equipment and Major Facilities Access grants, and
by Canada Foundation for Innovation grants (to FCH). We thank Mark Cooper for his assistance and

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valuable discussions.
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C18 0.099(5) 0.076(4) 0.093(5) 0.028(4) 0.030(4) 0.023(4)
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Long needles of the compound were obtained by crystallization
from
a saturated CH2Cl2 solution cooled to -20 deg.
A fragment of a transparent light-green needle was glued on
place on top of a thin glass capillary using epoxy glue.
The fragment showed some cracks perpendicular to its long
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dimension, but was the best we were able to obtain. Data quality was
poor. Diffraction spots were large (ca 2 deg), and no data was observed past 30 deg.

The solution was solved by Patterson methods using SHELXS (Sheldrick
1997) and refined using SHELXL (Sheldrick 1997). The Co and Cl atoms
were refined anisotropically, the non-hydrogen atoms were refined isotropically, and hydrogen atoms were placed at calculated positions and refined isotropically in riding mode.

A void of ca 50 <br>%A^3 was found near a chloride, and contained the highest peak in the electron density difference map. This was assumed to contain
a partially occupied water molecule (occupancy refined to ca 0.7). Its hydrogen atoms were not included in the refinement. ;
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\# 4. TEXT

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Crystal and Molecular Structure of zd01
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This work was supported by a Canada Research Chair
in Crystallography and Mineralogy (to Frank C. Hawthorne)
by Natural Sciences and Engineering Research Council
of Canada Discovery, Research Tools and Infrastructure
and Equipment and Major Facilities Access grants, and
by Canada Foundation for Innovation grants (to FCH).
We thank Mark Cooper for his assistance and
valuable discussions.
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    Refinement of F^^2^ against ALL reflections. The weighted R-
factor wR and
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goodness of fit $S$ are based on $\mathrm{F}^{\wedge} 2^{\wedge}$, conventional R-factors $R$ are based
on $F$, with $F$ set to zero for negative $\mathrm{F}^{\wedge} 2^{\wedge}$. The threshold expression of $F^{\wedge} 2^{\wedge}>2$ sigma ( $\mathrm{F}^{\wedge} 2^{\wedge}$ ) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. Rfactors based on $\mathrm{F}^{\wedge} 2^{\wedge}$ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger. ;
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_atom_sites_solution_secondary difmap
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N2 N 0.223(2) 0.0350(11) 0.7851(6) 0.049(5) Uiso 1 1 d . . .
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H12 H 0.5858 0.0719 0.9007 0.153 Uiso 1 1 calc R . .
H13 H 0.4551 0.0143 0.9310 0.153 Uiso 1 1 calc R . .
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C3 C 0.331(3) 0.0141(14) 0.8276(8) 0.050(6) Uiso 1 1 d . . .
C4 C 0.427(3) -0.0722(14) 0.8268(9) 0.071(7) Uiso 1 1 d . . .
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H91 H -0.0461 -0.0211 0.6305 0.090 Uiso 1 1 calc R . .
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C12 C 0.361(3) 0.3152(14) 0.8966(8) 0.056(6) Uiso 1 1 d . . .
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H131 H 0.4242 0.4460 0.9271 0.075 Uiso 1 1 calc R . .
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H151 H 0.0681 0.3218 0.9994 0.084 Uiso 1 1 calc R . .
C16 C 0.144(3) 0.2373(14) 0.9402(8) 0.056(6) Uiso 1 1 d . . .
C17 C 0.492(3) 0.3173(15) 0.8581(8) 0.078(8) Uiso 1 1 d . . .
H171 H 0.5535 0.3774 0.8619 0.117 Uiso 1 1 calc R . .
H172 H 0.4381 0.3126 0.8228 0.117 Uiso 1 1 calc R . .
H173 H 0.5674 0.2634 0.8648 0.117 Uiso 1 1 calc R . .
C18 C 0.233(3) 0.4845(17) 1.0019(9) 0.100(9) Uiso 1 1 d . . .
H181 H 0.1339 0.4801 1.0202 0.151 Uiso 1 1 calc R . .
H182 H 0.2279 0.5421 0.9805 0.151 Uiso 1 1 calc R . .
H183 H 0.3306 0.4876 1.0271 0.151 Uiso 1 1 calc R . .
C19 C 0.040(3) 0.1514(15) 0.9515(9) 0.088(8) Uiso 1 1 d . . .
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H191 H -0.0326 0.1349 0.9206 0.133 Uiso 1 1 calc R . .
H192 H -0.0263 0.1665 0.9799 0.133 Uiso 1 1 calc R . .
H193 H 0.1124 0.0971 0.9613 0.133 Uiso 1 1 calc R . .
C21 C -0.103(2) 0.1338(13) 0.6678(7) 0.043(6) Uiso 1 1 d . . .
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C23 C -0.143(3) 0.2375(15) 0.5912(9) 0.074(7) Uiso 1 1 d . . .
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C24 C -0.314(3) 0.2221(16) 0.5888(9) 0.070(7) Uiso 1 1 d . . .
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C27 C 0.155(3) 0.2028(15) 0.6297(9) 0.082(8) Uiso 1 1 d . . .
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H272 H 0.2033 0.2165 0.6649 0. 123 Uiso 1 1 calc R . .
H273 H 0.1805 0.2552 0.6068 0.123 Uiso 1 1 calc R . .
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H282 H -0.3581 0.3151 0.5262 0.142 Uiso 1 1 calc R . .
H283 H -0.5138 0.3050 0.5590 0.142 Uiso 1 1 calc R . .
C29 C - 0. 363(3) 0.0566(15) 0.7028(8) 0.075(7) Uiso 1 1 d . . .
H291 H -0.4013 0.0959 0.7305 0.112 Uiso 1 1 calc R . .
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    are estimated using the full covariance matrix. The cell esds
are taken
    into account individually in the estimation of esds in
distances, angles
    and torsion angles; correlations between esds in cell parameters
are only
    used when they are defined by crystal symmetry. An approximate
(isotropic)
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    treatment of cell esds is used for estimating esds involving
l.s. planes.
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Co1 Cl2 2.257(6) . ?
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N2 C7 1.37(2) . ?
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N3 C21 1.43(2) . ?
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C12 C17 H172 109.5 . . ?
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    University of Manitoba
    Fort Garry Campus
    Winnipeg, MB R3T 2N2
    Canada
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'Budz\overline{elaar, \overline{Peter H.M.'}}\mathbf{\prime}=\mp@code{'}
; Department of Chemistry
        University of Manitoba
        Fort Garry Campus
        Winnipeg, MB R3T 2N2
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Crystals suitable for X-ray structure determination
were obtained by layering a concentrated dichloromethane
solution of the complex with toluene.
A crystal fragment of approximate dimensions 0.3 x 0.2 x 0.03 mm,
broken off a larger needle, was mounted inside
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a thin-walled glass capillary.
Data were collected on a Bruker four-circle diffractometer with APEX detector, and were corrected for absorption using SADABS (Sheldrick, 1996). The structure was solved using direct methods with the SHELXS package (Sheldrick, 1997), and refined using SHELXL (Sheldrick, 1997).
One molecule dichloromethane of crystallization was located and refined. Analysis using PLATON (Spek, 2003) showed there were no further solvent-accessible voids.
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\# 4. TEXT

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Crystal and Molecular Structure of budz02
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International Tables for X-ray Crystallography (1974).
Vol. IV, Birmingham, England: Kynoch Press.

Sheldrick, G.M. (1996).
SADABS. Program for Emperical Absorption Correction.
University of $G \backslash$ "ottingen, Germany.

Sheldrick, G. M. (1997).
SHELXL-97, Program for the refinement of
crystal structures. University of $G$ ""ottingen, Germany.
Sheldrick, G. M. (1997).
SHELXS-97, Program for crystal structure solution.
University of $G \backslash$ "ottingen, Germany.
Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University,
Utrecht, The Netherlands.
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;
;
_publ_section_acknowledgements

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;
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by Canada Foundation for Innovation grants (to FCH).
We thank Mark Cooper for his assistance and
valuable discussions.
;
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    Refinement of F^2^ against ALL reflections. The weighted R-
factor wR and
    goodness of fit S are based on F^2^, conventional R-factors R
are based
    on F, with F set to zero for negative F^2^. The threshold
expression of
    F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt)
etc. and is
    not relevant to the choice of reflections for refinement. R-
factors based
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on $\mathrm{F}^{\wedge} 2^{\wedge}$ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger.
;

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$\mathrm{P}=\left(\mathrm{FO}^{\wedge} 2^{\wedge}+2 \mathrm{FC}^{\wedge} 2^{\wedge}\right) / 3^{\prime}$
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$\overline{\mathrm{C}}$ ○1 Cō $0.2 \overline{3} 292(10) \overline{0} .27054(3) 0.20338(4) 0.0389(3)$ Uani 1 d.
Cl1 Cl 0.0524(2) 0.23425(8) 0.27213(11) 0.0645(5) Uani 11 d.
Cl2 Cl $0.4559(2) 0.29676(8) 0.28019(9) 0.0564(5)$ Uani $11 \mathrm{~d} .$.

F11 F $0.2997(7) 0.1311(2)-0.0318(3) \quad 0.1025(18)$ Uani $11 d . \quad$. F12 F $0.5373(6) 0.1520(2) 0.0092(3) \quad 0.0943(16)$ Uani 11 d . . . F13 F $0.4196(7) 0.08995(19) 0.0715(3) 0.1008(19)$ Uani $11 \mathrm{~d} . \quad$. C1 C 0.4018(10) 0.1395(3) 0.0333(4) 0.065(2) Uani 11 d C2 C $0.3456(7) 0.1894(3) 0.0828(3) 0.0429(15)$ Uani $11 \mathrm{~d} . \quad$. C3 C $0.3137(7) 0.2459(3) 0.0404(3) 0.0407(14)$ Uani $11 \mathrm{~d} . \quad$. C4 C $0.3451(9) 0.2582(3)-0.0370(4) 0.0592(19)$ Uani $11 \mathrm{~d} . \quad$. H4 H $0.38780 .2300-0.06740 .071$ Uiso 1 calc R . .
C5 C 0.3122 (10) 0.3124(4) -0.0675(4) 0.069(2) Uani $11 \mathrm{~d} . \quad$.
H5 H $0.33510 .3217-0.11860 .083$ Uiso 11 calc R . .
C6 C $0.2451(9) 0.3534(3)-0.0228(4) 0.062(2) \quad U a n i 11 d . \quad$.
H6 H $0.21910 .3900-0.04390 .075$ Uiso 11 calc R . .
C7 C 0.2174(7) 0.3388(3) 0.0539(3) 0.0435(15) Uani $11 \mathrm{~d} . \quad$.
C8 C 0.1394(7) 0.3774(3) 0.1083(3) 0.0425(15) Uani $11 \mathrm{~d} . \quad$.
C9 C $0.0794(10) 0.4366(3) 0.0742(5) 0.064(2)$ Uani $11 d$. . .
F91 F $0.0113(7) 0.4684(2) 0.1230(3) 0.106(2)$ Uani $11 d$. . .
F92 F - 0.0212 (7) 0.4287(2) 0.0083(3) $0.1004(17)$ Uani $11 \mathrm{~d} . \quad$.
F93 F $0.1967(6) 0.46726(19) 0.0522(3) 0.0909(16)$ Uani $11 \mathrm{~d} . \quad$.
$\mathrm{N} 1 \mathrm{~N} 0.3216(6) 0.1858(2) 0.1562(3) 0.0407(12) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
$\mathrm{N} 2 \mathrm{~N} 0.2530(6) 0.2862(2) 0.0850(2) 0.0372(11) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
N3 N $0.1256(6) 0.3589(2) 0.1785(3) 0.0428(12)$ Uani $11 \mathrm{~d} . \quad$.
C11 C $0.3510(7) 0.1354(3) 0.2068(3) 0.0412(14)$ Uani $11 \mathrm{~d} . \quad$.
C12 C 0.2253(8) 0.0993(3) 0.2184(4) 0.0459(15) Uani $11 \mathrm{~d} . \quad . \quad$.
C13 C $0.2518(9) 0.0547(3) 0.2734(4) 0.0522(17)$ Uani $11 \mathrm{~d} . \quad . \quad$.
H13 H 0.16910 .03030 .28130 .063 Uiso 11 calc R.
C14 C 0.3961(9) 0.0454(3) 0.3168(4) 0.0559(18) Uani $11 d$. . .
C15 C 0.5195(8) 0.0805(3) 0.3033(4) 0.0546(17) Uani $11 \mathrm{~d} . \quad$.
H15 H 0.61820 .07380 .33190 .066 Uiso 11 calc R.
C16 C $0.4998(8) 0.1265(3) 0.2470(4) 0.0471(16)$ Uani $11 d$. . .
C17 C 0.0653(8) 0.1053(3) 0.1677(4) 0.0604(19) Uani $11 \mathrm{~d} . \quad$.
H171 H 0.02610 .14390 .17330 .091 Uiso 11 calc R . .
H172 H -0.00630 .07780 .18580 .091 Uiso 11 calc R . .
H173 H 0.07520 .09800 .11220 .091 Uiso 1 calc R . .
C18 C $0.4212(11)-0.0039(4) 0.3777(5) 0.086(3)$ Uani $11 \mathrm{~d} . \quad$.
H181 H $0.3287-0.00860 .40350 .128$ Uiso 1 calc R . .
H182 H 0.50890 .00500 .41750 .128 Uiso 1 1 calc R . .
H183 H $0.4416-0.03930 .35060 .128$ Uiso 11 calc R . .
C19 C 0.6392(8) 0.1624(3) 0.2309(5) 0.070(2) Uani $11 d$. . .
H191 H 0.61310 .20290 .23240 .106 Uiso 11 calc R . .
H192 H 0.66640 .15290 .17880 .106 Uiso 11 calc R . .
H193 H 0.72660 .15430 .27120 .106 Uiso 1 1 calc R . .
$\mathrm{C} 21 \mathrm{C} 0.0413(8) 0.3880(2) 0.2364(3) 0.0411(14) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
$\mathrm{C} 22 \mathrm{C} 0.1213(8) 0.4237(3) 0.2945(4) 0.0474(16) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
$\mathrm{C} 23 \mathrm{C} 0.0380(10) 0.4457(3) 0.3535(4) 0.0573(19)$ Uani $11 \mathrm{~d} . \quad$.
H23 H 0.08900 .46990 .39300 .069 Uiso 11 calc R . .
C24 C $-0.1188(10) 0.4325(3) 0.3552(4) 0.0567(18)$ Uani $11 d$. . .
C25 C - 0. 1931 (8) 0.3981 (3) 0.2954(4) 0.0565(18) Uani $11 \mathrm{~d} . \quad$.
H25 H -0.29890 .38990 .29560 .068 Uiso 11 calc R . .

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C26 C -0.1177(8) 0.3747(3) 0.2341(4) 0.0481(16) Uani 1 1 d . . .
C27 C 0.2901(9) 0.4407(3) 0.2937(5) 0.068(2) Uani 1 1 d . . .
H271 H 0.3243 0.4645 0.3398 0.102 Uiso 1 1 calc R . .
H272 H 0.2998 0.4622 0.2455 0.102 Uiso 1 1 calc R . .
H273 H 0.3539 0.4064 0.2954 0.102 Uiso 1 1 calc R . .
C28 C -0.2064(12) 0.4570(4) 0.4206(5) 0.091(3) Uani 1 1 d . . .
H281 H -0.1367 0.4808 0.4562 0.137 Uiso 1 1 calc R . .
H282 H -0.2445 0.4256 0.4504 0.137 Uiso 1 1 calc R . .
H283 H -0.2933 0.4800 0.3964 0.137 Uiso 1 1 calc R . .
C29 C -0.2059(9) 0.3387(3) 0.1687(4) 0.0642(19) Uani 1 1 d . . .
H291 H -0.2245 0.3612 0.1202 0.096 Uiso 1 1 calc R . .
H292 H -0.3044 0.3269 0.1846 0.096 Uiso 1 1 calc R . .
H293 H -0.1454 0.3049 0.1595 0.096 Uiso 1 1 calc R . .
C91 C -0.1780(12) 0.2647(4) 0.4235(5) 0.092(3) Uani 1 1 d . . .
H911 H -0.2719 0.2855 0.4012 0.111 Uiso 1 1 calc R . .
H912 H -0.1070 0.2639 0.3832 0.111 Uiso 1 1 calc R . .
Cl91 Cl 0.9111(4) 0.19914(17) 0.0087(2) 0.1429(13) Uani 1 1 d. .
Cl92 Cl -0.2265(5) 0.30480(17) -0.05336(19) 0.1556(15) Uani 1 1 d
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C
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0.0036(9)
Cl2 0.0548(10) 0.0681(11) 0.0460(9) -0.0033(8) 0.0061(8) -
0.0099(9)
F11 0.140(5) 0.098(4) 0.069(3) -0.045(3) 0.012(3) -0.010(3)
F12 0.104(4) 0.090(3) 0.103(4) -0.013(3) 0.067(3) 0.014(3)
F13 0.183(6) 0.051(3) 0.082(3) -0.007(2) 0.069(4) 0.017(3)
C1 0.090(6) 0.060(5) 0.052(4) -0.011(4) 0.035(4) -0.002(4)
C2 0.042(4) 0.053(4) 0.038(3) -0.012(3) 0.020(3) -0.008(3)
C3 0.046(4) 0.051(4) 0.028(3) -0.006(3) 0.014(3) -0.011(3)
C4 0.078(5) 0.067(5) 0.037(3) -0.008(3) 0.025(4) -0.005(4)
C5 0.092(6) 0.086(6) 0.034(3) 0.010(4) 0.027(4) -0.007(5)
C6 0.082(5) 0.065(5) 0.042(4) 0.013(3) 0.016(4) 0.000(4)
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C8 0.042(4) 0.047(4) 0.040(3) 0.011(3) 0.013(3) -0.002(3)
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F91 0.162(5) 0.073(3) 0.097(4) 0.039(3) 0.064(4) 0.059(3)
F92 0.107(4) 0.085(4) 0.100(4) 0.031(3) -0.021(3) 0.017(3)
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F93 0.100(4) 0.060(3) 0.119(4) 0.037(3) 0.039(3) 0.000(3)
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C12 0.047(4) 0.044(4) 0.047(3) -0.005(3) 0.008(3) 0.003(3)
C13 0.060(5) 0.045(4) 0.054(4) 0.008(3) 0.017(4) -0.003(3)
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C17 0.052(4) 0.052(4) 0.075(5) 0.003(4) 0.001(4) -0.010(4)
C18 0.101(7) 0.079(6) 0.076(5) 0.028(5) 0.009(5) 0.019(5)
C19 0.048(4) 0.075(5) 0.089(6) -0.005(4) 0.015(4) 0.003(4)
C21 0.053(4) 0.029(3) 0.045(3) 0.009(3) 0.016(3) 0.004(3)
C22 0.060(4) 0.030(3) 0.053(4) 0.007(3) 0.014(3) 0.004(3)
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C24 0.076(5) 0.039(4) 0.060(4) -0.002(3) 0.028(4) 0.004(4)
C25 0.053(4) 0.051(4) 0.071(5) 0.003(4) 0.028(4) 0.004(3)
C26 0.053(4) 0.041(4) 0.052(4) 0.002(3) 0.013(3) 0.001(3)
C27 0.072(5) 0.052(4) 0.079(5) -0.003(4) 0.006(4) -0.009(4)
C28 0.127(8) 0.074(6) 0.086(6) -0.018(5) 0.060(6) 0.007(6)
C29 0.055(4) 0.071(5) 0.068(5) -0.006(4) 0.015(4) -0.001(4)
C91 0.089(7) 0.131(9) 0.059(5) -0.007(5) 0.018(5) 0.010(6)
Cl91 0.118(2) 0.167(3) 0.130(2) 0.047(2) - 0.036(2) - 0.028(2)
Cl92 0.218(4) 0.147(3) 0.094(2) -0.0141(19) -0.010(2) 0.031(3)
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distances, angles
    and torsion angles; correlations between esds in cell parameters
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    treatment of cell esds is used for estimating esds involving
l.s. planes.
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F12 C1 1.314(9) . ?
F13 C1 1.307(9) . ?
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C5 H5 0.9300 . ?
C6 C7 1.379(8) . ?
C6 H6 0.9300 . ?
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C7 C8 1.493(8) . ?
C8 N3 1.272(7) . ?
C8 C9 1.540(9) . ?
C9 F91 1.294(8) . ?
C9 F92 1.322(9) . ?
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C15 H15 0.9300 . ?
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C17 H172 0.9600 . ?
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C18 H183 0.9600 . ?
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Vol. IV, Birmingham, England: Kynoch Press.
Sheldrick, G.M. (1996).
SADABS. Program for Emperical Absorption Correction.
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Utrecht, The Netherlands.
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in Crystallography and Mineralogy (to Frank C. Hawthorne)
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We thank Mark Cooper for his assistance and
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    Department of Chemistry
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    Canada
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_publ_contact_author_fax
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Crystals suitable for X-ray structure determination
were obtained by layering a concentrated dichloromethane
solution of the complex with toluene.
A crystal fragment of approximate dimensions 0.3 x 0.3 x 0.2 mm,
broken off a larger needle, was mounted inside
a thin-walled glass capillary.
Data were collected on a Bruker four-circle diffractometer
with APEX detector, and were corrected for absorption using
SADABS (Sheldrick, 1996). The structure was solved using
direct methods with the SHELXS package (Sheldrick, 1997),
and refined using SHELXL (Sheldrick, 1997).
Two disordered toluene molecules were found,
one located over an inversion centre and one in a general
position. They were refined as idealized rigid hexagons with
a methyl carbon attached at a fixed distance of 1.50 A,
and assigned one common isotropic temperature factor.
Analysis using PLATON (Spek, 2003) showed there were no further
solvent-accessible voids.
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International Tables for X-ray Crystallography (1974).
Vol. IV, Birmingham, England: Kynoch Press.
Sheldrick, G.M. (1996).
SADABS. Program for Emperical Absorption Correction.
University of G\"ottingen, Germany.
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crystal structures. University of G\"ottingen, Germany.
Sheldrick, G. M. (1997).
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SHELXS-97, Program for crystal structure solution. University of $G \backslash$ "ottingen, Germany.

Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands.

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This work was supported by a Canada Research Chair
in Crystallography and Mineralogy (to Frank C. Hawthorne)
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of Canada Discovery, Research Tools and Infrastructure
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We thank Mark Cooper for his assistance and
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17.3375(12)
_cell_length_c
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107.0897(12)
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90.00
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3775.1(5)
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(Bruker)'
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'SHELXL-97 (Sheldrick, 1997)'
'PLATON (Spek, 2003)'
_computing_molecular_graphics
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_refine_special_details
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    Refinement of F^^2^ against ALL reflections. The weighted R-
factor wR and
```

goodness of fit $S$ are based on $\mathrm{F}^{\wedge} 2^{\wedge}$, conventional R-factors $R$ are based
on $F$, with $F$ set to zero for negative $\mathrm{F}^{\wedge} 2^{\wedge}$. The threshold expression of $F^{\wedge} 2^{\wedge}>2$ sigma ( $\mathrm{F}^{\wedge} 2^{\wedge}$ ) is used only for calculating R-factors(gt) etc. and is
not relevant to the choice of reflections for refinement. Rfactors based on $\mathrm{F}^{\wedge} 2^{\wedge}$ are statistically about twice as large as those based on F, and R-
factors based on ALL data will be even larger. ;
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_refine_ls_weighting_details
${ }^{\prime}$ calc $\overline{\mathrm{w}}=1 /\left[\backslash \mathrm{s}^{\wedge} 2^{\wedge}\left(\mathrm{Fo}^{\wedge} 2^{\wedge}\right)+(0.1477 \mathrm{P})^{\wedge} 2^{\wedge}+0.0000 \mathrm{P}\right]$ where $\mathrm{P}=\left(\mathrm{FO}^{\wedge} 2^{\wedge}+2 \mathrm{FC}^{\wedge} 2^{\wedge}\right) / 3^{\prime}$
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_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
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_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
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_refine_ls_number_restraints 3
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Cl1 Cl 0.37314(15) 0.75095(9) 0.31211(11) 0.0686(5) Uani 11 d.
Cl2 Cl 0.52948(16) 0.73475(10) 0.17062(11) 0.0725(5) Uani 11 d.
C1 C 0.1533(5) 0.5490(4) 0.0550(5) 0.0643(18) Uani 11 d . . .
F11 F $0.0790(4) 0.6009(2) 0.0270(3) 0.1066(17)$ Uani $11 d$. . .
F12 F $0.1794(4) 0.5184(3)-0.0047(3) 0.0984(15)$ Uani $11 d$. . .
F13 F $0.1055(3) 0.4923(3) 0.0841(3) 0.1010(15)$ Uani $11 \mathrm{~d} . \quad . \quad$
C2 C 0.2547(5) 0.5768(3) 0.1185(4) 0.0500(15) Uani $11 \mathrm{~d} . \quad$.
C3 C 0.3375(5) 0.5180(3) 0.1571(4) 0.0496(15) Uani 11 d
C4 C $0.3348(5) 0.4405(3) 0.1361(4) 0.0664(19) \quad$ Uani $11 \mathrm{~d} . \quad . \quad$.
H4 H 0.27870 .42190 .09400 .080 Uiso 11 calc R.
C5 C 0.4157(6) 0.3919(4) 0.1781(4) 0.072(2) Uani 11 d . . .
H5 H 0.41410 .33980 .16530 .087 Uiso 1 calc R.
C6 C 0.4984(5) 0.4206(3) 0.2388(4) 0.0629(18) Uani $11 \mathrm{~d} . \quad$.
H6 H 0.55400 .38850 .26770 .075 Uiso 1 1 calc R. .
C7 C 0.4983(5) 0.4985(3) 0.2566(4) 0.0474(15) Uani 11 d . . .
C8 C 0.5827(5) 0.5376(3) 0.3217(4) 0.0493(15) Uani 1 1 d. . .
C9 C 0.6700(5) 0.4875(4) 0.3758(4) 0.0632(18) Uani 1 d d. .
F91 F $0.7385(4) 0.5247(2) 0.4330(3) 0.0993(16)$ Uani $11 \mathrm{~d} . \quad . \quad$.
F92 F $0.6255(3) 0.4327(2) 0.4075(3) 0.0919(14)$ Uani $11 \mathrm{~d} . \quad$.
F93 F $0.7286(4) 0.4529(3) 0.3347(3) 0.0978(15)$ Uani $11 \mathrm{~d} . \quad . \quad$.
N1 N $0.2738(4) 0.6460(3) 0.1411(3) 0.0473(12)$ Uani $11 \mathrm{~d} . \quad$.
$\mathrm{N} 2 \mathrm{~N} 0.4191(4) \quad 0.5461(2) \quad 0.2159(3) \quad 0.0451(12) \quad \operatorname{Uani} 11 \mathrm{~d} . \quad$.
N3 N $0.5731(4) 0.6111(3) 0.3278(3) 0.0478(12)$ Uani $11 \mathrm{~d} . \quad . \quad$.
C11 C 0.2005(5) 0.7099(3) 0.1100(4) 0.0496(15) Uani 11 d. . .
C12 C 0.2092(6) 0.7488(4) 0.0453(4) 0.0666(19) Uani $11 \mathrm{~d} . \quad$.
C13 C 0.1411(7) 0.8117(4) 0.0198(5) 0.084(2) Uani $11 \mathrm{~d} . \quad$.
H13 H $0.14550 .8387-0.02420 .101$ Uiso 1 1 calc R . .
C14 C 0.0672(7) 0.8351(4) 0.0577(6) 0.094(3) Uani $1 \quad 1$ d . . .
C15 C $0.0594(6) 0.7951(4) 0.1223(5) 0.079(2)$ Uani 11 d . . .
H15 H 0.00960 .81120 .14810 .095 Uiso 1 1 calc R.
C16 C 0.1252(5) 0.7308(3) 0.1500(4) 0.0631(18) Uani 11 d . . .
$\mathrm{C} 17 \mathrm{C} 0.2883(8) 0.7239(6) 0.0010(5) 0.103(3) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
H171 H $0.28970 .6686-0.00150 .155$ Uiso 1 1 calc R . .
H172 H 0.36030 .74260 .02770 .155 Uiso 11 calc R . .
H173 H $0.26490 .7446-0.05120 .155$ Uiso 1 calc R . .
C18 C $-0.0081(8) \quad 0.9048(4) \quad 0.0270(7) \quad 0.136(5)$ Uani $11 d$. . .
H181 H -0.08260 .89050 .02110 .205 Uiso 1 calc R . .
H182 H $-0.00090 .9206-0.02280 .205$ Uiso 1 calc R . .
H183 H 0.01240 .94660 .06370 .205 Uiso 11 calc R . .
C19 C $0.1100(6) 0.6854(5) 0.2170(5) 0.083(2)$ Uani $11 \mathrm{~d} . \quad$.
H191 H 0.18010 .66900 .25020 .125 Uiso 11 calc R . .

H192 H 0.06550 .64100 .19730 .125 Uiso 11 calc R . .
H193 H 0.07470 .71690 .24660 .125 Uiso 1 calc R . .
$\mathrm{C} 21 \mathrm{C} 0.6415(5) 0.6589(3) 0.3885(3) \quad 0.0478(15) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
$\mathrm{C} 22 \mathrm{C} 0.7359(5) 0.6931(3) 0.3771(4) \quad 0.0553(16) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
C23 C 0.7904(5) 0.7460(4) 0.4332(5) 0.0653(19) Uani $11 \mathrm{~d} . \quad$.
H23 H 0.85110 .77120 .42620 .078 Uiso 1 calc R.
$\mathrm{C} 24 \mathrm{C} 0.7592(6) 0.7632(4) 0.4988(4) 0.0663(19) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
C25 C 0.6674(6) 0.7265(4) 0.5081 (4) 0.0634(18) Uani $11 \mathrm{~d} . \quad$.
H 25 H 0.64500 .73800 .55200 .076 Uiso 1 calc R.
C26 C 0.6082(5) 0.6736(3) 0.4546(4) 0.0532(15) Uani $11 \mathrm{~d} . \quad$.
C27 C $0.7777(6) 0.6712(4) 0.3098(5) \quad 0.079(2)$ Uani 11 d . . .
H271 H 0.81180 .62140 .31950 .119 Uiso 11 calc R . .
H272 H 0.83030 .70880 .30440 .119 Uiso 11 calc R . .
H273 H 0.71780 .66960 .26230 .119 Uiso 11 calc R . .
$\mathrm{C} 28 \mathrm{C} 0.8205(6) 0.8216(4) 0.5594(5) 0.097(3) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
H281 H 0.84810 .79670 .60950 .146 Uiso 11 calc R . .
H282 H 0.77170 .86250 .56330 .146 Uiso 11 calc R . .
H283 H 0.88040 .84250 .54380 .146 Uiso 11 calc R . .
$\mathrm{C} 29 \mathrm{C} 0.5131(6) 0.6328(4) 0.4694(4) 0.074(2) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
H291 H 0.52450 .57810 .46910 .112 Uiso 11 calc R . .
H292 H 0.44730 .64610 .42900 .112 Uiso 11 calc R . .
H293 H 0.50640 .64810 .51960 .112 Uiso 11 calc R . .
$\mathrm{C} 77 \mathrm{C} 0.6640(7) 0.9777(5) 0.6322(7) 0.1488(19)$ Uiso 0.501 dPRD A -1
H77A H $0.72750 .96150 .6180 \quad 0.223$ Uiso 0.501 calc PR B -1
H77B H 0.64230 .93760 .66160 .223 Uiso 0.501 calc PR C -1
H77C H 0.68091 .02360 .66360 .223 Uiso 0.501 calc PR D -1
C71 C $0.5723(12) 0.9941(14) 0.5592(7) 0.1488(19)$ Uiso 0.501 d PGD A -1
C72 C $0.5362(13) 1.0657(13) 0.5267(9) 0.1488(19)$ Uiso 0.501 d PG A -1
H72 H 0.56581 .11060 .55320 .179 Uiso 0.501 calc PR A -1
C73 C $0.4557(13) 1.0703(14) 0.4548(9) 0.1488(19)$ Uiso 0.501 dPG A -1
H73 H 0.43161 .11820 .43310 .179 Uiso 0.501 calc PR A -1
$\mathrm{C} 74 \mathrm{C} 0.4114(11) 1.0033(15) 0.4153(8) 0.1488(19)$ Uiso 0.501 d PG A -1
H74 H 0.35761 .00640 .36720 .179 Uiso 0.501 calc PR A -1
C75 C $0.4476(12) 0.9317(14) 0.4477(10) 0.1488(19)$ Uiso 0.501 d PG A -1
H75 H 0.41790 .88680 .42130 .179 Uiso 0.501 calc PR A -1
C76 C $0.5280(13) 0.9271(13) 0.5197(9) 0.1488(19)$ Uiso 0.501 dPG A -1
H76 H 0.55220 .87920 .54140 .179 Uiso 0.501 calc PR A -1
C87 C $1.0405(9) 0.9505(11) 0.2998(8) 0.1488(19)$ Uiso $0.635(8) 1 \mathrm{~d}$ PGD E -2
H87A H 1.10070 .96640 .28160 .223 Uiso $0.635(8) 1$ calc PR E -2
H87B H 1.04940 .89720 .31510 .223 Uiso $0.635(8) 1$ calc PR E -2

H87C H 1.03860 .98140 .34400 .223 Uiso $0.635(8) 1$ calc PR E -2 C81 C $0.9355(7) 0.9604(8) 0.2352(5) 0.1488(19)$ Uiso $0.635(8) 1 \mathrm{~d}$ PGD E -2
C82 C 0.8818(10) 1.0149(6) 0.1800(5) 0.1488(19) Uiso 0.635(8) 1 d PG E -2
H82 H 0.91861 .05890 .17180 .179 Uiso $0.635(8) 1$ calc PR E -2 C83 C 0.7731(10) 1.0035(6) 0.1369(5) 0.1488(19) Uiso 0.635(8) 1 d PG E -2
н83 н 0.73721 .03990 .10000 .179 Uiso $0.635(8) 1$ calc PR E -2 C84 C $0.7180(8) 0.9377(8) 0.1491(5) 0.1488(19)$ Uiso $0.635(8) 1 \mathrm{~d}$ PG E -2
H84 н 0.64530 .93020 .12030 .179 Uiso $0.635(8) 1$ calc PR E -2 C85 C $0.7717(10) 0.8833(6) 0.2043(5) 0.1488(19)$ Uiso $0.635(8) 1 \mathrm{~d}$ PG E -2
H85 H 0.73480 .83930 .21240 .179 Uiso $0.635(8) 1$ calc PR E -2 C86 C $0.8804(9) 0.8947(6) 0.2473(5) 0.1488(19)$ Uiso $0.635(8) 1 \mathrm{~d}$ PG E -2
H86 H 0.91630 .85830 .28430 .179 Uiso $0.635(8) 1$ calc PR E -2 C97 C $0.7344(16) 0.9827(17) 1.1515(6) 0.1488(19)$ Uiso $0.365(8) 1$ d PGD E -3
H97A н 0.74261 .03561 .13850 .223 Uiso $0.365(8) 1$ calc PR E -3
н97B н 0.68420 .97941 .18230 .223 Uiso $0.365(8) 1$ calc $\operatorname{PR} E-3$
H97C н 0.70660 .95331 .10420 .223 Uiso $0.365(8) 1$ calc PR E -3
C91 C $0.8435(15) 0.9510(14) 1.1978(14) 0.1488(19)$ Uiso $0.365(8) 1$ d PGD E -3
C92 C $0.937(2) 0.9931(11) 1.2005(14) 0.1488(19)$ Uiso $0.365(8) 1 \mathrm{~d}$ PG E -3
H92 н 0.93161 .03831 .17150 .179 Uiso $0.365(8) 1$ calc PR E -3
C93 C $1.0388(16) 0.9676(13) 1.2464(14) 0.1488(19)$ Uiso $0.365(8) 1$ d PG E -3
н93 н 1.10140 .99581 .24820 .179 Uiso $0.365(8) 1$ calc PR E -3
C94 C $1.0470(15) 0.9000(14) 1.2897(12) 0.1488(19)$ Uiso $0.365(8) 1$ d PG E -3
н94 н 1.11500 .88301 .32050 .179 Uiso $0.365(8) 1$ calc PR E -3
C95 C 0.953(2) 0.8579(10) 1.2871(13) 0.1488(19) Uiso 0.365(8) 1 d PG E -3
н95 н 0.95890 .81271 .31600 .179 Uiso $0.365(8) 1$ calc PR E -3
C96 C $0.8516(15) 0.8834(13) 1.2411(15) 0.1488(19)$ Uiso $0.365(8) 1$ d PG E -3
н96 н 0.78900 .85521 .23930 .179 Uiso $0.365(8) 1$ calc PR E -3
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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
atom_site_aniso_U_12
Fē $0 . \overline{0} 517(\overline{6}) \quad 0.0 \overline{3} 1 \overline{2}(5) \quad 0.0534(6)-0.0021(4) \quad 0.0108(4)-0.0018(3)$ Cl1 0.0761(12) 0.0542(10) 0.0766(12) $-0.0155(8) 0.0243(9)$ $0.0016(8)$
Cl2 0.0813(12) 0.0695(11) 0.0705(12) 0.0067(9) 0.0280(10) 0.0152 (9)

C1 0.058(4) 0.046(4) 0.075(5) -0.009(4) -0.003(4) -0.001(3)
F11 0.073(3) 0.069(3) 0.135(4) -0.019(3) -0.037(3) 0.007(2)
F12 0.107(4) 0.099(3) 0.069(3) -0.027(3) $-0.006(3) 0.006(3)$
F13 $0.076(3) \quad 0.089(3) \quad 0.119(4) \quad 0.004(3)-0.001(3)-0.037(2)$
C2 0.047(4) 0.045(4) 0.052(4) -0.004(3) 0.005(3) 0.000(3)
C3 0.048(4) $0.040(3) \quad 0.056(4)-0.008(3) 0.009(3)-0.001(3)$
C4 0.069(4) 0.037(3) 0.080(5) -0.016(3) 0.000(4) -0.002(3)
C5 0.069(5) $0.041(4) \quad 0.092(6)-0.011(4) \quad 0.002(4) 0.007(3)$
C6 0.060(4) 0.041(4) 0.077(5) -0.005(3) 0.004(4) 0.012(3)
C7 0.045(3) 0.035(3) 0.061(4) 0.004(3) 0.014(3) 0.002(3)
C8 0.044(3) 0.040(3) 0.063(4) 0.002(3) 0.013(3) -0.003(3)
C9 0.053(4) 0.049(4) 0.075(5) 0.009(4) 0.000(4) 0.001(3)
F91 0.090(3) 0.060(3) 0.109(4) 0.008(2) -0.031(3) 0.007(2)
F92 $0.090(3) 0.071(3) 0.103(3) 0.041(2) 0.010(3) 0.005(2)$
F93 0.076(3) 0.094(3) 0.118(4) 0.015(3) 0.020(3) 0.041(3)
N1 0.050(3) 0.035(3) 0.052(3) 0.001(2) 0.007(2) 0.001(2)
N2 0.045(3) 0.039(3) 0.050(3) -0.004(2) 0.011(2) -0.001(2)
N3 $0.048(3) \quad 0.045(3) 0.050(3) \quad 0.000(2) 0.013(2) 0.001(2)$
C11 0.043(3) 0.038(3) 0.059(4) -0.001(3) 0.000(3) -0.002(3)
C12 0.067(4) 0.061(4) 0.059(4) 0.010(4) 0.000(4) -0.009(3)
C13 $0.086(6) 0.064(5) \quad 0.077(5) 0.028(4)-0.015(5)-0.015(4)$
C14 0.082(6) 0.041(4) 0.122(8) 0.009(5) -0.027(5) 0.000(4)
C15 0.064(5) 0.061(5) 0.104(6) -0.011(5) 0.010(4) 0.014(4)
C16 0.048(4) 0.048(4) 0.086(5) 0.000(4) 0.009(4) 0.008(3)
$\mathrm{C} 170.113(7) 0.136(8) 0.061(5) 0.011(5) 0.027(5)-0.034(6)$
C18 0.119(8) 0.056(5) 0.189(11) 0.018(6) -0.024(7) 0.024(5)
C19 0.068(5) 0.111(6) 0.076(5) 0.009(5) 0.030(4) 0.008(4)
C21 0.045(3) 0.044(3) 0.050(4) -0.001(3) 0.008(3) 0.000(3)
C22 0.051(4) 0.047(3) 0.064(4) 0.000(3) 0.011(3) -0.006(3)
C23 0.049(4) 0.054(4) 0.085(5) 0.005(4) 0.008(4) -0.010(3)
C24 0.064(5) 0.050(4) 0.069(5) -0.003(3) -0.004(4) 0.005(3)
C25 0.069(5) 0.063(4) 0.053(4) -0.004(3) 0.009(3) 0.005(4)
C26 0.047(4) 0.054(4) 0.053(4) 0.003(3) 0.007(3) -0.002(3)
$\mathrm{C} 270.064(5) 0.094(6) 0.084(5)-0.008(4) 0.029(4)-0.019(4)$
C28 0.087(6) 0.066(5) 0.108(7) -0.029(5) -0.019(5) -0.006(4)
C29 0.089(5) 0.084(5) 0.057(4) -0.001(4) 0.031(4) -0.009(4)
_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;
loop
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Crystals suitable for X-ray structure determination
were obtained by layering a dichloromenthane solution with
diethyl ether and pentane.
A crystal of approximate dimensions 0.2 x 0.2 x 0.05 mm was
mounted on top of a thin glass fiber using epoxy glue.
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Data were collected on a Bruker four-circle diffractometer with APEX detector, and were corrected for absorption using SADABS (Sheldrick, 1996).
The crystal quality deteriorated during the data collection, as evidenced from the increase in diffraction spot sizes.
The structure was solved using
direct methods with the SHELXS package (Sheldrick, 1997),
and refined using SHELXL (Sheldrick, 1997).
One molecule dicloromethane of crystallization
was located and refined; analysis using PLATON
(Spek, 2003) revealed no further significant
solvent-accessible voids.
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\# 4. TEXT

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Crystal and Molecular Structure of budz02
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International Tables for X-ray Crystallography (1974).
Vol. IV, Birmingham, England: Kynoch Press.

Sheldrick, G.M. (1996).
SADABS. Program for Emperical Absorption Correction.
University of $G \backslash$ "ottingen, Germany.

Sheldrick, G. M. (1997).
SHELXL-97, Program for the refinement of
crystal structures. University of $G$ "ottingen, Germany.

Sheldrick, G. M. (1997).
SHELXS-97, Program for crystal structure solution.
University of $G \backslash$ "ottingen, Germany.

Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands.
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This work was supported by a Canada Research Chair
in Crystallography and Mineralogy (to Frank C. Hawthorne)
by Natural Sciences and Engineering Research Council
of Canada Discovery, Research Tools and Infrastructure
and Equipment and Major Facilities Access grants, and
by Canada Foundation for Innovation grants (to FCH).
We thank Mark Cooper for his assistance and
valuable discussions.
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expression of
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$\mathrm{F}^{\wedge} 2^{\wedge}>2$ sigma $\left(\mathrm{F}^{\wedge} 2^{\wedge}\right)$ is used only for calculating $R$-factors ( $\left.\mathrm{g} t\right)$ etc. and is
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C6 C $0.1341(6) 0.3017(3)-0.1602(3) 0.0591(15)$ Uani $11 \mathrm{~d} .$.
H106 H $0.15710 .3345-0.18910 .071$ Uiso 11 calc R. .

C7 C 0.1679(5) 0.2996(2) -0.0803(3) 0.0444(12) Uani 1 d . . . N2 N 0.1383(4) 0.25292(19) -0.0383(2) 0.0420(10) Uani $11 d$. . . P1 P 0.26281(13) 0.35837(6) -0.02487(8) 0.0427(4) Uani 11 d. C20 C $0.2000(6) 0.4300(3)-0.0612(3) \quad 0.0537(14)$ Uani $11 \mathrm{~d} . \quad$. C21 C 0.0671(8) 0.4374(4) -0.0738(4) 0.074(2) Uani 1 d . . . H128 H 0.01480 .4041 -0.0682 0.089 Uiso 1 calc R . . C22 C $0.0102(10) 0.4924(5)-0.0945(5) 0.098(3)$ Uani $11 \mathrm{~d} . \quad$. H129 H -0.0790 0.4963-0.1045 0.117 Uiso 1 1 calc R . . C23 C 0.0910(16) 0.5419(4) -0.0998(5) 0.119(4) Uani $11 \mathrm{~d} . \quad$. H130 H $0.05510 .5798-0.11260 .143$ Uiso 1 calc R. C24 C 0.2213(14) 0.5357(4) -0.0868(6) 0.110(4) Uani $11 \mathrm{~d} . \quad$. H131 H $0.27380 .5693-0.09020 .132$ Uiso 1 calc R . . C25 C 0.2753(9) 0.4800(3) -0.0686(4) 0.081(2) Uani 1 d . . . H132 H 0.3646 $0.4760-0.06120 .097$ Uiso 1 calc R . .
C26 C $0.4230(6) 0.3490(3)-0.0477(4) \quad 0.0548(14)$ Uani $11 d$. . . $\mathrm{C} 27 \mathrm{C} 0.5136(7) 0.3240(3) 0.0072(5) 0.0749(19) \mathrm{Uani} 11 \mathrm{~d} . \quad$. H133 H 0.49110 .31400 .05560 .090 Uiso 11 calc R . . C28 C $-0.3626(8) 0.3131(5)-0.0067(7) 0.106(3)$ Uani $11 d . \quad . \quad$. H134 H -0.30250 .29560 .03160 .127 Uiso 1 calc R . . C29 C $-0.3289(9) 0.3284(6)-0.0773(10) 0.127(4)$ Uani $11 d . \quad . \quad$. H135 H $-0.24460 .3226-0.08660 .152$ Uiso 11 calc R . . C30 C $0.5827(12) 0.3518(6)-0.1338(8) 0.130(4)$ Uani $11 d$. . . H136 H $0.60600 .3599-0.18250 .157$ Uiso 1 calc R . . C31 C 0.4559(8) 0.3642(4) -0.1203(5) 0.088(2) Uani $11 d$. . . H137 H $0.39610 .3819-0.15860 .105$ Uiso 1 calc R . .
$\mathrm{N} 3 \mathrm{~N} 0.2458(5) 0.3444(2) 0.0632(3) 0.0483(11) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
$\mathrm{C} 32 \mathrm{C} 0.2808(5) 0.3871(2) 0.1243(3) 0.0479(13) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
C33 C $0.2188(6) 0.3852(3) 0.1886(4) 0.0583(15)$ Uani $11 d$. . .
H138 H 0.15630 .35580 .19200 .070 Uiso 1 1 calc R . .
C34 C 0.2479(8) 0.4264(3) 0.2484(4) 0.076(2) Uani $11 \mathrm{~d} . \quad$.
H139 H 0.2039 0.4244 0.2913 0.091 Uiso 1 1 calc R . .
C35 C $-0.3385(8)-0.0307(4) 0.2537(5) \quad 0.083(2)$ Uani $11 \mathrm{~d} . \quad$.
H140 H $-0.3580-0.00360 .21260 .099$ Uiso 1 1 calc R . .
C36 C 0.4007(8) 0.4725(4) 0.1833(5) 0.085(2) Uani $11 \mathrm{~d} . \quad$.
H141 H 0.4630 0.50220 .18100 .102 Uiso 11 calc R . .
$\mathrm{C} 37 \mathrm{C} 0.3728(7) 0.4317(3) 0.1218(4) 0.0682(18) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
H142 H 0.41620 .43460 .07880 .082 Uiso 11 calc R . .
C91 C $0.5426(18) 0.3251(10) 0.2902(15) 0.261(13)$ Uani $11 \mathrm{~d} . \quad$.
H911 H 0.47250 .34910 .26310 .313 Uiso 11 calc R . .
H912 H 0.51330 .28370 .29540 .313 Uiso 1 1 calc R . .
Cl91 Cl $-0.3110(8) 0.1721(5)-0.2610(7) 0.353(5)$ Uani $11 d . \quad$.
Cl92 Cl $-0.4057(16) 0.1476(5)-0.1311(6) 0.498(11)$ Uani 11 d.
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Cl2 0.0703(10) 0.0705(10) 0.0549(9) 0.0032(7) -0.0223(8)
0.0032(8)
N1 0.040(2) 0.048(2) 0.040(3) 0.0002(19) 0.0033(19) -0.0060(19)
C8 0.076(4) 0.050(3) 0.048(3) -0.002(3) 0.003(3) -0.025(3)
C9 0.101(6) 0.069(4) 0.062(4) -0.012(3) 0.023(4) -0.040(4)
C10 0.201(13) 0.084(6) 0.076(6) -0.001(5) 0.047(7) -0.074(8)
C11 0.244(17) 0.082(7) 0.073(7) 0.018(6) -0.009(9) -0.044(9)
C12 0.162(10) 0.066(5) 0.106(8) 0.027(5) -0.029(7) -0.005(6)
C13 0.087(5) 0.061(4) 0.085(5) 0.008(4) -0.017(4) -0.001(4)
C14 0.108(7) 0.099(7) 0.142(10) -0.009(6) 0.062(7) -0.043(6)
C15 0.148(10) 0.186(12) 0.174(12) -0.091(10) 0.095(10) -0.086(9)
C16 0.116(10) 0.30(2) 0.115(10) 0.026(12) 0.039(8) 0.043(12)
C17 0.097(7) 0.079(6) 0.155(10) 0.019(6) 0.011(7) 0.030(5)
C18 0.088(8) 0.152(11) 0.31(2) -0.016(13) -0.019(10) 0.050(8)
C19 0.165(13) 0.171(13) 0.185(15) -0.001(12) 0.040(11) 0.056(11)
C1 0.102(6) 0.069(4) 0.065(4) -0.018(3) 0.012(4) -0.036(4)
C2 0.047(3) 0.052(3) 0.049(3) -0.011(3) 0.009(3) -0.011(2)
C3 0.041(3) 0.054(3) 0.035(3) -0.007(2) -0.001(2) 0.000(2)
C4 0.064(4) 0.073(4) 0.039(3) -0.013(3) 0.001(3) -0.005(3)
C5 0.088(5) 0.088(5) 0.028(3) -0.006(3) -0.002(3) 0.002(4)
C6 0.075(4) 0.070(4) 0.034(3) 0.007(3) 0.014(3) 0.000(3)
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C21 0.090(5) 0.080(5) 0.054(4) 0.008(3) 0.018(4) 0.028(4)
C22 0.127(7) 0.102(7) 0.065(5) 0.006(5) 0.018(5) 0.059(6)
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C24 0.191(12) 0.056(5) 0.078(6) 0.008(4) 0.003(7) -0.001(6)
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C26 0.048(3) 0.057(3) 0.060(4) 0.006(3) 0.008(3) -0.003(3)
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N3 0.059(3) 0.049(2) 0.036(2) 0.0021(19) 0.004(2) -0.013(2)
C32 0.056(3) 0.041(3) 0.045(3) 0.002(2) 0.002(3) -0.001(2)
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    and torsion angles; correlations between esds in cell parameters
are only
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(isotropic)
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l.s. planes.
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publ-contact author name 'Dr. Peter H.M. Budzelaar'
_publ_contact_author_address
;Department of Chemistry
University of Manitoba
Fort Garry Campus
    Winnipeg, MB R3T 2N2
    Canada
;
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;Department of Chemistry
University of Manitoba
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'Zhu, Di'
;Department of Chemistry
University of Manitoba
Fort Garry Campus
    Winnipeg, MB R3T 2N2
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expression of
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etc. and is
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on F}\mp@subsup{\textrm{F}}{}{\wedge}\mp@subsup{2}{}{\wedge}\mathrm{ are statistically about twice as large as those based on
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C4 C 0.1944(7) 0.8510(5) 1.3042(4) 0.047(2) Uani 1 1 d . . .
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H1 H 0.0810 0.8775 1.1446 0.080 Uiso 1 1 calc R . .
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H2 H 0.2118 0.9246 1.2334 0.081 Uiso 1 1 calc R . .
C7 C - 0.0589(9) 0.6596(5) 1.2285(5) 0.075(3) Uani 1 1 d . . .
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H5 H -0.0254 0.6507 1.1791 0.112 Uiso 1 1 calc R . .
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C8 C $-0.0844(10) 0.6008(6) 1.4098(6) 0.073(3)$ Uani $11 \mathrm{~d} .$. C9 C $0.0752(13) 0.5629(6) 1.3487(7) 0.089(4)$ Uani $11 \mathrm{~d} .$. C10 C $-0.0547(8) 0.7819(5) 0.7975(5) 0.058(3)$ Uani $1 \mathrm{~d} . .$. C11 C $-0.2693(7) 0.7210(5) 0.8150(5) 0.056(3)$ Uani $11 \mathrm{~d} . .$. C12 C $-0.0585(10) 0.8082(5) 0.7243(5) 0.071(3)$ Uani $11 \mathrm{~d} .$. н43 н -0.11810 .82630 .70920 .086 Uiso 11 calc R . .
C13 C $0.0238(9) 0.8069(6) 0.6766(6) 0.070(3)$ Uani $11 \mathrm{~d} . \quad$. H44 H 0.02130 .82370 .62810 .083 Uiso 11 calc R .
C14 C $0.0451(8) 0.7963(6) 1.1988(5) 0.064(3)$ Uani $11 \mathrm{~d} .$. H3 H -0.00420 .77631 .16220 .077 Uiso 11 calc R .
C15 C $0.4195(8) 0.8874(5) 1.3415(6) 0.065(3)$ Uani $11 \mathrm{~d} .$.
C16 C $0.0457(16) 0.4979(8) 1.3664(9) 0.119(6)$ Uani $11 \mathrm{~d} .$.
н19 н 0.08840 .46391 .35320 .143 Uiso 11 calc R.
C17 C $-0.1483(11) 0.6553(8) 1.4347(7) 0.096(4)$ Uani $11 \mathrm{~d} .$.
н88 н -0.11610 .69641 .41510 .144 Uiso 11 calc R. .
C18 C $0.2688(7) 0.6723(5) 0.9133(5) 0.054(2)$ Uani $11 \mathrm{~d} . \quad$.
C19 C $0.3486(9) 0.7818(6) 0.9856(6) 0.076(3)$ Uani $11 \mathrm{~d} .$.
н87 н 0.29090 .79860 .95890 .115 Uiso 1 calc R.
C20 C $0.3414(8) 0.7080(6) 0.9663(5) 0.061(3)$ Uani $11 \mathrm{~d} . .$.
C21 C $0.4503(12) 0.8198(7) 0.9598(11) 0.147(7)$ Uani $11 \mathrm{~d} .$.
н49 н 0.50880 .79900 .97730 .220 Uiso 11 calc R.
н50 н 0.45420 .86560 .98230 .220 Uiso 11 calc R. .
H51 н 0.45120 .81850 .90380 .220 Uiso 11 calc R . .
C22 C $0.3377(12) 0.8019(8) 1.0742(7) 0.124(6)$ Uani $11 \mathrm{~d} .$.
H52 н 0.27460 .77971 .09270 .187 Uiso 11 calc R. .
H53 н 0.33560 .84961 .08330 .187 Uiso 11 calc R..
H54 н 0.39610 .78891 .10160 .187 Uiso 11 calc R . .
C23 C $0.1136(8) 0.7800(5) 0.7001(5) 0.066(3)$ Uani $11 \mathrm{~d} .$.
н45 н 0.17110 .77820 .66760 .079 Uiso 11 calc R. .
C24 C $0.1146(7) 0.7558(5) 0.7743(5) 0.052(2)$ Uani $11 \mathrm{~d} .$.
C25 C 0.2033(7) 0.7249(4) 0.8067(5) 0.048(2) Uani $11 \mathrm{~d} .$.
C26 C $0.2927(9) 0.7101(7) 0.7544(6) 0.095(4)$ Uani $11 \mathrm{~d} .$.
н46 н 0.32340 .75100 .73620 .143 Uiso 11 calc R.
н47 н 0.26830 .67940 .71050 .143 Uiso 11 calc R. .
Н48 н 0.34370 .69050 .78310 .143 Uiso 11 calc R . .
$\mathrm{C} 27 \mathrm{C}-0.2029(7) 0.8592(5) 0.8760(5) 0.052(2) \mathrm{Uani} 1 \mathrm{~d} . .$.
C28 C $-0.1237(9) 0.9115(6) 0.9005(6) 0.074(3)$ Uani $11 \mathrm{~d} .$.
H64 н -0.05490 .90180 .90440 .089 Uiso 11 calc R. .
C29 C $-0.4360(10) 0.6589(6) 0.8215(7) 0.090(4)$ Uani $11 \mathrm{~d} .$.
H69 H -0.49830 .65030 .84760 .108 Uiso 11 calc R..
C30 C $-0.3582(8) 0.7059(5) 0.8557(6) 0.062(3)$ Uani $1 \mathrm{~d} .$.
н70 н -0.36700 .72670 .90580 .075 Uiso 11 calc R . .
C31 C 0.5039(10) 0.9037(6) 1.3914(7) 0.084(3) Uani $11 \mathrm{~d} .$.
н23 н 0.49310 .91271 .44480 .101 Uiso 11 calc R . .
C32 C $0.4375(10) 0.8717(8) 1.2652(6) 0.123(6)$ Uani $11 \mathrm{~d} .$.
н22 н 0.38190 .85911 .23080 .148 Uiso 1 calc R. .
C33 C $0.2570(8) 0.9676(5) 1.4068(5) 0.051(2)$ Uani $11 \mathrm{~d} .$.

C34 C 0.1561(9) 0.9776(6) 1.4239(6) 0.074(3) Uani $11 \mathrm{~d} . \quad$. H27 H 0.10550 .94131 .42190 .089 Uiso 11 calc R . .
C35 C 0.1293(10) 1.0426(6) 1.4442(7) 0.091(4) Uani 11 d... H28 H 0.06051 .04921 .45620 .109 Uiso 11 calc R . .
C36 C $0.3020(11) 1.0865(6) 1.4296(8) 0.094(4)$ Uani $11 \mathrm{~d} . \quad$. H29 H 0.35241 .12291 .43180 .113 Uiso 11 calc R . .
C37 C $0.2034(11) 1.0980(6) 1.4471(7) 0.083(4)$ Uani $11 \mathrm{~d} . \quad$. H30 H 0.18531 .14121 .46060 .100 Uiso 11 calc R. . C38 C $0.3387(9) 0.8280(6) 1.5084(7) 0.071(3)$ Uani $11 d . \quad$. C39 C $-0.0498(19) \quad 0.4839(8) 1.4047(9) 0.125(8)$ Uani $11 d$. . . H20 H -0.07040 .44031 .41600 .150 Uiso 1 calc R . C40 C $0.1795(11) 0.5774(7) 1.3135(9) 0.103(4)$ Uani $11 d$. . . H89 H 0.19390 .62621 .31540 .154 Uiso 1 1 calc R.
C41 C $-0.1520(15) 0.6671(9) 1.5267(7) 0.162(8)$ Uani $11 d . \quad$.
H7 H -0.18560 .62791 .54700 .243 Uiso 11 calc R . .
H8 H -0.19020 .70491 .54180 .243 Uiso 1 1 calc R . .
H9 H -0.08240 .67571 .54730 .243 Uiso 11 calc R . .
$\mathrm{C} 42 \mathrm{C}-0.3330(11) 0.6406(8) \quad 0.7092(8) 0.117(5) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
H71 H -0.32570 .61920 .65920 .140 Uiso 11 calc R . .
C43 C $-0.2533(9) 0.6879(6) 0.7415(6) 0.086(4)$ Uani $11 \mathrm{~d} . \quad . \quad$.
H72 H -0.19190 .69680 .71450 .104 Uiso 1 1 calc R.
C44 C $-0.4206(13) \quad 0.6260(8) \quad 0.7508(8) 0.131(6)$ Uani $11 d$. . .
H73 H -0.47080 .59270 .73000 .157 Uiso 1 1 calc R . .
C45 C $-0.1489(13) 0.9764(6) 0.9185(8) 0.098(4)$ Uani $11 d$. . .
H65 H -0.09721 .01000 .93530 .118 Uiso 11 calc R . .
C46 C $-0.3017(9) 0.8759(6) 0.8697(7) 0.073(3)$ Uani $11 d . \quad$.
H66 H -0.35420 .84280 .85260 .088 Uiso 11 calc R . .
$\mathrm{C} 47 \mathrm{C} 0.4081(10) 0.6002(8) 0.9852(8) 0.093(4) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
H61 H 0.45500 .57561 .00830 .111 Uiso 11 calc R . .
C48 C 0.4123(9) 0.6704(7) 1.0012(6) 0.081(4) Uani $11 \mathrm{~d} . \quad . \quad$.
H62 H 0.46290 .69251 .03540 .098 Uiso 11 calc R.
C49 C $0.3317(10) 0.5691(6) 0.9340(8) 0.089(4)$ Uani $11 \mathrm{~d} . \quad$.
H63 H 0.32800 .52270 .92330 .106 Uiso 11 calc R . .
C50 C $0.2603(9) 0.6036(6) 0.8976(6) \quad 0.073(3)$ Uani 11 d . . .
C51 C 0.1806(13) 0.5633(7) 0.8414(10) 0.121(6) Uani $11 \mathrm{~d} . \quad$.
H86 H 0.14160 .59550 .81720 .182 Uiso 1 1 calc R.
C52 C $0.1016(13) 0.5215(8) 0.8932(11) 0.150(7)$ Uani $11 \mathrm{~d} . \quad$.
H55 H 0.05470 .49170 .85970 .225 Uiso 1 calc R . .
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C53 C 0.2249(14) 0.5200(8) 0.7772(8) 0.142(7) Uani $11 d$. . .
H58 H 0.24680 .54640 .73550 .213 Uiso 11 calc R . .
H59 H 0.17300 .48490 .75800 .213 Uiso 11 calc R . .
H60 H 0.28360 .50050 .79670 .213 Uiso 11 calc R . .
C54 C $-0.2468(14) 0.9911(7) 0.9121(8) 0.105(5)$ Uani $11 \mathrm{~d} . \quad$.
H67 H -0.26261 .03510 .92360 .127 Uiso 11 calc R . .
C55 C $-0.3262(12) 0.9408(8) 0.8879(8) 0.106(4)$ Uani $11 \mathrm{~d} . \quad . \quad$.
H68 H -0.39460 .95110 .88430 .127 Uiso 11 calc R . .

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C59 C -0.2807(9) 0.7427(7) 1.1180(6) 0.075(3) Uani 1 1 d . . .
H74 H -0.3018 0.7722 1.1588 0.090 Uiso 1 1 calc R . .
C60 C -0.1668(11) 0.8407(6) 1.0723(6) 0.092(4) Uani 1 1 d . . .
H77 H -0.1086 0.8475 1.0381 0.137 Uiso 1 1 calc R . .
H78 H -0.1445 0.8524 1.1256 0.137 Uiso 1 1 calc R . .
H79 H -0.2198 0.8684 1.0599 0.137 Uiso 1 1 calc R . .
C61 C - 0. 3181(8) 0.6777(8) 1.1142(6) 0.077(3) Uani 1 1 d . . .
C62 C -0.3959(10) 0.6513(7) 1.1759(8) 0.114(5) Uani 1 1 d . . .
H80 H -0.3595 0.6489 1.2241 0.171 Uiso 1 1 calc R . .
H81 H -0.4271 0.6075 1.1570 0.171 Uiso 1 1 calc R . .
H82 H -0.4492 0.6814 1.1848 0.171 Uiso 1 1 calc R . .
C63 C - 0. 2593(15) 0.6410(11) 1.4001(11) 0.184(9) Uani 1 1 d . . .
H10 H -0.2556 0.6332 1.3442 0. 276 Uiso 1 1 calc R . .
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C64 C - 0.1103(13) 0.5327(9) 1.4248(7) 0.103(5) Uani 1 1 d . . .
H21 H -0.1727 0.5218 1.4498 0.123 Uiso 1 1 calc R . .
C65 C 0.2693(12) 0.5508(9) 1.3541(12) 0.157(7) Uani 1 1 d . . .
H13 H 0.2567 0.5530 1.4094 0. 236 Uiso 1 1 calc R . .
H14 H 0.3328 0.5776 1.3447 0.236 Uiso 1 1 calc R . .
H15 H 0.2751 0.5051 1.3340 0.236 Uiso 1 1 calc R . .
C66 C 0.6167(12) 0.8908(10) 1.2843(10) 0.144(7) Uani 1 1 d . . .
H24 H 0.6837 0.8919 1.2640 0.172 Uiso 1 1 calc R . .
C67 C 0.6028(11) 0.9067(7) 1.3631(9) 0.107(5) Uani 1 1 d . . .
H25 H 0.6595 0.9192 1.3964 0.129 Uiso 1 1 calc R . .
C68 C 0.3322(9) 1.0231(6) 1.4083(6) 0.072(3) Uani 1 1 d . . .
H31 H 0.4010 1.0173 1.3953 0.086 Uiso 1 1 calc R . .
C69 C 0.3280(12) 0.8698(8) 1.5797(7) 0.100(5) Uani 1 1 d . . .
C70 C 0.2420(14) 0.9153(7) 1.5891(6) 0.114(6) Uani 1 1 d . . .
H34 H 0. 2637 0.9570 1.5684 0.171 Uiso 1 1 calc R . .
H35 H 0.2261 0.9238 1.6436 0.171 Uiso 1 1 calc R . .
H36 H 0.1812 0.8943 1.5613 0.171 Uiso 1 1 calc R . .
C71 C 0.4117(11) 0.7822(8) 1.5026(9) 0.096(4) Uani 1 1 d . . .
C72 C 0.4201(12) 0.7333(8) 1.4324(11) 0.133(6) Uani 1 1 d . . .
H37 H 0.3833 0.6911 1.4414 0.199 Uiso 1 1 calc R . .
H38 H 0.4920 0.7273 1.4226 0.199 Uiso 1 1 calc R . .
H39 H 0.3904 0.7500 1.3878 0.199 Uiso 1 1 calc R . .
C73 C - 0. 1854(9) 0.6043(5) 0.9335(6) 0.076(3) Uani 1 1 d . . .
H83 H -0.2393 0.5932 0.8947 0.115 Uiso 1 1 calc R . .
H84 H -0.1719 0.5646 0.9571 0.115 Uiso 1 1 calc R . .
H85 H -0.1231 0.6222 0.9093 0.115 Uiso 1 1 calc R
C74 C - 0. 2898(8) 0.6341(6) 1.0531(7) 0.073(3) Uani 1 1 d . . .
H75 H -0.3173 0.5895 1.0494 0.088 Uiso 1 1 calc R .
C75 C 0.1739(16) 0.5486(12) 1.2250(11) 0.201(10) Uani 1 1 d . . .
H16 H 0.1339 0.5057 1.2199 0.301 Uiso 1 1 calc R . .
```

H17 H 0.24300 .54371 .20590 .301 Uiso 11 calc R . .
H18 н 0.14140 .57891 .19500 .301 Uiso 11 calc R . .
C76 C $0.5365(12) 0.8740(11) 1.2376(10) 0.178(10)$ Uani $11 \mathrm{~d} .$.
н26 н 0.54740 .86331 .18440 .213 Uiso 1 calc R. .
C77 C $0.474(2) 0.8217(14) 1.6372(14) 0.174(14)$ Uani $11 \mathrm{~d} .$.
C78 C $0.4781(11) 0.7805(10) 1.5748(14) 0.154(9)$ Uani $11 \mathrm{~d} . .$.
н32 н 0.52440 .74771 .57420 .185 Uiso 11 calc R . .
C79 C $0.3999(17) 0.8648(10) 1.6415(9) 0.142(9)$ Uani $11 \mathrm{~d} .$. н33 н 0.39520 .89291 .68740 .171 Uiso 11 calc R . .
C80 C $0.5453(15) 0.8190(14) 1.7062(12) 0.278(18)$ Uani $11 \mathrm{~d} .$.
H40 H 0.54530 .77341 .71820 .417 Uiso 11 calc R . .
H41 H 0.52100 .84581 .75070 .417 Uiso 11 calc R . .
H42 H 0.61460 .83611 .69370 .417 Uiso 11 calc R . .
Cl8 Cl $0.8694(15) 0.0124(9) 0.2049(11) 0.510(10)$ Uiso $11 \mathrm{~d} .$.
$\mathrm{Cl} 9 \mathrm{Cl} 0.6953(19) 0.0311(11) 0.1425(14) 0.637(15) \mathrm{Uiso} 1 \mathrm{~d} . \quad$.
loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_-22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
-atom_site_aniso_U_12
$\overline{\mathrm{F}}=10.0572 \overline{(9)} 0 . \overline{0} 6 \overline{2} 2(9) \quad 0.0322(6) \quad 0.0046(6)-0.0056(6) \quad 0.0006(7)$
$\mathrm{Fe} 20.0632(9) \quad 0.0559(9) \quad 0.0353(6) 0.0049(6)-0.0083(6)-0.0059(7)$
P1 0.0518(15) 0.0565(16) 0.0375(11) 0.0035(10) -0.0029(11)
$0.0032(12)$
P2 0.0554(16) 0.0594(17) 0.0399(12) 0.0013(11) -0.0055(11) -
$0.0058(13)$
Cl3 0.0790(19) 0.0709(18) 0.0597(14) 0.0057(12) 0.0112(13)
$0.0078(15)$
Cl5 0.0721(18) $0.0631(17) 0.0665(15) 0.0015(12)-0.0141(13)$
$0.0000(14)$
C14 0.0819(19) 0.094(2) 0.0479(13) 0.0244(13) -0.0019(13)
0.0127 (16)

Cl2 $0.101(2) 0.0716(18) \quad 0.0567(14) 0.0202(13)-0.0239(14)-$
$0.0096(16)$
N1 0.062(5) 0.070(6) 0.032(4) 0.003(4) 0.000(4) -0.007(4)
N2 0.059(5) 0.065(5) 0.029(4) 0.003(3) -0.004(3) 0.003(4)
N3 $0.057(5) \quad 0.048(5) \quad 0.039(4) \quad 0.005(3)-0.007(3) 0.009(4)$
N4 0.057(5) 0.053(5) 0.038(4) 0.001(3) -0.001(3) -0.001(4)
N5 0.058(5) 0.055(5) 0.040(4) -0.001(3) 0.000(4) -0.001(4)
N6 0.066(5) 0.065(5) 0.032(3) 0.011(3) -0.022(3) -0.005(4)
C1 $0.052(6) 0.055(6) 0.041(5)-0.002(4) 0.004(4) 0.010(5)$
C2 $0.074(7) 0.066(7) 0.025(4)-0.008(4)-0.009(4)-0.002(6)$
C3 $0.090(9) 0.042(7) 0.059(6) 0.004(5)-0.024(6)-0.018(6)$


```
C52 0.116(13) 0.098(12) 0.22(2) -0.013(12) -0.013(13) -0.026(11)
C53 0.197(19) 0.121(13) 0.091(10) -0.005(9) -0.029(11) -0.051(13)
C54 0.137(14) 0.073(10) 0.113(11) 0.035(8) -0.006(10) 0.011(10)
C55 0.089(10) 0.094(11) 0.135(12) 0.015(9) -0.016(9) 0.009(9)
C56 0.052(6) 0.061(7) 0.064(6) 0.026(5) 0.002(5) 0.005(5)
C57 0.058(6) 0.070(7) 0.037(5) 0.007(5) -0.009(4) 0.019(5)
C58 0.078(8) 0.089(9) 0.049(6) 0.017(6) -0.012(5) 0.015(7)
C59 0.074(8) 0.101(10) 0.051(6) 0.011(6) 0.001(6) 0.015(7)
C60 0.139(12) 0.075(9) 0.060(6) -0.005(6) -0.017(7) 0.019(8)
C61 0.045(6) 0.130(12) 0.063(7) 0.035(7) 0.012(5) 0.019(7)
C62 0.077(9) 0.162(14) 0.114(10) 0.075(10) 0.030(8) 0.007(9)
C63 0.143(18) 0.25(3) 0.152(17) -0.003(16) -0.001(14) -0.009(17)
C64 0.129(13) 0.115(12) 0.054(7) 0.028(8) -0.034(7) -0.062(11)
C65 0.095(12) 0.149(16) 0.23(2) 0.016(15) -0.020(13) 0.035(11)
C66 0.068(10) 0.22(2) 0.126(13) -0.043(13) 0.008(9) -0.004(11)
C67 0.082(10) 0.115(12) 0.113(11) -0.032(9) -0.013(9) -0.010(9)
C68 0.064(7) 0.080(9) 0.068(6) 0.000(6) 0.012(5) 0.000(6)
C69 0.123(12) 0.116(12) 0.049(7) 0.031(7) -0.033(7) -0.067(9)
C70 0.195(17) 0.097(11) 0.041(6) -0.003(6) -0.008(8) -0.028(11)
C71 0.071(9) 0.089(10) 0.127(11) 0.053(9) -0.033(8) -0.034(8)
C72 0.089(11) 0.109(13) 0.208(19) 0.037(13) -0.005(12) 0.025(10)
C73 0.092(9) 0.052(7) 0.086(8) 0.014(6) -0.007(7) 0.004(6)
C74 0.065(7) 0.077(8) 0.084(8) 0.044(7) -0.006(6) 0.002(6)
C75 0.152(19) 0.28(3) 0.151(17) -0.030(18) 0.012(14) -0.030(18)
C76 0.061(10) 0.32(3) 0.128(14) -0.072(16) 0.017(10) -0.012(13)
C77 0.19(2) 0.20(3) 0.128(16) 0.101(18) -0.102(18) -0.11(2)
C78 0.055(9) 0.164(18) 0.26(2) 0.140(18) -0.068(13) -0.050(10)
C79 0.19(2) 0.149(18) 0.074(9) 0.059(11) -0.058(12) -0.102(15)
C80 0.168(19) 0.45(4) 0.21(2) 0.23(3) -0.155(17) -0.17(2)
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;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
    into account individually in the estimation of esds in
distances, angles
    and torsion angles; correlations between esds in cell parameters
are only
    used when they are defined by crystal symmetry. An approximate
(isotropic)
    treatment of cell esds is used for estimating esds involving
l.s. planes.
;
loop
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Fe1 N4 2.259(7) . ?
Fe1 Cl4 2.267(3) . ?
Fe1 Cl5 2.378(3) . ?
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P1 C10 1.803(10) . ?
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P2 C4 1.820(9) . ?
P2 C15 1.820(11) . ?
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N1 C4 1.362(11) . ?
N2 C1 1.292(10) . ?
N2 C3 1.459(12) . ?
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N4 C25 1.322(10) . ?
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C6 H2 0.9300 . ?
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C7 H5 0.9600 . ?
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C8 C17 1.464(17) . ?
C9 C16 1.391(19) . ?
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C21 H51 0.9600 . ?
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С30 H70 0.9300 . ?
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C31 н23 0.9300 . ?
C32 C76 1.361(17) . ?
C32 н22 0.9300 . ?

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C71 C78 1.51(2) . ?
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C72 H38 0.9600 . ?
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C75 H18 0.9600 . ?
C76 H26 0.9300 . ?
C77 C78 1.29(3) . ?
C77 C79 1.35(3) . ?
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C25 N4 Fe1 116.8(6) . . ?
C18 N4 Fe1 123.9(5) . . ?
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C10 N5 Fe1 119.4(6) . . ?
C24 N5 Fe1 119.6(6) . . ?
C38 N6 P2 122.6(6) . . ?
C38 N6 Fe2 117.8(6) . . ?
P2 N6 Fe2 119.7(4) . . ?
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C8 C3 N2 119.0(11) . . ?
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C3 C9 C40 122.6(11) . . ?
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N5 C10 C12 121.3(9) . . ?
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C19 C22 H53 109.5 . . ?
H52 C22 H53 109.5 . . ?
C19 C22 H54 109.5 . . ?
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C24 C23 H45 120.8 . . ?
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N5 C24 C25 113.8(8) . . ?
C23 C24 C25 124.5(8) . . ?
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N4 C25 C26 126.0(9) . . ?
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expression of
    F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt)
etc. and is
    not relevant to the choice of reflections for refinement. R-
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N2 N 0.0304(4) 0.4654(2) 0.7727(3) 0.0487(11) Uani $11 d$
N4 N $0.2008(4) 0.6200(2) 0.8099(3) 0.0458(11)$ Uani $11 \mathrm{~d} . \quad . \quad$. C51 C 0.0353(4) 0.5168(3) 0.6564(3) 0.0474(13) Uani $11 \mathrm{~d} . \quad$. C52 C $0.0127(5) 0.5250(3) 0.5785(4) 0.0579(15)$ Uani $11 \mathrm{~d} . \quad . \quad$. H1 H -0.02230 .49650 .54920 .069 Uiso 1 calc R .
C53 C $0.0418(5) 0.5749(3) 0.5446(3) 0.0620(16)$ Uani $11 \mathrm{~d} . \quad$. H2 H 0.02710 .58040 .49220 .074 Uiso 1 calc R . .
C54 C 0.0929(5) 0.6169(3) 0.5881(3) 0.0580(16) Uani $11 \mathrm{~d} . \quad$. H3 H 0.11090 .65180 .56620 .070 Uiso 1 1 calc R . .
C55 C $0.1173(4) 0.6061(2) 0.6660(3) 0.0468(13)$ Uani $11 \mathrm{~d} . \quad$. C6 C 0.0082(4) 0.4645(2) 0.6995(3) 0.0475(13) Uani 1 1 d . . C56 C - 0.0446(7) 0.4160(3) 0.6550(4) 0.0734(19) Uani $11 \mathrm{~d} . \quad$. H24 H -0.0073 0.40600 .61240 .110 Uiso 11 calc R . . H25 H -0.1116 0.4282 0.6364 0.110 Uiso 1 1 calc R . . H26 H -0.04860 .38270 .68760 .110 Uiso 1 1 calc R . . C11 C 0.1150(5) 0.7214(2) 0.7233(3) 0.0529(14) Uani $11 \mathrm{~d} . \quad$. C12 C 0.0235(6) 0.7228(4) 0.7543(5) 0.082(2) Uani 11 d . . . H4 H 0.00140 .69070 .78030 .099 Uiso 1 calc R . .
C13 C $0.1440(6) 0.7708(3) 0.6824(4) 0.0648(17)$ Uani $11 \mathrm{~d} . \quad$. H8 H 0.20560 .77130 .66080 .078 Uiso 1 calc R . .
C14 C 0.0799(7) 0.8182(3) 0.6748(5) 0.079(2) Uani $11 \mathrm{~d} . \quad . \quad$. H7 H 0.09780 .85070 .64750 .095 Uiso 11 calc R.
C15 C $-0.0086(8) 0.8174(4) 0.7070(6) 0.100(3)$ Uani $11 \mathrm{~d} . \quad . \quad$. H6 H -0.05170 .84930 .70130 .120 Uiso 11 calc R . .
C16 C $-0.0347(7) 0.7719(4) 0.7466(6) 0.100(3)$ Uani $11 \mathrm{~d} . \quad . \quad$. H5 H -0.09480 .77320 .77010 .120 Uiso 11 calc R.
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H9 H 0.29920 .61860 .60190 .090 Uiso 1 calc R . .
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H13 H 0.34620 .73480 .77340 .079 Uiso 1 1 calc R.
C31 C 0.2793(5) 0.6361 (2) 0.8689(3) 0.0479(13) Uani $11 \mathrm{~d} . \quad$.
C32 C 0.2549(6) 0.6732(3) 0.9285(3) 0.0577(16) Uani $11 \mathrm{~d} . \quad . \quad$.
C33 C $0.3303(7) 0.6890(3) 0.9843(4) 0.070(2)$ Uani $11 \mathrm{~d} . \quad . \quad$.
H14 H 0.31480 .71351 .02380 .084 Uiso 1 calc R.
C34 C 0.4301(8) 0.6686(4) 0.9824(5) 0.087(3) Uani 11 d . . .
H15 H 0.48160 .68041 .01870 .104 Uiso 1 calc R.
C35 C 0.4487(6) 0.6303(3) 0.9241(4) 0.0691(18) Uani $11 \mathrm{~d} . \quad . \quad$.
H16 H 0.51400 .61580 .92300 .083 Uiso 11 calc R .
C36 C $0.3766(5) 0.6128(3) 0.8685(3) 0.0542(15)$ Uani $11 \mathrm{~d} . \quad . \quad$.
C70 C $0.1510(6) 0.6938(3) 0.9386(4) 0.0667(18)$ Uani $11 \mathrm{~d} . \quad$.

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C71 C 0.4047(5) 0.5665(3) 0.8111 (4) 0.0633(16) Uani $11 \mathrm{~d} . \quad$.
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C41 C 0.0056(5) 0.4156(2) 0.8177(3) 0.0501(14) Uani 1 1 d. . .
C42 C 0.0835(6) 0.3755(3) 0.8396(4) 0.0625(17) Uani $11 \mathrm{~d} . \quad$.
C43 C $0.0587(8) 0.3270(3) 0.8805(5) \quad 0.082(2)$ Uani 11 d . . .
H17 H 0.10810 .29930 .89430 .098 Uiso 11 calc R . .
C44 C $-0.0399(8) 0.3189(3) 0.9014(5) 0.091(3)$ Uani $11 \mathrm{~d} . \quad . \quad$.
H18 H -0.05500 .28620 .92930 .109 Uiso 1 calc R.
C45 C $-0.1143(7) 0.3590(3) 0.8809(4) 0.076(2)$ Uani $11 \mathrm{~d} . \quad . \quad$.
H19 H -0.17940 .35330 .89540 .092 Uiso 11 calc R.
C46 C $-0.0932(5) \quad 0.4082(3) \quad 0.8389(4) 0.0601(16)$ Uani $11 d \quad . \quad$.
C72 C 0.1876(6) 0.3827(3) 0.8151(5) 0.076(2) Uani $11 d$. . .
H20 H 0.19430 .42360 .80070 .091 Uiso 11 calc R.
C57 C 0.2723(8) 0.3704(5) 0.8799(7) 0.112(3) Uani $11 d$. . .
H 27 H 0.25470 .38780 .92670 .168 Uiso 11 calc R . .
H 28 H 0.33500 .38670 .86630 .168 Uiso 1 1 calc R . .
H29 H 0.27980 .32920 .88690 .168 Uiso 1 calc R . .
C58 C $0.2012(8) 0.3465(5) 0.7432(6) 0.109(3) \quad U a n i 11 d . \quad . \quad$.
H30 H 0.20460 .30600 .75650 .163 Uiso 1 calc R . .
H31 H 0.26270 .35780 .72230 .163 Uiso 11 calc R . .
H32 H 0.1448 0.3530 0.7059 0.163 Uiso 1 1 calc R . .
C73 C $-0.1777(6) 0.4514(3) 0.8214(5) 0.0721(19)$ Uani $11 d . \quad$.
H21 H - 0. 15050.48270 .79130 .087 Uiso 11 calc R . .
C59 C $-0.2132(9) 0.4791(5) 0.8920(6) 0.111(3)$ Uani $11 d . \quad . \quad$.
H33 H -0.25230 .45150 .91800 .167 Uiso 11 calc R . .
H34 H -0.25440 .51230 .87760 .167 Uiso 11 calc R . .
H35 H -0.15560 .49110 .92550 .167 Uiso 1 1 calc R . .
C60 C $-0.2678(8) 0.4246(6) 0.7711(7) 0.121(4)$ Uani $11 d$. . .
H36 H -0.24820 .41760 .72050 .181 Uiso 11 calc R . .
H37 H -0.32410 .45100 .76830 .181 Uiso 11 calc R . .
H38 H -0.28690 .38850 .79320 .181 Uiso 1 calc R . .
C63 C 0.1124(8) 0.6701(5) 1.0122(6) 0.105(3) Uani $11 d$. . .
H45 H 0.12650 .62921 .01630 .157 Uiso 1 1 calc R . .
H46 H 0.04060 .67631 .01090 .157 Uiso 1 1 calc R . .
H47 H 0.14570 .68991 .05560 .157 Uiso 11 calc R . .
C64 C 0.1420(9) 0.7607(4) 0.9339(6) 0.106(3) Uani $11 \mathrm{~d} . \quad$.
H48 H 0.17990 .77780 .97750 .160 Uiso 11 calc R. .
H49 H 0.07210 .77170 .93350 .160 Uiso 11 calc R . .
H50 H 0.16830 .77420 .88790 .160 Uiso 1 1 calc R. .

Cl81 Cl 0.2907(3) 0.47650(18) 0.63978(17) 0.1375(11) Uani $11 \mathrm{~d} D$

Cl82 Cl 0.4857(3) 0.4799(2) 0.5845(3) 0.1730(18) Uani 1 d D. . C91 C 0.3592(7) 0.4655(6) 0.5637(6) 0.130(5) Uani $11 d \mathrm{D}$. .
H51 H 0.33280 .49020 .52170 .156 Uiso 1 calc R . .
H52 H 0.35110 .42540 .54700 .156 Uiso 1 calc R . .
Cl13 Cl 0.7162(13) 0.6868(7) 0.8706(7) 0.1784(16) Uiso 0.301(5) 1 d PD A 1
Cl14 Cl 0.7517(13) 0.6677(7) 1.0316(6) 0.1784(16) Uiso 0.301(5) 1 d PD A 1
C92 C 0.7704(4) 0.6490(2) 0.9455(3) 0.206(8) Uiso 0.301(5) 1 d PD A 1
H53A H 0.74860 .60890 .9388 0.247 Uiso $0.301(5) 1$ calc PR A 1 H54A H 0.84290 .64950 .94180 .247 Uiso $0.301(5) 1$ calc PR A 1 Cl84 Cl 0.7991(4) 0.7120(2) 0.9986(3) 0.1784(16) Uiso 0.699(5) 1 d PRD A 2

Cl83 Cl 0.7200(4) 0.6067(2) 1.0171(3) 0.1784(16) Uiso 0.699(5) 1 d PRD A 2
C94 C 0.7704(4) 0.6490(2) 0.9455(3) 0.206(8) Uiso 0.699(5) 1 d PRD A 2
H53B H 0.83040 .63130 .92760 .247 Uiso $0.699(5) 1$ calc PR A 2 H54B H 0.72080 .65610 .90230 .247 Uiso $0.699(5) 1$ calc PR A 2 Cl85 Cl 0.2346(6) 0.9474(4) 0.1147(5) 0.291(4) Uani $11 d \mathrm{~d}$. Cl86 Cl 0.2876(9) 0.8295(4) 0.1305(8) 0.398(8) Uani 1 1 d D. . C93 C 0.2552(18) 0.8918(6) 0.1749(10) 0.212(8) Uiso $11 \mathrm{~d} D$. H55 H 0.19450 .88480 .20050 .255 Uiso 1 1 calc R . . H56 H 0.30910 .90210 .21380 .255 Uiso 1 1 calc R. .

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Cl8 0.1139(16) 0.0843(12) 0.0434(8) 0.0161(8) -0.0125(9) -
0.0375(11)
Cl9 0.0611(10) 0.0712(10) 0.1069(15) -0.0127(9) 0.0346(10) -
0.0050(8)
N3 0.045(3) 0.048(2) 0.036(2) -0.0032(18) 0.002(2) -0.003(2)
N2 0.055(3) 0.048(2) 0.042(3) -0.0026(19) 0.003(2) -0.007(2)
N4 0.046(3) 0.053(3) 0.039(2) 0.0006(19) 0.005(2) -0.006(2)
C51 0.044(3) 0.059(3) 0.039(3) -0.003(2) 0.003(2) 0.002(3)
C52 0.058(4) 0.067(4) 0.048(3) -0.009(3) 0.000(3) -0.003(3)
C53 0.074(5) 0.074(4) 0.037(3) 0.002(3) -0.005(3) 0.003(3)
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C54 0.074(4) 0.061(4) 0.039(3) 0.011(3) 0.008(3) 0.001(3)
C55 0.052(3) 0.049(3) 0.040(3) 0.003(2) 0.003(3) -0.003(3)
C6 0.046(3) 0.049(3) 0.047(3) -0.009(2) 0.001(3) -0.001(2)
C56 0.092(5) 0.066(4) 0.060(4) -0.015(3) -0.004(4) -0.014(4)
C11 0.062(4) 0.050(3) 0.046(3) 0.007(2) 0.006(3) -0.008(3)
C12 0.077(5) 0.076(5) 0.097(6) 0.025(4) 0.020(5) 0.013(4)
C13 0.076(5) 0.059(4) 0.058(4) 0.007(3) -0.002(3) -0.005(3)
C14 0.096(6) 0.062(4) 0.075(5) 0.018(3) -0.011(4) -0.010(4)
C15 0.098(7) 0.081(6) 0.122(8) 0.013(5) 0.016(6) 0.037(5)
C16 0.077(6) 0.079(5) 0.147(9) 0.031(5) 0.036(6) 0.023(4)
C21 0.050(3) 0.062(4) 0.056(3) 0.015(3) 0.010(3) -0.003(3)
C22 0.068(5) 0.093(5) 0.067(4) 0.005(4) 0.024(4) -0.009(4)
C23 0.108(8) 0.164(10) 0.096(7) 0.036(7) 0.055(7) 0.007(8)
C24 0.065(5) 0.132(8) 0.115(8) 0.048(7) 0.016(5) -0.025(6)
C25 0.078(6) 0.093(6) 0.112(7) 0.026(5) 0.002(5) -0.017(5)
C26 0.054(4) 0.066(4) 0.076(4) 0.012(3) -0.001(3) -0.016(3)
C31 0.054(4) 0.052(3) 0.037(3) 0.010(2) 0.003(2) -0.017(3)
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C34 0.106(7) 0.088(5) 0.060(4) 0.014(4) -0.021(4) -0.043(5)
C35 0.062(4) 0.083(5) 0.060(4) 0.005(3) -0.008(3) -0.019(4)
C36 0.060(4) 0.057(3) 0.046(3) 0.012(2) 0.003(3) -0.010(3)
C70 0.086(5) 0.065(4) 0.051(3) -0.014(3) 0.017(3) -0.011(4)
C71 0.062(4) 0.067(4) 0.061(4) 0.004(3) 0.006(3) 0.000(3)
C61 0.109(7) 0.085(6) 0.107(7) 0.004(5) 0.025(6) 0.002(5)
C62 0.067(5) 0.111(6) 0.098(6) 0.009(5) 0.028(5) 0.014(5)
C41 0.060(4) 0.043(3) 0.048(3) -0.005(2) 0.005(3) -0.013(3)
C42 0.076(5) 0.055(3) 0.057(4) -0.006(3) 0.009(3) -0.002(3)
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C46 0.071(4) 0.056(3) 0.053(3) -0.013(3) 0.007(3) -0.017(3)
C72 0.092(6) 0.048(4) 0.087(5) 0.007(3) 0.006(4) 0.011(4)
C57 0.090(7) 0.096(7) 0.143(9) 0.023(6) -0.023(6) 0.007(5)
C58 0.097(7) 0.122(8) 0.110(8) -0.022(6) 0.027(6) 0.030(6)
C73 0.054(4) 0.084(5) 0.079(5) -0.003(4) 0.009(4) -0.021(4)
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C60 0.075(6) 0.173(11) 0.110(8) -0.009(8) -0.013(6) -0.023(7)
C63 0.110(7) 0.112(7) 0.100(7) -0.014(5) 0.048(6) -0.004(6)
C64 0.133(9) 0.078(5) 0.110(7) -0.024(5) 0.021(6) -0.006(6)
Cl81 0.145(3) 0.177(3) 0.0918(18) -0.0275(19) 0.0200(18) 0.002(2)
Cl82 0.119(3) 0.232(4) 0.165(3) -0.086(3) 0.000(2) -0.015(3)
C91 0.122(9) 0.173(10) 0.089(7) -0.070(7) -0.032(6) 0.041(8)
Cl85 0. 203(6) 0.390(11) 0.283(9) 0.084(8) 0.033(6) 0.069(7)
Cl86 0.315(10) 0.349(11) 0.494(17) -0.210(12) -0.164(11) 0.082(9)
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All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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expression of
    F^2^ > 2sigma( }\mp@subsup{\textrm{F}}{}{\wedge}\mp@subsup{2}{}{\wedge})\mathrm{ is used only for calculating R-factors(gt)
etc. and is
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factors based
on F^^2^ are statistically about twice as large as those based on
F, and R-
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N8 N 0.99381(15) 0.40598(8) 0.20787(6) 0.0495(4) Uani 1 1 d . . .
N9 N 0.91230(14) 0.20189(8) -0.08018(5) 0.0434(4) Uani 1 1 d . .
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C8 C 0.9218(2) 0.37460(10) 0.28339(8) 0.0546(5) Uani 1 1 d . . .
C9 C 0.9248(3) 0.33640(13) 0.32608(10) 0.0734(7) Uani 1 1 d . . .
H4 H 0.9780 0.2983 0.3308 0.088 Uiso 1 1 calc R . .
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C10 C 0.8480(3) 0.35528(15) 0.36164(10) 0.0853(8) Uani $11 \mathrm{~d} .$.
н5 н 0.84920 .33010 .39050 .102 Uiso 11 calc R . .
C11 C $0.7699(3) 0.41181(14) 0.35380(8) 0.0730(7)$ Uani $11 \mathrm{~d} .$. H6 H 0.71810 .42530 .37740 .088 Uiso 1 calc R . .
C12 C $0.7691(2) 0.44837(12) 0.31051(7) 0.0543(5)$ Uani $11 \mathrm{~d} .$.
C13 C $0.9973(2) 0.36355(10) 0.24379(9) 0.0581(5)$ Uani $11 \mathrm{~d} .$.
C14 C 1.0929(2) 0.38368(12) 0.17646(10) 0.0670(6) Uani 11 d.
C15 C 1.2063(2) 0.42925(17) 0.18766(12) 0.0926(9) Uani 11 d.
н23 н 1.18380 .47750 .18310 .139 Uiso 11 calc R. .
н24 н 1.26870 .41720 .16620 .139 Uiso 11 calc R . .
H25 H 1.23850 .42190 .22080 .139 Uiso 11 calc R. .
C16 C $1.0490(3) 0.38918(16) 0.12272(10) 0.0894(9)$ Uani 11 d.
н26 н 0.97640 .36080 .11600 .134 Uiso 11 calc R . .
H27 H 1.11360 .37320 .10350 .134 Uiso 11 calc R. .
H28 H 1.02950 .43700 .11480 .134 Uiso 11 calc R. .
C17 C $1.1149(3) 0.30879(15) 0.19348(13) 0.1022(11)$ Uani 11 d.
H7 H 1.06660 .27630 .17260 .123 Uiso 11 calc R. .
н8 H 1.20210 .29660 .19380 .123 Uiso 11 calc R . .
C18 C $0.69057(19) 0.50699(12) 0.29591(8) 0.0549(5)$ Uani 11 d.
C19 C $0.5185(3) 0.36692(16) 0.10208(10) 0.0856(8)$ Uani 11 d.
н35 н 0.45800 .40270 .10630 .128 Uiso 11 calc R. .
н36 н 0.47950 .32190 .10280 .128 Uiso 11 calc R. .
н37 н 0.55280 .37320 .07140 .128 Uiso 11 calc R. .
C20 C 0.99626(18) 0.22385(11) -0.11167(7) 0.0480(4) Uani 11 d.
C21 C $0.5638(3) 0.59626(19) 0.30268(11) 0.1024(11)$ Uani 1 d.
н9 н $0.60340 .63720 .3178 \quad 0.123$ Uiso 11 calc R. .
H10 H 0.47480 .60010 .30450 .123 Uiso 11 calc R . .
C22 C $0.5951(2) 0.58960(14) 0.24972(9) 0.0678(6)$ Uani $11 \mathrm{~d} .$.
C23 C $0.6439(3) 0.65783(16) 0.23063(12) 0.0969(10)$ Uani 11 d.
.
н29 н 0.71590 .67220 .25080 .145 Uiso 11 calc R. .
н30 н 0.58080 .69310 .23110 .145 Uiso 11 calc R. .
H31 н 0.66570 .65130 .19790 .145 Uiso 11 calc R . .
C24 C $0.4867(3) 0.5621(2) 0.21688(13) 0.1071(11)$ Uani $11 \mathrm{~d} .$.
н32 н 0.51470 .54980 .18590 .161 Uiso 11 calc R. .
н33 н 0.42390 .59760 .21250 .161 Uiso 11 calc R. .
н34 н 0.45280 .52150 .23140 .161 Uiso 11 calc R . .
C25 C 0.73311(19) 0.45539(10) 0.15147(7) 0.0481(4) Uani 11 d.

H21 н 0.67350 .49250 .14390 .058 Uiso 11 calc R . .
H22 н 0.78560 .45280 .12460 .058 Uiso 11 calc R . .
C26 C 1.0019(2) 0.19572(14) -0.15732(8) 0.0674(6) Uani 11 d. .
H1 H $1.05980 .2121-0.17770 .081$ Uiso 11 calc R . . C27 C $0.7493(3) 0.29497(13) 0.14613(11) 0.0800(7)$ Uani 11 d. н38 н 0.78990 .29900 .11660 .120 Uiso 11 calc R. .
H39 н 0.70040 .25300 .14520 .120 Uiso 11 calc R . .
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C28 C $0.5706(3) 0.36046(16) 0.21065(10) 0.0862(9)$ Uani $11 \mathrm{~d} .$.
H41 н 0.63360 .35440 .23700 .129 Uiso 11 calc R. .
H42 H 0.51820 .31990 .20810 .129 Uiso 11 calc R. .
H43 H 0.52160 .40090 .21670 .129 Uiso 11 calc R . .
C29 C 0.83345(19) 0.14961(11) -0.09616(8) 0.0531(5) Uani 11 d.
C30 C $0.8359(3) 0.11952(14)-0.14156(9) 0.0739(7) \operatorname{Uani} 11 \mathrm{~d}$.
н3 н $0.78070 .0838-0.15110 .089$ Uiso 11 calc R. .
C31 C 0.9203(3) 0.14269(16) -0.17259(9) 0.0840(8) Uani $11 \mathrm{~d} .$.
н2 н $0.92270 .1231-0.20330 .101$ Uiso 11 calc R . .
C32 C 1.07420(17) 0.27920(11) -0.09106(7) 0.0477(4) Uani 11 d. C33 C $1.1576(2) 0.35876(12)-0.03908(9) 0.0600(6)$ Uani $11 \mathrm{~d} .$. C34 C $1.2106(3) 0.36540(16)-0.08855(10) 0.0860(9)$ Uani 11 d.

H11 H $1.18350 .4087-0.10440 .103$ Uiso 11 calc R. .
H12 н $1.30070 .3648-0.08480 .103$ Uiso 11 calc R..
C35 C $1.2543(2) 0.33342(17)-0.00018(10) 0.0871(9)$ Uani 11 d. .
H68 H 1.21480 .32230 .02880 .131 Uiso 11 calc R. .
H69 н 1.31490 .36950 .00690 .131 Uiso 11 calc R. .
н70 H $1.29430 .2924-0.01150 .131$ Uiso 11 calc R. .
C36 C $1.0996(3) 0.42628(15)-0.02325(14) 0.1038(11)$ Uani $11 d$.
H71 H $1.03840 .4418-0.04820 .156$ Uiso 1 calc R. .
H72 н $1.16280 .4614-0.01790 .156$ Uiso 11 calc R. .
н73 н 1.06080 .41850 .00640 .156 Uiso 11 calc R. .
C37 C $0.75060(19) 0.13032(11)-0.06012(9) 0.0557(5)$ Uani 11 d. C38 C $0.6575(2) 0.12814(14) 0.00938(10) 0.0721(7)$ Uani 11 d. C39 C $0.5993(3) 0.07554(19)-0.02706(13) 0.1118(12)$ Uani 11 d. H13 н $0.60640 .0286-0.01380 .134$ Uiso 11 calc R. .

H14 H $0.51200 .0860-0.03450 .134$ Uiso 1 calc R . .
$\mathrm{C} 40 \mathrm{C} 0.7162(3) 0.0917(2) \quad 0.05419(14) 0.1344(16) \mathrm{Uani} 11 \mathrm{~d} . \quad$. H74 H 0.77380 .05700 .04470 .202 Uiso 1 calc R . .
H75 H 0.65270 .06950 .07110 .202 Uiso 1 1 calc R . .
H76 H 0.75920 .12530 .07520 .202 Uiso 1 calc R . .
C41 C 0.5876(3) 0.43808(18) -0.04576(14) 0.1197(13) Uani 11 d .
H62 H $0.53140 .4214-0.02320 .179$ Uiso 11 calc R . .
H63 H $0.54120 .4541-0.07480 .179$ Uiso 11 calc R . .
H64 H $0.63580 .4760-0.03130 .179$ Uiso 11 calc R . .
C42 C 0.5913(3) 0.29825(16) $-0.09216(13) 0.1120(12)$ Uani 11 d .
H65 H $0.64120 .2623-0.10510 .168$ Uiso 11 calc R. .
H66 H $0.54020 .3197-0.11820 .168$ Uiso 11 calc R . .
H67 H $0.53950 .2780-0.06920 .168$ Uiso 11 calc R . .
C43 C $0.78688(19) 0.33042(11)-0.00793(8) 0.0529(5)$ Uani 11 d .
H15 н 0.72950 .31800 .01590 .063 Uiso 11 calc R . .
H16 H 0.83740 .36860 .00590 .063 Uiso 11 calc R . .
$\mathrm{C} 44 \mathrm{C} 0.9495(3) 0.6323(2) 0.31414(12) 0.1148(13) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
H44 H 0.89290 .66670 .29990 .172 Uiso 11 calc R. .
H45 H 1.00020 .65300 .34060 .172 Uiso 11 calc R . .
H46 H 0.90350 .59390 .32610 .172 Uiso 1 1 calc R . .
C45 C 1.1621(3) 0.67191(17) 0.25603(14) 0.1123(12) Uani 11 d.
H47 H 1. 20380.66110 .22750 .168 Uiso 1 calc R . .
H48 H 1. 22210.67620 .28350 .168 Uiso 11 calc R . .
H49 H 1.11780 .71520 .25120 .168 Uiso 11 calc R . .
C46 C $1.1455(3) 0.52853(14) 0.29662(11) 0.0875(9)$ Uani $11 d$.
H50 H 1.09240 .49100 .30510 .131 Uiso 11 calc R . .
H51 H 1. 19100.54590 .32550 .131 Uiso 11 calc R . .
H52 H 1. 20260.51170 .27440 .131 Uiso 11 calc R . .
C51 C 0.95728(18) 0.57308(10) 0.21149(7) 0.0473(4) Uani 11 d.
-
H19 H 1.01440 .56530 .18670 .057 Uiso 11 calc R . .
H20 H 0.90500 .61230 .20080 .057 Uiso 11 calc R . .
C50 C $1.00755(19) 0.21087(11) 0.04750(7) 0.0518(5)$ Uani 11 d.
H17 H 1.05160 .25120 .06150 .062 Uiso 11 calc R . .
H18 H 0.94890 .19680 .07040 .062 Uiso 1 1 calc R . .
$\mathrm{C} 47 \mathrm{C} 1.1854(3) 0.12877(15)-0.01455(9) 0.0812(8) \mathrm{Uani} 11 \mathrm{~d}$.
H53 H $1.12010 .1140-0.03800 .122$ Uiso 11 calc R . .
H54 H $1.25000 .0942-0.01210 .122$ Uiso 11 calc R . .
H55 H $1.21860 .1725-0.02460 .122$ Uiso 11 calc R . .
C48 C $1.2594(3) 0.1572(2) 0.09076(12) 0.1160(13)$ Uani $11 \mathrm{~d} . \quad$.
H56 H 1. 29970.19960 .08200 .174 Uiso 11 calc R. .

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H57 H 1.3168 0.1190 0.0903 0.174 Uiso 1 1 calc R . .
H58 H 1.2320 0.1620 0.1228 0.174 Uiso 1 1 calc R . .
C49 C 1.0573(3) 0.05329(16) 0.06225(14) 0.1134(13) Uani 1 1 d . .
H59 H 1.0269 0.0560 0.0939 0.170 Uiso 1 1 calc R . .
H60 H 1.1212 0.0184 0.0624 0.170 Uiso 1 1 calc R . .
H61 H 0.9903 0.0410 0.0387 0.170 Uiso 1 1 calc R . .
C52 C 0.5680(3) 0.1826(2) 0.02286(18) 0.1388(17) Uani 1 1 d . . .
H77 H 0.6103 0.2161 0.0442 0.208 Uiso 1 1 calc R . .
H78 H 0.5027 0.1610 0.0391 0.208 Uiso 1 1 calc R . .
H79 H 0.5332 0.2058 -0.0060 0.208 Uiso 1 1 calc R . .
C53 C 0.7925(3) 0.4001(3) -0.10727(14) 0.1477(19) Uani 1 1 d . .
H80 H 0.8477 0.4349 -0.0926 0.222 Uiso 1 1 calc R . .
H81 H 0.7410 0.4208 -0.1334 0.222 Uiso 1 1 calc R . .
H82 H 0.8400 0.3627 -0.1197 0.222 Uiso 1 1 calc R . .
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0.00092(11)
Fe2 0.04610(16) 0.04834(17) 0.03943(16) -0.00079(12) 0.00344(12)
0.00422(12)
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0.0346(10)
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0.0373(10)
N7 0.0515(9) 0.0463(9) 0.0418(9) 0.0046(7) 0.0023(7) -0.0011(7)
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N9 0.0448(8) 0.0449(8) 0.0407(8) -0.0007(7) 0.0047(7) -0.0006(7)
N10 0.0486(9) 0.0563(10) 0.0488(10) -0.0011(8) 0.0040(8)
0.0079(8)
N11 0.0448(8) 0.0511(9) 0.0454(9) 0.0023(7) 0.0010(7) -0.0049(7)
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N12 0.0503(9) 0.0556(10) 0.0579(11) 0.0049(9) 0.0117(8) -
0.0056(8)
C8 0.0627(12) 0.0433(11) 0.0565(12) 0.0088(9) -0.0038(10) -
0.0002(9)
C9 0.0899(17) 0.0560(14) 0.0724(16) 0.0216(12) -0.0051(14)
0.0029(13)
C10 0.118(2) 0.0816(18) 0.0548(15) 0.0273(14) 0.0004(15) -
0.0071(17)
C11 0.0888(17) 0.0841(18) 0.0475(13) 0.0091(12) 0.0142(12) -
0.0114(15)
C12 0.0599(12) 0.0617(13) 0.0415(11) 0.0020(10) 0.0057(9) -
0.0080(10)
C13 0.0579(12) 0.0398(11) 0.0758(15) 0.0033(10) 0.0006(11)
0.0097(9)
C14 0.0640(13) 0.0583(13) 0.0814(17) -0.0073(12) 0.0222(12)
0.0147(11)
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0.0021(15)
C16 0.097(2) 0.096(2) 0.0790(19) -0.0205(16) 0.0311(16)
0.0048(17)
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0.0002(10)
C19 0.0767(17) 0.095(2) 0.0821(19) -0.0106(16) -0.0132(14) -
0.0171(15)
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0.0032(9)
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C22 0.0573(13) 0.0791(16) 0.0675(15) -0.0068(13) 0.0078(11)
0.0246(12)
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C24 0.0626(16) 0.132(3) 0.122(3) -0.022(2) -0.0186(17) 0.0319(18)
C25 0.0531(11) 0.0493(11) 0.0413(10) 0.0007(9) 0.0000(8) -
0.0043(9)
C26 0.0737(15) 0.0832(17) 0.0471(12) -0.0047(12) 0.0161(11) -
0.0043(13)
C27 0.0840(17) 0.0556(14) 0.101(2) 0.0007(14) 0.0092(15) -
0.0081(13)
C28 0.097(2) 0.095(2) 0.0691(16) -0.0068(15) 0.0273(15) -
0.0388(17)
C29 0.0570(12) 0.0487(11) 0.0530(12) -0.0071(9) 0.0017(9) -
0.0055(9)
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0.0174(13)
C31 0.106(2) 0.095(2) 0.0523(14) -0.0277(14) 0.0161(14) -
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0.0006(9)
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C33 0.0522(12) 0.0607(13) 0.0661(14) 0.0047(11) -0.0010(10) -
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C34 0.0877(18) 0.098(2) 0.0720(17) 0.0119(15) 0.0066(14) -
0.0426(16)
C35 0.0690(16) 0.110(2) 0.0780(18) 0.0118(16) -0.0181(13) -
0.0276(16)
C36 0.091(2) 0.0646(17) 0.155(3) -0.0207(19) 0.000(2) -0.0132(15)
C37 0.0525(11) 0.0466(11) 0.0682(14) -0.0007(10) 0.0059(10) -
0.0094(9)
C38 0.0603(13) 0.0755(16) 0.0832(17) 0.0102(14) 0.0230(13) -
0.0151(12)
C39 0.099(2) 0.122(3) 0.118(3) -0.002(2) 0.034(2) -0.053(2)
C40 0.112(3) 0.174(4) 0.119(3) 0.079(3) 0.016(2) -0.029(3)
C41 0.118(3) 0.093(2) 0.142(3) -0.013(2) -0.024(2) 0.051(2)
C42 0.123(3) 0.0790(19) 0.122(3) -0.0030(19) -0.062(2) 0.0023(18)
C43 0.0534(11) 0.0520(11) 0.0537(12) -0.0018(9) 0.0072(9)
0.0049(9)
C44 0.0793(19) 0.170(4) 0.092(2) -0.071(2) -0.0094(16) 0.014(2)
C45 0.112(2) 0.087(2) 0.130(3) 0.013(2) -0.037(2) -0.0470(19)
C46 0.097(2) 0.0656(16) 0.091(2) -0.0062(14) -0.0402(17)
0.0109(14)
C51 0.0496(10) 0.0421(10) 0.0497(11) 0.0015(8) 0.0011(9) -
0.0011(8)
C50 0.0577(12) 0.0585(12) 0.0390(10) 0.0004(9) 0.0030(9)
0.0062(10)
C47 0.0905(18) 0.0895(19) 0.0665(16) 0.0100(14) 0.0244(14)
0.0342(15)
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C49 0.131(3) 0.0750(19) 0.144(3) 0.027(2) 0.067(3) 0.0209(19)
C52 0.099(2) 0.116(3) 0.216(5) 0.017(3) 0.097(3) 0.004(2)
C53 0.086(2) 0.244(5) 0.112(3) 0.109(3) 0.002(2) -0.005(3)
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;
All esds (except the esd in the dihedral angle between two l.s.
planes)
are estimated using the full covariance matrix. The cell esds
are taken
        into account individually in the estimation of esds in
distances, angles
and torsion angles; correlations between esds in cell parameters
are only
    used when they are defined by crystal symmetry. An approximate
(isotropic)
    treatment of cell esds is used for estimating esds involving
l.s. planes.
;
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Fe1 N10 2.2599(16) . ?
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Fe2 C50 2.072(2) . ?
Fe2 N12 2.2796(17) . ?
Fe2 N11 2.2949(16) . ?
Si3 C51 1.842(2) . ?
Si3 C44 1.857(3) . ?
Si3 C46 1.858(3) . ?
Si3 C45 1.875(3) . ?
Si4 C25 1.844(2) . ?
Si4 C28 1.873(2) . ?
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Si4 C27 1.877(3) . ?
Si5 C50 1.839(2) . ?
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Si5 C47 1.871(2) . ?
Si5 C48 1.878(3) . ?
Si6 C43 1.838(2) . ?
Si6 C53 1.848(3) . ?
Si6 C42 1.857(3) . ?
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O5 C34 1.441(3) . ?
O6 C37 1.344(2) . ?
O6 C39 1.429(4) . ?
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N9 C20 1.373(2) . ?
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N10 C22 1.498(3) . ?
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C8 C13 1.432(3) . ?
C9 C10 1.384(4) . ?
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C10 H5 0.9300 . ?
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C14 C16 1.522(4) . ?
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C15 H25 0.9600 . ?
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C50 H17 0.9700 . ?
C50 H18 0.9700 . ?
C47 H53 0.9600 . ?
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C25 Si4 C28 112.19(11) . . ?
C25 Si4 C19 112.65(11) . . ?
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C28 Si4 C27 106.52(14) . . ?
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C50 Si5 C49 112.52(13) . . ?
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C13 O2 C17 104.18(19) . . ?
C32 O5 C34 104.68(17) . . ?
C37 06 C39 105.1(2) . . ?
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C8 N7 Fe1 121.09(14) . . ?
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C13 N8 Fe1 111.24(14) . . ?
C14 N8 Fe1 141.81(14) . . ?
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C18 N10 Fe1 111.28(14) . . ?
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C32 N11 Fe2 110.40(13) . . ?
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N7 C8 C13 111.16(17) . . ?
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C14 C17 H7 110.9 . . ?
O2 C17 H8 110.9 . . ?
C14 C17 H8 110.9 . . ?
H7 C17 H8 108.9 . . ?
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Si4 C19 H36 109.5 . . ?
H35 C19 H36 109.5 . . ?
Si4 C19 H37 109.5 . . ?
H35 C19 H37 109.5 . . ?
H36 C19 H37 109.5 . . ?
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C26 C20 C32 125.50(19) . . ?
N9 C20 C32 111.75(17) . . ?
O1 C21 C22 105.4(2) . . ?
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C22 C21 H9 110.7 . . ?
O1 C21 H10 110.7 . . ?
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H9 C21 H10 108.8 . . ?
N10 C22 C24 108.6(2) . . ?
N10 C22 C23 111.4(2) . . ?
C24 C22 C23 111.4(3) . . ?
N10 C22 C21 101.2(2) . . ?
C24 C22 C21 112.2(2) . . ?
C23 C22 C21 111.7(3) . . ?
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H29 C23 H30 109.5 . . ?
C22 C23 H31 109.5 . . ?
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H30 C23 H31 109.5 . . ?
C22 C24 H32 109.5 . . ?
C22 C24 H33 109.5 . . ?
H32 C24 H33 109.5 . . ?
C22 C24 H34 109.5 . . ?
H32 C24 H34 109.5 . . ?
H33 C24 H34 109.5 . . ?
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Si4 C25 H21 107.4 . . ?
Fe1 C25 H21 107.4 . . ?
Si4 C25 H22 107.4 . . ?
Fe1 C25 H22 107.4 . . ?
H21 C25 H22 107.0 . . ?
C20 C26 C31 119.3(2) . . ?
C20 C26 H1 120.3 . . ?
C31 C26 H1 120.3 . . ?
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H39 C27 H40 109.5 . . ?
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Si4 C28 H42 109.5 . . ?
H41 C28 H42 109.5 . . ?
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Fe2 C43 H16 107.1 . . ?
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Si3 C45 H47 109.5 . . ?
Si3 C45 H48 109.5 . . ?
H47 C45 H48 109.5 . . ?
Si3 C45 H49 109.5 . . ?
H47 C45 H49 109.5 . . ?
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'-x, y+1/2, -z+1/2'
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expression of
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etc. and is
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N1 N 0.7346(4) 0.1924(2) 0.16948(19) 0.0594(9) Uani 1 1 d . . .
C11 C 0.9662(6) 0.0720(5) 0.0575(4) 0.101(2) Uani 1 1 d . . .
H111 H 0.9234 0.0589 0.0139 0.151 Uiso 1 1 calc R . .
H112 H 1.0090 0.0181 0.0729 0.151 Uiso 1 1 calc R . .
H113 H 1.0233 0.1209 0.0494 0.151 Uiso 1 1 calc R . .
C12 C 0.8763(4) 0.1008(4) 0.1145(3) 0.0659(12) Uani 1 1 d . . .
C13 C 0.8138(4) 0.1863(3) 0.1123(3) 0.0667(13) Uani 1 1 d . . .
C14 C 0.8197(6) 0.2580(4) 0.0631(3) 0.0835(17) Uani 1 1 d . . .
H14 H 0.8733 0.2552 0.0246 0.100 Uiso 1 1 calc R . .
C15 C 0.7446(7) 0.3335(4) 0.0723(3) 0.098(2) Uani 1 1 d . . .
H15 H 0.7483 0.3814 0.0394 0.117 Uiso 1 1 calc R . .
C16 C 0.6652(6) 0.3394(4) 0.1282(3) 0.0807(16) Uani 1 1 d . . .
H16 H 0.6143 0.3900 0.1330 0.097 Uiso 1 1 calc R . .
C17 C 0.6620(4) 0.2689(3) 0.1776(3) 0.0627(12) Uani 1 1 d . . .
C18 C 0.5903(4) 0.2585(3) 0.2424(3) 0.0608(12) Uani 1 1 d . . .
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C19 C 0.4995(5) 0.3290(4) 0.2663(4) 0.0831(15) Uani $11 \mathrm{~d} . \quad . \quad$ H191 H 0.42560 .29890 .28040 .125 Uiso 1 1 calc R . .
H192 H 0.48290 .37050 .22760 .125 Uiso 1 1 calc R . .
H193 H 0.53190 .36260 .30610 .125 Uiso 1 1 calc R . .
N2 N $0.8444(3) 0.0486(3) 0.1702(2) \quad 0.0610(10)$ Uani $11 d$. . .
C21 C 0.8935 (4) -0.0443(4) 0.1772 (3) 0.0642 (12) Uani $11 \mathrm{~d} . \quad$.
$\mathrm{C} 22 \mathrm{C} 0.8262(5)-0.1163(4) 0.1488(3) 0.0723(14)$ Uani $11 \mathrm{~d} . \quad$.
C23 C $0.8662(9)-0.2052(5) \quad 0.1612(4) \quad 0.120(3) \quad$ Uani $11 d$. . .
H23 H $0.8219-0.25440 .14310 .145$ Uiso 1 1 calc R.
$\mathrm{C} 24 \mathrm{C} 1.0301(14) 0.2785(9) 0.3003(6) 0.175(6) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
H24 H 1.00350 .21860 .29290 .210 Uiso 11 calc R . .
C25 C $0.9660(9) 0.3504(8) 0.2729(6) \quad 0.150(4)$ Uani 11 d . . .
H 25 H 0.89600 .33970 .24630 .180 Uiso 11 calc R . .
C26 C $0.9951(6)-0.0610(6) 0.2155(4) 0.105(2)$ Uani $11 d$. . .
$\mathrm{C} 27 \mathrm{C} 0.7132(6)-0.0979(4) 0.1046(3) 0.0929(17) \mathrm{Uani} 11 \mathrm{~d} . \quad$.
H271 H $0.6642-0.05230 .12800 .139$ Uiso 1 calc R . .
H272 H $0.6673-0.15360 .09970 .139$ Uiso 11 calc R . .
H273 H $0.7366-0.07600 .05820 .139$ Uiso 11 calc R . .
$\mathrm{C} 28 \mathrm{C} 1.0690(7) 0.0189(7) 0.2434(6) 0.159(4) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
H281 H 1.01910 .05620 .27390 .238 Uiso 11 calc R. .
H282 H 1.09750 .05520 .20400 .238 Uiso 1 1 calc R . .
H283 H $1.1373-0.00380 .27010 .238$ Uiso 1 1 calc R . .
N3 N $0.6136(3) 0.1804(3) 0.2766(2) 0.0572(9)$ Uani $11 \mathrm{~d} . \quad . \quad$.
C31 C 0.5450(4) 0.1616(3) 0.3403(3) 0.0598(12) Uani $11 \mathrm{~d} . \quad$.
C32 C $0.4354(5) 0.1114(4) 0.3336(3) 0.0750(15)$ Uani $11 \mathrm{~d} . \quad$.
C33 C $0.3695(6) 0.0940(5) 0.3943(5) 0.100(2)$ Uani $11 \mathrm{~d} . \quad$.
H33 H 0.29610 .06250 .39070 .120 Uiso 11 calc R
C34 C 0.4083(9) 0.1213(6) 0.4587(5) 0.112(3) Uani $11 \mathrm{~d} . \quad$.
H34 H 0.36180 .10730 .49880 .134 Uiso 11 calc R.
C35 C 0.5146(9) 0.1691(5) 0.4672(3) 0.110(3) Uani $11 \mathrm{~d} . \quad . \quad$.
H35 H 0.53880 .18770 .51260 .131 Uiso 11 calc R .
C36 C 0.5886(6) 0.1906(4) 0.4064(3) 0.0823(16) Uani $11 \mathrm{~d} . \quad . \quad$.
C37 C 0.3919(5) 0.0837(4) 0.2593(4) 0.0989(19) Uani $11 \mathrm{~d} . \quad$.
H371 H 0.3403 0.03070 .26300 .148 Uiso 11 calc R . .
H372 H 0.46090 .06940 .22980 .148 Uiso 11 calc R . .
H373 H 0.34720 .13350 .23830 .148 Uiso 1 1 calc R . .
C38 C 0.7023(7) 0.2438(6) 0.4123(4) 0.119(3) Uani $11 \mathrm{~d} . \quad$.
H381 H 0.76460 .21480 .38420 .178 Uiso 1 1 calc R . .
H382 H 0.72740 .24620 .46140 .178 Uiso 1 1 calc R . .
H383 H 0.68900 .30510 .39500 .178 Uiso 1 1 calc R . .
$\mathrm{N} 4 \mathrm{~N} 0.7265(5) 0.0140(3) 0.2972(2) 0.0838(13) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
C41 C 0.7431(5) -0.0438(4) 0.3468(3) 0.0802(15) Uani $11 d$. . .
H41 H 0.6928-0.0951 0.3482 0.096 Uiso 1 1 calc R .
C42 C 0.8387(6) -0.0350(4) 0.4035(3) 0.0828(16) Uani $11 \mathrm{~d} . \quad$.
C43 C $0.8523(6)-0.1038(5) 0.4542(3) 0.0967(19)$ Uani $11 \mathrm{~d} . \quad$.
H43 H $0.8016-0.15490 .45280 .116$ Uiso 11 calc R . .
$\mathrm{C} 44 \mathrm{C} 0.9417(7)-0.0969(6) 0.5075(3) 0.100(2) \mathrm{Uani} 11 \mathrm{~d} . \quad . \quad$.
H44 H 0.9516-0.1440 0.5406 0.120 Uiso 11 calc R. .

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C45 C 1.0145(6) -0.0204(6) 0.5105(4) 0.100(2) Uani 1 1 d . . .
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C46 C $1.0021(8) 0.0472(6) 0.4620(5) 0.120(3)$ Uani $11 \mathrm{~d} .$.
H46 H 1.05290 .09820 .46410 .144 Uiso 11 calc R . .
C47 C $0.9144(7) 0.0416(5) 0.4088(4) 0.102(2)$ Uani $11 \mathrm{~d} .$.
H47 H 0.90590 .08950 .37630 .122 Uiso 11 calc R . .
Cl4 Cl 1.1254(2) -0.0140(2) 0.57662(11) 0.1525(10) Uani 11 d.
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N1 $0.062(2) \quad 0.052(2) 0.064(2)-0.0032(17) \quad 0.002(2)-0.0009(19)$
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C12 $0.061(2) \quad 0.059(3) \quad 0.078(3)-0.003(3) 0.018(2)-0.011(3)$
C13 0.065(3) 0.056(3) 0.079(3) 0.004(3) 0.009(3) -0.012(2)
C14 0.109(4) 0.059(3) 0.083(4) 0.010(3) 0.018(3) -0.025(3)
C15 0.143(6) 0.059(3) 0.091(4) 0.018(3) 0.019(4) -0.014(4)
C16 0.100(4) 0.051(3) 0.090(4) 0.014(3) -0.003(3) 0.000(3)
C17 0.068(3) 0.048(3) 0.071(3) 0.005(2) 0.001(3) -0.005(2)
C18 0.068(3) 0.044(2) 0.070(3) 0.001(2) 0.000(2) 0.006(2)
C19 0.097(4) 0.063(3) 0.089(4) 0.006(3) 0.014(4) 0.022(3)
N2 $0.052(2) \quad 0.058(2) \quad 0.073(3)-0.005(2) \quad 0.0015(19)-0.0046(18)$
C21 0.057(3) 0.063(3) 0.072(3) 0.001(3) 0.003(2) 0.011(2)
C22 0.089(3) 0.056(3) 0.071(3) -0.005(3) 0.026(3) 0.001(3)
C23 0.191(9) 0.068(5) 0.102(5) 0.009(4) 0.075(6) 0.005(5)
C24 0.256(15) 0.148(10) 0.120(8) -0.038(7) 0.043(9) -0.124(10)
C25 0.132(7) 0.178(10) 0.139(8) 0.006(8) -0.019(6) -0.102(7)
$\mathrm{C} 260.071(4) 0.136(6) 0.108(5)-0.019(4)-0.010(4) 0.036(4)$
C27 0.100(4) 0.091(4) 0.088(4) -0.010(4) 0.008(3)-0.036(4)
C28 0.080(4) 0.199(10) 0.197(10) -0.044(8) -0.039(6) 0.003(5)
N3 $0.061(2) \quad 0.055(2) \quad 0.056(2)-0.0007(18)-0.0013(19)-0.0026(16)$
$\mathrm{C} 310.061(3) 0.057(3) 0.062(3) 0.004(2) 0.004(2) 0.016(2)$
C32 0.068(3) 0.063(3) 0.094(4) 0.016(3) 0.017(3) 0.014(3)
C33 0.090(4) 0.071(4) 0.138(6) 0.018(5) 0.043(4) 0.020(4)
C34 0.132(6) 0.090(6) 0.113(6) 0.034(5) 0.051(5) 0.051(5)
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C36 0.095(4) 0.078(4) 0.074(4) -0.003(3) -0.004(3) 0.020(3)
C37 0.083(3) 0.093(4) 0.121(5) -0.016(4) -0.015(4) -0.015(3)
C38 0.136(7) 0.127(6) 0.093(5) -0.035(4) -0.031(4) 0.007(5)
N4 0.107(3) 0.067(3) 0.077(3) 0.015(2) 0.023(3) 0.044(3)
C41 0.080(4) 0.065(3) 0.096(4) 0.012(3) 0.004(3) 0.008(3)
C42 0.092(4) 0.074(4) 0.083(4) 0.017(3) 0.010(3) 0.004(3)

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C43 0.110(5) 0.085(4) 0.095(4) 0.031(4) 0.020(4) 0.023(4)
C44 0.108(5) 0.118(6) 0.074(4) 0.021(4) 0.013(4) 0.036(5)
C45 0.090(4) 0.130(7) 0.079(4) -0.005(4) 0.019(4) 0.014(4)
C46 0.108(6) 0.127(7) 0.125(7) 0.026(6) 0.013(5) -0.002(5)
C47 0.109(5) 0.091(5) 0.105(5) 0.021(4) 0.011(4) 0.004(4)
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0.0377(18)
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distances, angles
    and torsion angles; correlations between esds in cell parameters
are only
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l.s. planes.
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Co1 N3 1.899(4) . ?
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C11 H112 0.9600 . ?
C11 H113 0.9600 . ?
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C18 N3 C31 117.5(4) . . ?
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C41 N4 Col 169.9(5) . . ?
N4 C41 C42 124.3(6) . . ?
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```


[^0]:    ${ }^{\text {I }}$ Roles of MAO: 1) scavenging catalyst poisons (water, $\mathrm{O}_{2}$ etc.); 2) generating active species by reacting with catalyst. And so on.

[^1]:    ${ }^{\text {II }}$ The activities of iron catalysts were in many cases comparable or even higher than those of metallocenes under analogous conditions reported by Gibson ${ }^{17}$ and comparable to the most active Ziegler-Natta systems reported by Brookhart. ${ }^{16}$

[^2]:    ${ }^{\text {III }}$ The two $\pi^{*}$ orbitals are labelled according to the symmetry with respect to the xz mirror plane.

[^3]:    ${ }^{\text {IV }}$ Modifications at 3,5-positions of central pyridine are normally not considered, because substituents at those positions will repulse imine-arms to make pyridine and imine arms not coplanar any more; as a result, the $\pi$-conjugate system is destroyed.
    ${ }^{\mathrm{V}}$ Other transition metal complexes have also been tried, but $\mathrm{Fe}, \mathrm{Co}$ and Cr are the most common ones.

[^4]:    ${ }^{\text {VI }}$ In this situation, the DIP ligand is trianion with one unpaired electron antiferromagnetically coupled to the low-spin cobalt(II).

[^5]:    ${ }^{\text {VII }}$ Fermi contact interaction refers to the spin-spin coupling between the electron and the nucleus when the electron formally is inside the nucleus. Pseudo-contact interaction is the dipolar interaction between the magnetic moments of the electron and the nucleus when the electron is outside of the nucleus.

[^6]:    ${ }^{\text {VIII }}$ Refers to Coulomb and exchange integrals in Eq. 2.10.

[^7]:    x a) Orbitals of "paired" spins are allowed to be spatially different. For further details, see 1) Noodleman, L. Chem. Phys. 1981, 74, 5737. 2) Noodleman, L.; Davidson, E.R. Chem. Phys. 1986, 109, 131. b) The broken symmetry treatment typically results in energies that are significantly lower than those from doubly-occupied restricted calculations.

[^8]:    ${ }^{\mathrm{XI}}$ This methodology is to deduce the "pure" energy from the "spin-contaminated" energy.

    XII One determinant in the expression of DFT wave functions is called single configuration. A configuration which is used as the basis to generate other excited configurations is called a reference. DFT/MRCI seems to work well for organic olefins, but the validity in computing transition metal complexes is not yet clear.
    ${ }^{\text {XIII }}$ The main systems studied by the fractional occupancy approach are simple organic systems and compounds.

[^9]:    ${ }^{\text {xiv }}$ Corresponding triplet: related to the broken-symmetry solution by a single spin flip.

[^10]:    xv Turnstile rotation or " 3 vs 2 rotation" looks superficially different, but is in fact equivalent to pseudorotation. So there is no need to define a separate reaction coordinate for turnstile rotation.

[^11]:    ${ }^{\text {XVIII }}$ The metal deviation out of $\mathrm{N}_{3}$ plane follows automatically the trend of the tilting of the $\mathrm{MCl}_{2}$ unit, as Figure A. 2 shows.

[^12]:    ${ }^{\mathrm{XX}} \mathrm{Cr}^{2+}$ was expected to have the same geometry preference as $\mathrm{Cu}^{2+}$. The reason why it does not show SP preference as $\mathrm{Cu}^{2+}$ does here is not so clear. One possible reason is that, as Figure 4.11 indicates, the $\pi$-basicity of $\mathrm{Cr}^{2+}$ is not negligible; as a result, a significant amount of electron might transfer from $\mathrm{Cr}^{2+}$ to the DIP ligand, which might lead to the unexpected geometry preference here.
    ${ }^{\mathrm{xxI}}$ Although there are no degenerate orbitals in these systems, two orbitals, of which energies are close, are to be distorted.

[^13]:    ${ }^{\text {xxiv }}$ The information here will be used to estimate the $\alpha(\mathrm{CoMe})$ later.

[^14]:    xxviI According to Figure 4.4, the strength of $\pi$-basicity of CoMe is similar to that of Lewis acidity of $\mathrm{ZnCl}_{2}$, thus I think $\alpha(\mathrm{CoMe})$ is reasonably assumed to be less than 0.5 . As Figure 4.5 clearly shows that Lewis acidity of CoMe cannot be neglected in their DIP complexes, so I think $\alpha(\mathrm{CoMe})$ can be reasonably regarded as higher than 0.15 .

[^15]:    Xxx The synthesis of $(\mathrm{Py})_{2} \mathrm{CoPh}_{2}$ and $(\mathrm{Py})_{2} \mathrm{CoMe}_{2}$ using the same synthesis procedure for $(\mathrm{Py})_{2} \mathrm{Co}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{2}$ was not successful. For experimental details, see Section 9.3 in Chapter 9.

[^16]:    ${ }^{\text {a }}$ Geometry was optimized at b3-lyp/TZVP. R: - $\mathrm{CH}_{2} \mathrm{SiMe}_{3} ; \mathrm{R}^{\prime}:-\mathrm{CH}_{2} \mathrm{C}\left(\mathrm{Me}_{2}\right) \mathrm{Ph}$;
    ${ }^{\mathrm{b}}$ correction to the published data.

[^17]:    xxxII Figures, part of tables, part of schemes and part of the texts of the corresponding

[^18]:    ${ }^{\mathrm{a}} \mathrm{CoCH}_{2}$ and $\mathrm{FeCH} \mathrm{H}_{2}$ were not observed, probably due to the broadness of the peaks and the large chemical shift induced directly by iron and cobalt. ${ }^{\text {b }}$ (6) $\mathrm{FeR}_{2}$ was studied in Chapter 3.

[^19]:    ${ }^{x x x v}$ In the normal calculation of the equilibrium constant for an equilibrium reaction, the absolute error is hard to judge only based on the functional and the basis set. The only way to determine this is to compare with experimental data. Here the equilibrium constant obtained from ${ }^{1} \mathrm{H}$ NMR has itself a certain experimental error margin (normally $\sim 5 \%$ ) and the result from b3-lyp calculation is very close to the experimental value. In addition, the error associated with the spin state change in DFT calculation is normally quite large, which is the case in b-p calculation. Within acceptable error margin, I believe the result from the b3-lyp calculation is consistent with the experimental value.

[^20]:    ${ }^{\text {a }}$ For Co complexes of $\mathbf{6}$, the Gaussian 03 SCF calculations needed for calculating $\delta^{\text {orb }}$ did not converge, therefore we used the values calculated for the free ligand and for the $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ group in (TMEDA) $\mathrm{CoR}_{2}$. The errors this introduces should be of the order of $1-2 \mathrm{ppm}$, which is small relative to the $\delta^{\mathrm{FC}}$ contribution.

[^21]:    xxxviII The error margin is $\pm 4 \mathrm{~cm}^{-1}$ in the IR measurement of the KBr pellet here. In addition, the difference of the NN stretching frequency by the KBr pellet measurement from that in toluene solution is expected. Thus the $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ made from hydrogenolysis or Na-amalgam are considered to be same.

    XXXIX The eelectronic structure of $(\mathbf{1}) \mathrm{Co}\left(\mathrm{N}_{2}\right)$ is describes as the low-spin cobalt(I) bound to the ligand anion.

[^22]:    ${ }^{\mathrm{XL}}$ The ${ }^{1} \mathrm{H}$ NMR spectrum of an immediate mixture of (1)CoR and $\mathrm{PhC} \equiv \mathrm{CH}$ (1:1 ratio) showed that two products $((\mathbf{1}) \mathrm{CoC} \equiv \mathrm{CPh}$ and $(\mathbf{1}) \mathrm{CoC}(\mathrm{Ph})=\mathrm{C}(\mathrm{H}) \mathrm{C} \equiv \mathrm{CPh})$ were generated and there was still unreacted (1)CoR left. In contrast, 1:2 ratio of the two reactants led completely to one product $(\mathbf{1}) \mathrm{CoC}(\mathrm{Ph})=\mathrm{C}(\mathrm{H}) \mathrm{C} \equiv \mathrm{CPh}$. The further increase in the amount of $\mathrm{PhC} \equiv \mathrm{CH}$ did not affect the product.

[^23]:    ${ }^{\text {XLI }}$ See also Section 2.4.4 in Chapter 2.

[^24]:    ${ }^{\text {XLIII }}$ If MS database does not contain mass spectra for all of the regio-isomers of the expected product, or if it does not have any relevant mass spectrum of the expected product from these CC-coupling reactions, the regiochemistry of the product cannot be determined. However, the peak of the molecular ion and the information of fragment ions are useful for the identification of the product.

[^25]:    ${ }^{\text {a }}$ Electronic energies calculated using b3-lyp/TZVP or b-p86/TZVP; ZPE, enthalpy and entropy corrections for 298K, 1bar, gas phase, taken from SV(P) calculations

[^26]:    ${ }^{\text {a }}$ For Co complexes of $\mathbf{6}$, the Gaussian 03 SCF calculations needed for calculating $\delta{ }^{\text {orb }}$ did not converge, therefore we used the values calculated for the free ligand and (for the $\mathrm{CH}_{2} \mathrm{SiMe}_{3}$ group) (TMEDA)CoR ${ }_{2}$. The errors this introduces should be of the order of 12 ppm , which is small relative to the $\delta^{\mathrm{FC}}$ contribution.

