Non-innocence of the diiminepyridine ligand in its cobalt complexes

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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 ω 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 kcal/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 σ -donor and π -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 σ -donor and a strong π -acceptor, and inferior only to the bis(carbene)pyridine ligand. The strong π -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 (Py)₂Co(CH₂SiMe₃)₂ in this thesis is simple and easy to reproduce. This compound is stable at room temperature and can be further converted to (TMEDA)Co(CH₂SiMe₃)₂ in high yield. The X-ray structure of the analogous (Py)₂Co(CH₂CMe₂Ph)₂ showed a structure similar to its iron analog. Application to DIP ligands indicates that the π -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 $2,6-[2,6-Me_2C_6H_3N=C(CH_3)]_2C_5H_3N$ (L) ligand was explored in more detail. This ligand is less hindered than the often-used 2,6-¹Pr₂C₆H₃ ligand and might induce more interesting chemistry. Hydrogenolysis of $LCoCH_2SiMe_3$ 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 N₂ 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. $LCo(N_2)$ 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:

- Andrew Chalaturnyk wrote part of the code for the "calcGeom" program in Chapter 3.
- 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.
- 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
CCSD(T)	Coupled cluster with single and double substitution operators
CSD	Cambridge Structural Database
COSY	Correlation Spectroscopy
Ср	Cyclopentadienyl
DFT	Density Functional Theory
^{<i>i</i>Pr} ADIP	2,6-(RN=CMe) ₂ C ₅ H ₃ N, R = CHMe ₂ (i Pr)
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
МО	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
Ру	pyridine
QM	Quantum mechanics
SP	Square pyramid
SVP	Split valence polarization
SQUID	Superconducting Quantum Interference Device
TBP	Trigonal bipyramid
THF	Tetrahydrofuran
TMEDA	Tetramethylethylenediamine

TMS	Tetramethylsilane
TZVP	Triple Zeta Valence Plus Polarization
TZVPP	Valence triple-zeta plus polarization
VB	Valence bond
VWN	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 catalysts⁴ and metallocene catalysts.⁵

The Phillips catalyst was first discovered by Hogan and Banks of Phillips Petroleum in the 1950s: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 TiCl₃ or TiCl₄ supported on silica or MgCl₂ 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 Cp₂TiCl₂ activated by Et₃Al or Et₂AlCl.⁹ The discovery of MAO (methylaluminoxane) boosted the development of metallocene catalysts significantly^{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. Cp₂Ti⁺-R, Scheme 1.1),¹¹ while we are less sure about the active species in the heterogeneous Ziegler-Natta and Phillips catalysts.¹²

¹ Roles of MAO: 1) scavenging catalyst poisons (water, O_2 etc.); 2) generating active species by reacting with catalyst. And so on.



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 coworkers¹³ in 1995, although there were a few scattered reports dating before that time.¹⁴ Bulky α -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 can from the application of the diiiminepyridine (DIP) ligand in this field.^{15a} In 1998, Brookhart¹⁶ and Gibson¹⁷ 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^{II}. Since then, similar systems (Figure 1.1) have also been studied extensively.

^{II} The activities of iron catalysts were in many cases comparable or even higher than those of metallocenes under analogous conditions reported by Gibson¹⁷ and comparable to the most active Ziegler-Natta systems reported by Brookhart.¹⁶



M = Co, FeR = substituents

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.^{15b} 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 C-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)MX₂ (Chapter 3), ligand parameter studies of DIP type ligands (Chapter 4), synthesis exploration of the labile-ligand cobalt dialkyls (Chapter 5), their applications to the synthesis of DIP cobalt(I) monoalkyl complexes (Chapter 6), and binuclear oxidative addition of 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 P, N, O, 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, Co^{3+} is not stable in water because it is a strong enough oxidant to oxidize water to oxygen (standard reduction potential of Co^{3+}/Co^{2+} : 1.82 V). After being coordinated by ammonia, Co^{3+} is very stable in water and indeed $Co(NH_3)_6^{2+}$ is a very strong reductant (reduction potential of Co(NH₃)₆³⁺/Co(NH₃)₆²⁺: 0.1 V).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 (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.^{27a} Cp ligands are used mainly in metallocene or half-metallocene chemistry;⁵ the Cp ligand is a good ligand with strong σ -donor ability. DIP ligands (good π -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: σ -interactions and π -interactions (Figure 1.2). σ -Interactions exist in any complex while π -interactions have to go together with σ -interactions (to the best of my knowledge, there is no report of systems with only π -interactions and without σ interactions). In terms of the ligand, σ -interaction is usually σ -donation from ligand to metal, while depending on the position of lone-pair electrons, the π -interaction can be π donation (from ligand π -orbital to metal) or π -backdonation (from metal d non-bonding electrons to empty ligand π^* orbital).



 σ -interaction (head to head overlap)



 π -interaction (side by side overlap)

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. σ -Coordination of a ligand to a metal center will raise the d_{σ} orbital energy as shown schematically in Scheme 1.2 using NH₃ 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.^{27b}



Scheme 1.2. Interaction between metal d orbitals and ammonia

Where ligands have the ability to participate in both σ and π 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 d_{σ} orbital; as a result, it will raise the energy of this orbital. On the other hand, each π^* orbital of CO is close in energy to one of the other metal d_{π} 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 d_{π} orbital and CO π^* orbital are quite large. Thus, the energy gap between HOMO (d_{π} orbital lowered by π -interaction) and LUMO (d_{σ} orbital raised by σ -interaction) will be larger than for a ligand with only σ -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 π -interaction is between orbitals having relatively small overlap, due to the large spread of π^* orbital with most of its density far away from the coordination center. As a result, this π -interaction is quite weak. If the original ligand π^* 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 π^* 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 π^*) 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 π^* 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



R = Me Ar: aryl groups

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 Brookhart¹⁶ and Gibson¹⁷ 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 π -system with two low-lying π^* orbitals (π^*_{asym} and π^*_{sym} in Figure 1.4) is formed.³⁴ These two π^* orbitals are the combinations of two imine and central pyridine π^* orbitals.



Figure 1.4. Two lowest π^* orbitals of diiminepyridine ligands (Picture generated from electron density plot)^{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 π^* orbitals. In the situation with ideal symmetry, the π^*_{asym} orbital can overlap with the

^{III} The two π^* orbitals are labelled according to the symmetry with respect to the xz mirror plane.

metal d_{yz} orbital while the π^*_{sym} orbital can overlap with the metal d_{xz} 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 13

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 σ -donor and good π -acceptor ligand while CO is a poor σ -donor but a good π -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).^{35a} 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).^{35b}



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 AcOH/EtOH was used to synthesize the aldimine variation of DIP^{35c} and base/MeI was used to modify the imine methyl groups (Scheme 1.7).^{35d}



Ar = 2,4,6-trimethylphenyl or 2,6-di*iso*propylphenyl

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, CH₃CN 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)MX₂ complexes

Entry	Metal-salt/solvent	Entry	Metal-salt/solvent
1	ScCl ₃ (THF) ₃ /Toluene ³⁷	11	$(Et_4N)_2(Fe_2OCl_6)/Methanol^{38}$
2	TiCl ₄ /Toluene ³⁹	12	CoCl ₂ /THF ⁴⁰
3	ZrCl ₄ /Toluene or ZrCl ₄ (THF) ₂ /CH ₂ Cl ₂ ³⁹	13	RhCl ₃ (H ₂ O) ₃ /Ethanol ⁴¹
4	VCl ₃ (THF) ₃ /THF ⁴²	14	NiCl ₂ ·6H ₂ O/Ethanol ⁴³
5	CrCl ₃ (THF) ₃ /CH ₂ Cl ₂ or acetone ⁴⁴	15	$CuCl_2 \cdot 2H_2O/CH_3CN^{45}$
6	$[NH_4]_2[IrCl_6]/(CH_2OH)_2^{46}$	16	RuCl ₃ /EtOH ⁴⁷
7	Na ₂ [OsCl ₆]/MeOH ⁴⁸	17	MoCl ₃ (THF) ₃ /THF ⁴⁹
8	$MnCl_2 \cdot (THF)_2 / Toluene^{50}$	18	ZnCl ₂ /EtOH ⁵¹
9	FeCl ₂ / <i>n</i> -butanol ⁵²	19	$MnCl_2{\cdot}4H_2O/EtOH^{51}$
10	CdCl ₂ ·2.5H ₂ O/CH ₃ CN or CH ₂ Cl ₂ ⁵³	20	HgCl ₂ /MeCN ⁵⁴

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

1.10 Modification of DIP-type ligands

1.10.1 Modification vs Reactivity

After the discovery of the catalytic efficiency of (DIP)FeCl₂ and (DIP)CoCl₂, 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)^{IV.55} The corresponding iron(II) and cobalt(II) dihalides and chromium halide complexes^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-Di*iso*propylphenyl works quite well in ethylene polymerization. However, further reducing the steric hindrance down to N-

^{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 π -conjugate system is destroyed.

^V Other transition metal complexes have also been tried, but Fe, Co and Cr are the most common ones.

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. phosphinimine⁵⁸ or alkyl phosphine⁵⁹ leads to loss of activity; replacement by e.g. thiophenyl⁶⁰ or carbene,⁶¹ results in catalysts that promote oligomerization; replacement by carbonyl⁶² 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 oligomerization⁶³).



Diiminepyridine (DIP) Highly active in ethylene polymerization



oligomerization active



Bis(imino)pyrimidine slightly active in ethylene polymerization



Bisphosphiniminepyridine Inactive

Figure 1.6. Effect of structural changes on catalytic activity of Fe/Co complexes in ethylene polymerization.

The replacement of the central pyridine by a relatively electron-poor core such as pyrimidine⁶⁴ (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 carbazoles⁶⁵ 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 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^{66b} systematically explored this steric effect by reacting ligands **1-3** with (CH₃CN)₂Fe(OTf)₂ (Table 1.2). For the bulky DIP ligand **1**, only (**1**)Fe(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.

 CH_2CI_2 (CH₃CN)₂Fe(OTf)₂ products N. `Ar Ar Entry Ligands **Products** Ar 1 1 $2,6^{-i}Pr_2C_6H_3$ $(1)Fe(OTf)_2$ $(2)Fe(OTf)_2 + [(2)_2Fe]^{2+} 2[OTf]^{-1}$ 2 2 $2-MeC_6H_4$

 $(3)_2$ Fe(OTf)₂

No data

3

4

3

4

 C_6H_5

2,4,6-Me₃C₆H₂

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

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 β -H transfer is in cobalt alkyl complexes:⁶⁷ the rate of hydride transfer in (1)Co(Bu-*n*) is 16.3 faster than that of (4)Co(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 β -H transfer

1.11 Electron-accepting ability of DIP ligands

As DIP ligands have two low-lying π^* 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 group⁶⁷ found that $(DIP)CoCl_2$ can be reduced the cobalt dinitrogen anion to $[Na(solvent)_3][(^{iPr}ADIP)Co(N_2)]$ (^{iPr}ADIP: $2,6-(^{i}PrN=CMe)_{2}C_{5}H_{3}N)$ by 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 π^* orbitals to form a singlet biradical situation^{VI} (singlet biradical character will be illustrated in detail in section 2.4.4 on four coordinate cobalt(I) complex in Chapter 2). The ¹H NMR spectrum of Na(THF)[($^{iPr}ADIP$)CoN₂] in benzene- d_6 and THF (1:1) clearly showed that it is diamagnetic.

^{VI}In this situation, the DIP ligand is trianion with one unpaired electron antiferromagnetically coupled to the low-spin cobalt(II).



Scheme 1.10. Reduction of (^{*i*Pr}ADIP)CoCl₂ 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 non-innocent 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 $(DIP)Fe(N_2)_2$ complex reported by the group of Chirik.^{70a} This complex can promote a number of interesting reactions, such as hydrogenation and hydrosilylation of olefins^{70b} and hydrogenation of ketones,⁷¹ cyclization of enynes and diynes,⁷² the breaking of C-O bonds of esters⁷³ 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)^{13d} or to change the magnetic or optical properties of their metal complexes (e.g. Semiquinone in copper(II) complexes)^{28b} or optoelectronic properties of organoboron compounds^{28c} 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 C2 position has been observed with alkyl magnesium and alkyl zinc reagents. Alkyl aluminum reagents can alkylate at the imine carbon and at the pyridine C4 position (although this product is not stable and easily dimerizes). Alkylation at C3 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 NaH⁸⁰ 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)CoCl₂ 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 N₃ 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.





Although DIP cobalt(I) alkyl complexes are diamagnetic, the spectra show some rather abnormal features. The pyridine H4 peak in the ¹H NMR spectrum shifts significantly to low field (δ : around 10 ppm) and the imine methyl group shifts significantly to higher field (δ : 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 cross-coupling 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 (4d+5d) 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 ¹H NMR spectra of organic compounds are normally quite sharp (half widths are normally less than 0.5 Hz) and the total ¹H 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 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 ¹H 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 $[Rh(H)_2(P^iBu_3)_2][BArF_4]$ is located at -21.55 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, ¹H 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 $\delta = 7.2$ ppm, while in the ¹H 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 ¹³C spectra and the broadness of the peaks caused by fast electron spin-relaxation often prevents observation of ¹³C NMR signals. In addition, due to the wide spread of peaks in ¹H NMR spectra, the ¹H decoupling technique normally used in ¹³C 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

$$\delta (\text{in ppm}) = 10^6 (\upsilon - \upsilon_{\text{ref}}) / \upsilon_{\text{ref}} = 10^6 (\sigma_{\text{ref}} - \sigma) / (1 - \sigma_{\text{ref}}) \approx 10^6 (\sigma_{\text{ref}} - \sigma)$$

- v is the resonance frequency of a target nucleus (Hz)
- υ_{ref} is the resonance frequency of the same nucleus in a reference compound (Hz)
- σ is the shielding of a target nucleus
- σ_{ref} is the shielding of a reference nucleus (normally TMS or solvent residue)

For closed-shell diamagnetic compounds, the shielding parameter σ has been interpreted as the sum of the paramagnetic (σ_p) and diamagnetic (σ_d) contributions (for details about how to calculate these two components, see ref. 86):

Where,

- Diamagnetic shielding (σ_d) 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 (σ_p) 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 δ^{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 (δ^{FC}) and the pseudo-contact shift

 (δ^{PC}) . The observed chemical shift (δ^{obs}) can be interpreted according to following equation:⁹¹

$$\delta^{\text{obs}} = \delta^{\text{orb}} + \delta^{\text{FC}} + \delta^{\text{PC}}$$
 Eq. 2.2

The Fermi contact shift (δ^{FC}) is caused by Fermi contact^{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

^{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.

However, the expected peak splitting in the ¹H 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 ($m_S = +1/2$) and spin-down ($m_S = -1/2$) states affects the chemical shift of the adjacent proton according to the following equation (Eq. 2.3):

Average
$$v = N_{+1/2} v_{+1/2} + N_{-1/2} v_{-1/2}$$
 Eq. 2.3

- $N_{+1/2}$ and $N_{-1/2}$ correspond to the fraction of each spin population
- $v_{+1/2} = v 1/2J_{e-H}$ and $v_{-1/2} = v + 1/2J_{e-H}$
- J_{e-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 $(N_{+1/2} > N_{-1/2})$ to the time average of v.

Thus the magnitude of the contact shift can be estimated according to the following equation:⁹⁰

$$\delta^{FC} = A_{iso} \frac{g\beta_e S(S+1)}{g_N \beta_N 3\kappa T}$$
 Eq. 2.4

Where:

- \overline{g} is the rotationally averaged electronic g-value,
- g_N is the nuclear g-value,
- β_e and β_N are the Bohr and nuclear magnetons, respectively,

- A_{iso} is the isotropic hyperfine coupling constant (the analog of a *J* coupling) which can be positive or negative,
- κ is the Boltzmann constant and T is the absolute temperature,
- S is the total electron spin of the molecule (1/2, 1, 3/2,...).

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:^{90,92a}

$$\delta^{PC} = \beta_e^2 S(S+1) \frac{3(\cos^2 \Omega - 1)}{3\kappa T R^3} F(g)$$
 Eq. 2.5

Where:

- Ω 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.

• F(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 (δ^{obs}) of a target nucleus in a paramagnetic compound, the orbital contribution (δ^{orb}) is small but not negligible. For example, in the organic radical 2-methylphenyl-tert-butylnitroxide, the ratio $|\delta^{orb}/\delta^{FC}|$ is calculated to be less than 15% while pseudocontact shifts δ^{PC} contribute less than 0.1 ppm to any of the ¹H shifts.⁹² In addition, in the calculation of the acetylacetonate complexes of Mn, Fe, Cr, ^{91b,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 d⁶ and d¹⁰ transition metals (including cobalt complexes like the ones studied in this thesis). Only δ^{orb} and δ^{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.^{92b} 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 α than β

electrons, but this is not the case. A large spin density in one orbital (due to a single electron of e.g. spin α) also affects other formally doubly occupied orbitals, which will get an excess of spin β 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 1000Hz). 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 T₂ value.

2.1.2 Interpretation of paramagnetic ¹H 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 δ^{orb} and δ^{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:^{98b}

$$\mu_{eff} = 798 \sqrt{\chi_M T}$$
 Eq. 2.6

$$\chi_M = \left(-\frac{3\Delta \nu}{\nu m} + \chi_{mass,0}\right) \bullet MW$$

Where:

• μ_{eff} : the effective magnetic moment (μ_B)

- T: temperature (K)
- MW: molecular weight (kg/mol)
- v: the frequency of the external magnetic field (Hz)
- Δυ: 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 (m³/kg)
- m: mass concentration (kg/m³)
- χ_M : molar susceptibility of the complex in the magnetic susceptometer (m³/mol)

The number of unpaired electrons can be derived by comparing the value of this effective magnetic moment, μ_{eff} , to the value μ_s from the ideal "spin-only" formula (where the orbital contribution is neglected):

$$\mu_s = g_e \sqrt{S(S+1)} \approx 2\sqrt{\frac{n}{2}(\frac{n}{2}+1)}$$
 Eq. 2.7

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 ¹H NMR. Thus, the theory in ¹H 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 ¹H 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

$$2d \sin\theta = n \lambda$$
 Eq. 2.8

Where:

- d is the distance between two atom arrays
- θ is the angle between the incident X-ray beam and the atom array
- λ 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 K α radiation ($\lambda = 0.71073$ Å), one 360 degree φ run and then a number of ω 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 2σ are analyzed and indexed using the Bruker smart suite¹⁰¹ 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 -3 51" was used to remove 47

all reflections with 20 value above 51° and to modify very negative F_o^2 (all reflections with $F_o^2 < -1.5\sigma(F_o^2)$ are replaced by $1.5\sigma(F_o^2)$).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 solvent-accessible voids with PLATON;^{106a} Mercury¹⁰⁷ is used to view the structure. For co-crystallized 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^{106a} software to remove the contribution of the solvent molecules from the diffraction data.^{106b-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):

$$\hat{H} \Psi = E \Psi$$
 Eq. 2.9

- \hat{H} : Hamiltonian Operator
- Ψ : 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 Φ_{SD} ; one-electron wave functions are called spin orbitals). The total Hartree-Fock energy of the system is calculated according to the following equation:

$$E_{\rm HF} = \left\langle \Phi_{SD} \middle| \hat{H} \middle| \Phi_{SD} \right\rangle = \sum_{i}^{N} (\chi_i \mid -\frac{1}{2} \nabla^2 - \sum_{A}^{M} \frac{Z_A}{r_{1A}} \mid \chi_i) + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} (\chi_i \chi_i \mid \chi_j \chi_j) - (\chi_i \chi_j \mid \chi_j \chi_i)$$
Eq. 2.10

The first two terms are the contributions from the electronic kinetic energy $\left(-\frac{1}{2}\nabla^2\right)$ and the electron-nucleus attraction $\left(\frac{Z_A}{r_{1A}}\right)$; the second two terms are the Coulomb $(\chi_i\chi_i|\chi_j\chi_j)$ and exchange $(\chi_i\chi_i|\chi_i\chi_i)$ integrals $(\chi_i$ and χ_j are spin orbitals).

Thus E_{HF} is a functional of the spin orbitals (χ_i). 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 (ε_i); this is expressed as follows:

$$f_i \chi_i = \varepsilon_i \chi_i$$
 Eq. 2.11

$$f_{i} = -\frac{1}{2}\nabla_{i}^{2} - \sum_{k}^{nuclei} \frac{Z_{k}}{r_{ik}} + V_{i}^{HF} \{j\}$$

 $V_i^{HF}\{j\}$ is the Hartree-Fock potential, which is the average interaction potential of one electron with all of the other electrons occupying orbitals $\{j\}$. 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 wave-function 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 N⁴ (theoretically, due to the four-index integrals; here N stands for the number of basis functions used) or as $\sim N^{2.7}$ (in practice, due to efficient pre-screening methods). Post-HF methods scale as N⁵(MP2), N⁶(MP3), N⁷(CCSD(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 (ρ), which can be expressed as follows:

$$\mathbf{E} = \mathbf{E}_{\mathbf{o}}[\boldsymbol{\rho}]$$

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:

$$E[\rho] = T_{ni}[\rho] + V_{ne}[\rho] + V_{ee}[\rho] + E_{XC}[\rho]$$
 Eq. 2.12

- $T_{ni}[\rho]$: kinetic energy of the non-interacting electrons
- $V_{ne}[\rho]$: the nuclear-electron interaction
- $V_{ee}[\rho]$: the classical electron-electron repulsion
- $E_{XC}[\rho]$: 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 $E[\rho]$ with respect to independent variations in the orbitals (χ_i). 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:

$$h_i^{ks} \chi_i = \varepsilon_i \chi_i$$
 Eq. 2.13

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 - \sum_{k=1}^{nuclei} \frac{Z_k}{|r_i - r_k|} + \int \frac{\rho(r')}{|r_i - r'|} dr' + V_{XC}$$

- χ_i is the Kohn-Sham (KS) orbital
- h_i^{ks} is the Kohn-Sham one-electron operator

- V_{xc} is the exchange-correlation potential which is unknown
- ε_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 *ab 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 N^2-N^3 .

If V_{XC} were known explicitly, the energy calculated would be the exact energy. However, it is not. Current theory only states that a V_{XC} exists, but not what it would look like. Thus, approximating the V_{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 functional¹¹⁰ combined with the Perdew 86¹¹¹ correlation functional works quite well for many transition metal systems.^{112a-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^{112c} functional, which includes around 20% of HF exchange, was shown to work

VIII Refers to Coulomb and exchange integrals in Eq. 2.10.

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

One problem with the DFT methods is that there is no systematic way to approach the exact energy of the system. For *ab 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 SV(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 ("b3-lyp' 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 VWN(V) and Perdew 86 as correlation functionals. In Turbomole, the correlation functional in b3-lyp¹¹⁴ 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 VWN(III) is much less well founded than VWN(V).

The group of Budzelaar has done numerous DFT studies on cobalt systems using the Turbomole program¹¹⁷ and the b3-lyp functional combined with SV(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 Gaussian¹¹⁸ and Orca programs¹¹⁹ 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 $\langle \hat{S}^2 \rangle$ (\hat{S} is the spin operator) value can be used as an indicator of such contamination (ideal $\langle \hat{S}^2 \rangle$ values: $\frac{n}{2} \left(\frac{n}{2}+1\right)$). Although spin projection^{120a} 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 $\langle \hat{S}^2 \rangle$ values always checked for spin contamination.

2.4.4 DFT study of (DIP)CoR

Introduction

The X-ray structures of (DIP)CoR complexes⁸¹ 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 ¹H 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 broken-symmetry (BS) treatment^X based on the Unrestricted Hartree-Fock (UHF)/Unrestricted Kohn-Sham (UKS) formalism^{120b-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 ($\hat{S}^2 = 0$) and pure triplet ($\hat{S}^2 = 2$).

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.

^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.

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:^{120d}

- eliminate or correct spin contamination from electronic energies^{XI} (for example, spin projection^{120a});
- 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^{XII} (e.g. DFT/MRCI^{120e-f}) to take care of the non-dynamic correlation. However, these methods are too expensive for large molecules;
- change the treatment of full-spin occupancy to fractional-spin occupancy (this approach is also called the fractional occupancy approach).^{121a-f}

As the application of the fractional occupancy approach to transition metal complexes has not been validated,^{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.^{120a} Apart

^{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.

^{XIII} The main systems studied by the fractional occupancy approach are simple organic systems and compounds.

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.^{120b-c,121g}

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.^{120b}

$$E_s - E_t = 2(E_u(BS) - E_u(T))$$
 Eq. 2.14

- $E_u(T)$ is the UHF or UKS energy of the triplet state
- E_u(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^{121h-i}.

$$E_s - E_t = \frac{2(E_u(BS) - E_u(T))}{2 - \langle S^2 \rangle}$$
 Eq. 2.15

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

(negligible triplet contribution). In the limit of strong coupling ($\hat{S}^2 \approx 0$), Eq. 2.15 converts to Eq. 2.16.

$$E_s - E_t = E_u(BS) - E_u(T)$$
 Eq. 2.16

Both Ruiz^{121j} and Bachler^{121g} 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,^{121g} 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^{XIV} and their \hat{S}^2 values. However, to derive the "pure" singlet energy is not trivial for DIP cobalt(I) systems.

XIV Corresponding triplet: related to the broken-symmetry solution by a single spin flip.

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 kcal/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.



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 π^* 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 well-defined (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 S_{N2} reactions at $C(sp^3)$ centers¹²² 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 PF_5 with geometries of trigonal bipyramidal (TBP, left) and square pyramidal (SP, right)

The IR spectrum of PF_5 supports a TBP structure. However, the ¹⁹F 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 rotation¹²⁸ is in principle the same as Berry pseudorotation^{XV}) is

^{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.

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 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 (C, 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 (δ and τ , 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 δ parameter

In 1974, Muetterties and Guggenburger approached five-coordinate molecules in a quite different way, considering only the dihedral angle δ_{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 δ_{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 (53.1°) and the angle formed by two norms to the adjacent faces within one pyramid (116.5°). When changing from TBP to SP, δ_{24} will change from 53.1° to 0°. By comparing all δ_{ij} values (they are also called δ 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 $D_{3h} \leftrightarrow C_{4v}$ path.¹³³ Later Homes and Deiters reported that, for a certain five-coordinate molecular structure (C), if the quantities $\sum_{i} |\delta_i(C) - \delta_i(TBP)|$ and 217.7- $\sum_{i} |\delta_i(C) - \delta_i(SP)|$ are same, this structure (C) lies on the TBP-SP Berry pseudorotation

pathway.^{132a} The percentage of SP can be calculated according to the definition of τ parameter^{132b} which will be illustrated in the following section. These δ parameters normally work well for complexes with five identical and non-chelating ligands.

3.2.2 τ parameters

Reedijk and coworkers defined a τ 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 β and the other (second-largest) is defined as α (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, $\tau = 0$.



Figure 3.3. Definition of τ parameter

The τ parameter works quite well for a variety of five-coordinate copper(II) complexes. For example, the correlation of the τ parameter with EPR hyperfine coupling constant A_{//} values of five-coordinate Cu(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^{125a} 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 (S_4 , S_{6a} , S_{6b} , S_{7a} , S_{7b} , S_{8a} , and S_{8b} for TBP; S_3 , S_5 , S_6 , S_{8a} , S_{8b} , S_{9a} and S_{9b} for SP).



Name of angle: e.g. $\theta_{12} = D^1 - M - D^2$

Name of bond length: e.g. $r_1 = \Delta(D^1-M)$

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
$S_1 = 2^{-1/2}(r_1 + r_5)$	$S_1 = r_3$
$S_2 = 3^{-1/2}(r_2 + r_3 + r_4)$	$S_2 = 1/2 (r_1 + r_2 + r_4 + r_5)$
$S_3 = 2^{-1/2} (r_1 - r_5)$	$\mathbf{S}_3 = 2^{-1/2} (\Delta \theta_{15} + \Delta \theta_{24})$
$S_4 = 6^{-1/2} (\Delta \theta_{12} + \Delta \theta_{13} + \Delta \theta_{14} - \Delta \theta_{25} - \Delta \theta_{35} - \Delta \theta_{45})$	$S_4 = \frac{1}{2} (r_1 + r_5 - r_2 - r_4)$
$S_{5a} = 6^{-1/2} (2r_3 - r_2 - r_4)$	$S_5 = 2^{-1/2} (\Delta \theta_{15} - \Delta \theta_{24})$
$S_{5b} = 2^{-1/2} (r_2 - r_4)$	$S_6 = \frac{1}{2} \left(\Delta \theta_{12} + \Delta \theta_{45} - \Delta \theta_{14} - \Delta \theta_{25} \right)$
$\mathbf{S}_{6a} = 6^{-1/2} (\ 2\Delta\theta_{24} - \Delta\theta_{34} - \Delta\theta_{23})$	$S_{7a} = 2^{-1/2} (r_1 - r_5)$

Symmetry coordinates of TBP	Symmetry coordinates of SP
$S_{6b} = 2^{-1/2} (\Delta \theta_{34} - \Delta \theta_{23})$	$S_{7b} = 2^{-1/2} (r_4 - r_2)$
$S_{7a} = 12^{-1/2} (\ 2\Delta\theta_{13} - \Delta\theta_{12} - \Delta\theta_{14} + 2\Delta\theta_{35} - \Delta\theta_{25} - \Delta\theta_{45} \)$	$\mathbf{S}_{8a} = 2^{-1/2} (\Delta \theta_{13} - \Delta \theta_{35})$
$S_{7b} = 1/2(\Delta\theta_{12} - \Delta\theta_{14} + \Delta\theta_{25} - \Delta\theta_{45})$	$S_{8b} = 2^{-1/2} (\Delta \theta_{34} - \Delta \theta_{23})$
$S_{8a} = 12^{-1/2} (\ 2\Delta\theta_{13} - \Delta\theta_{12} - \Delta\theta_{14} - 2\Delta\theta_{35} + \Delta\theta_{25} + \Delta\theta_{45} \)$	$S_{9a} = 2^{-1/2} (\Delta \theta_{12} - \Delta \theta_{45})$
$S_{8b} = 1/2 \left(\Delta \theta_{12} - \Delta \theta_{14} - \Delta \theta_{25} + \Delta \theta_{45} \right)$	$\mathbf{S}_{9b} = 2^{-1/2} (\Delta \theta_{14} - \Delta \theta_{25})$

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:

$$|\text{Dist}(\text{TBP})| = \sqrt{S_4^2 + S_{6a}^2 + S_{6b}^2 + S_{7a}^2 + S_{7b}^2 + S_{8a}^2 + S_{8b}^2}$$
$$|\text{Dist}(\text{SP})| = \sqrt{S_3^2 + S_5^2 + S_6^2 + S_{8a}^2 + S_{8b}^2 + S_{9a}^2 + S_{9b}^2}$$

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° for two apical positions, 120° among three basal positions and 90° between apical and basal positions, there is no unique choice for the ideal SP (Figure 3.5). Any structure having four equal apical-equatorial (θ_{13} , θ_{23} , θ_{34} and θ_{35}) and four equal equatorial-

equatorial angles (θ_{12} , θ_{25} , θ_{45} and θ_{14}) should probably be classified as SP regardless of the value of this apical-equatorial angle.



Figure 3.5. TBP and SP reference structures

Without the choice of one specific θ_{24} value for ideal SP, the S₃ 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 (θ_{24}) 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.^{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.^{81a,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.

^{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)CoCl₂¹³⁷ and (B) SP-like (5)FeCl₂¹⁶

Structure analysis of all (DIP)MX₂ complexes (M: Fe, Co; X: F, Cl, Br, 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 τ parameter values for these complexes are all low, leading to a classification of *every* system as SP^{XVII}; thus it appears not to be suitable for our systems. For example, for (1)CoCl₂ (Figure 3.6) which is "clearly TBP", τ was calculated to be 0.45, indicating SP. FAA similarly leads to the non-discriminating results

^{XVII} For (DIP)CoX₂, $\tau \le 0.48$; for (DIP)FeX₂, with two exceptions, τ is less than 0.44. One of these exceptions is the somewhat atypical (**11**)FeCl₂, 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)MX₂ complexes. For example, all *cis*-NMN angles in these complexes are close to 74° which deviate significantly from the ideal 90° or 120° 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} Carugo¹³⁹ used a flat SP in which the *trans* basal L-M-L angle is 180° and the angle between apical and basal positions is 90° (Figure 3.7(b)); Bürgi used a so-called bent SP with 150° for the trans basal L-M-L angle and 105° between the apical and basal positions^{125a} (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.^{125a} After screening through all available X-ray structures of FeX₂ and CoX₂ 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° 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: N¹MN² = 74.0°, N¹MN⁵ = 148.0°.



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

Analysis

Using these modified reference geometries, all (DIP)MX₂ (M: Fe, Co; X: F, Cl, Br, I) in the 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-di*iso*propyl 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)MX₂ (M: Fe, Co), visual inspection shows that the main variation is in the two chlorine positions relative to the N_3 plane, and in the movement of the metal center out of the 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 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 N3 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 N(Py)-M-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: MCl₂ unit tilts (A in Scheme 3.3), and at the same time, the metal moves up from N₃ plane (B in Scheme 3.3). The repulsion between the N-aryl ring and the MCl₂ unit is the main cause for the MCl₂ unit to move out of the N₃ 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 MCl₂ unit and the metal movement out of the N₃ 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 N²-M-X³ and N²-M-X⁴ in Figure 3.8 is used to define a reaction path between TBP and SP for this specific system. Metal distortion out of the N₃ plane as a function of ω is summarized in Figure A.2 in the Appendix A; it shows that the tilting of the MCl₂ is much more significant than the metal deviation from the N₃ plane in terms of energy^{XVIII}.

^{XVIII} The metal deviation out of N_3 plane follows *automatically* the trend of the tilting of the MCl₂ unit, as Figure A.2 shows.
3.5.3 Two-angle criterion

The larger of the two N(Py)-M-X angles is defined as α and the smaller one is defined as β (Scheme 3.4). We propose to use $\omega = (\alpha - \beta)/90$ as a parameter describing the interconversion. If ω is zero, we have "perfect" TBP; when ω is 1, the structure is "perfect" SP (within the limitations imposed by the ligand framework). Using the ω criterion, the structures is assigned as TBP ($\omega < 0.5$) or SP ($\omega > 0.5$). In contrast to the FAA classification, this ω 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 ω -based assignment corresponds to that using the modified FAA. The distributions of structures over ω values are plotted in Figure 3.10. (DIP)FeX₂ structures are seen to cluster around ω values near 0.1 (preference for TBP 82

geometries) while the geometries of (DIP)CoX₂ tend to spread over the whole ω space. Values close to $\omega = 1$ ("flat SP") are rare.



Figure 3.10. Distribution of observed structures over ω 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 **3** and **5-12**, in Figure 3.11) and DFT computations (ligands **1-6**, in Figure 3.11).



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

Analysis of X-ray structures

Structures of (3)FeCl₂,¹⁴¹ (5)CoCl₂,¹⁶ (5)FeCl₂,¹⁶ (6)FeCl₂,⁵² (11)FeCl₂¹⁴² and (12)FeCl₂¹⁴³ were obtained from the CSD database,¹⁴⁰ while ligands 7, 8, 9, 10 and their corresponding metal dihalides and (3)CoCl₂ complexes were prepared by me to obtain their X-ray structures.

Synthesis of cobalt and iron dichloride complexes

The complex (3)CoCl₂ can be easily obtained by reaction of CoCl₂ with the free ligand in THF solvent or butanol (for more details about the preparation of CoCl₂ 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 CF₃ groups at the imine carbons is a very weak σ -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 CH_2Cl_2 was also unsuccessful. However, the reaction of 7 with $CoCl_2(THF)_{1.5}$ in CH_2Cl_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 $CoCl_2(THF)_{1.5}$ will dissociate THF to generate the "naked" $CoCl_2$ which can be captured by the free ligand. However, washing (7)CoCl₂ with toluene seemed to release part of the ligand and produce some off-white powder, tentatively identified as CoCl₂. Thus the complex is not very stable to dissociation into 2

and bulk $CoCl_2$. X-ray structures of the corresponding iron and cobalt complex are shown in Figure 3.12 and Figure 3.13. The complex (7)CoCl₂ co-crystallized with one molecule of dichloromethane, while (7)FeCl₂ co-crystallized with toluene. The metal centers in both complexes have a distorted TBP environment with a small metal distortion from the N₃ plane, similar to the corresponding complex of ligand **3**.



Figure 3.12. X-ray structure of (7)FeCl₂ (thermal ellipsoids drawn at 30% probability, hydrogen atoms and co-crystallized toluene are omitted for clarity). Selected bond distances (Å) and angles (deg): Fe(1)-N(1): 2.248(5); Fe(1)-N(2): 2.124(4); Fe(1)-N(3): 2.267(5); Fe(1)-Cl(1): 2.255(2); Fe(1)-Cl(2): 2.279(2); C(2)-N(1): 1.264(7); C(2)-C(3): 1.478(8); C(3)-N(2): 1.335(7); C(7)-N(2): 1.345(7); C(7)-C(8): 1.493(8); C(8)-N(3): 1.284(7); N(1)-Fe(1)-N(2): 72.9(2); N(2)-Fe(1)-N(3): 72.9(2); N(1)-Fe(1)-N(3): 145.3(2); N(2)-Fe(1)-Cl(1): 136.01(14); N(2)-Fe(1)-Cl(2): 116.35(14).



Figure 3.13. X-ray structure of (7)CoCl₂ (thermal ellipsoids drawn at 30% probability, hydrogen atoms and co-crystallized CH₂Cl₂ have been omitted for clarity). Selected bond distances (Å) and angles (deg):): Co(1)-N(1): 2.274(5); Co(1)-N(2): 2.047(4); Co(1)-N(3): 2.249(5); Co(1)-Cl(1): 2.216(2); Co(1)-Cl(2): 2.245(2); C(2)-N(1): 1.278(7); C(2)-C(3): 1.491(9); C(3)-N(2): 1.339(7); C(7)-N(2): 1.338(7); C(7)-C(8): 1.493(8); C(8)-N(3): 1.272(7); N(1)-Co(1)-N(2): 74.9(2); N(2)-Co(1)-N(3): 75.3(2); N(1)-Co(1)-N(3): 149.3(2); N(2)-Co(1)-Cl(1): 136.6(2); N(2)-Co(1)-Cl(2): 109.42(14).

Ligands (8-10) were prepared from 2,6-dibromopyridine through several steps (acylation,¹⁴⁵ condensation,¹⁴⁶ C-P coupling reaction and the oxidation by $azide^{142}$); the representative synthesis of ligand **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 $CoCl_2$ and $FeCl_2$ can be prepared according to the standard procedure for the DIP ligand.¹⁶ CoCl₂ complexes of ligands **8-10** have been prepared; however, only (**10**)CoCl₂ formed X-ray quality crystals (Figure 3.14). X-ray structures of FeCl₂ complexes for all three ligands **8-10** (see Section 9.1, experimental section for Chapter 3) could be obtained. Although the quality of the crystals of (**8**)FeCl₂ (X-ray structure, see Figure 9.4) and (**10**)FeCl₂ (X-ray structure, see Figure 9.3) was not high, it was sufficient to establish the connectivity of the atoms and allow FAA and ω analysis.



Figure 3.14. X-ray structure of (**10**)CoCl₂ (thermal ellipsoids drawn at 30% probability, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Co(1)-N(1): 2.311(2); Co(1)-N(2): 2.060(2); Co(1)-N(3): 2.109(2); Co(1)-Cl(1): 2.2550(6); Co(1)-Cl(2): 2.2940(6); N(1)-C(68): 1.276(3) ; C(11)-C(68): 1.485(3); N(2)-C(11): 1.339(3); N(2)-C(15): 1.337(3); C(15)-P(2): 1.824(2); N(3)-P(2): 1.598(2); N(1)-Co(1)-N(2): 73.39(6); N(2)-Co(1)-N(3): 84.94(6); N(1)-Co(1)-N(3): 157.10(6); N(2)-Co(1)-Cl(1): 135.03(5); N(2)-Co(1)-Cl(2): 100.96(5).

Analysis of selected X-ray structures

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

Entry	Metal complex	FAA analysis results	ω	Metal deviation (Å)
1	(3)CoCl ₂	TBP	0.04	0.01
2	(3)FeCl ₂	TBP	0.14	0.09
3	$(7)CoCl_2$	TBP	0.30	0.20
4	(7)FeCl ₂	TBP	0.22	0.16
5	$(5)CoCl_2$	SP	0.64	0.56
6	(5)FeCl ₂	SP	0.59	0.56
7	(10)CoCl ₂	TBP	0.38	0.18
8	(10)FeCl ₂	TBP	0.44	0.17
9	(8)FeCl ₂	SP	$0.67 (0.76)^{a}$	$0.41(0.42)^{a}$
10	(9)FeCl ₂	SP	0.66	0.44
11	(11)FeCl ₂	TBP	$0.00(0.05)^{a}$	$0.05(0.11)^{a}$
12	(6)FeCl ₂	TBP	$0.35(0.14)^{a}$	$0.35(0.09)^{a}$
13	(12)FeCl ₂	TBP	0.44	0.40

Table 3.2. Analysis results for selected complexes

^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 N₃ plane (0.56 Å in entry 6 vs 0.44 Å 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 ω at 0.11 intervals and fully optimizing all other structural parameters.¹⁴⁷ Ligands **1-6** in Figure 3.11 and their CoCl₂ and FeCl₂ 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) FeCl₂ and (B) CoCl₂ complexes of DIP ligands(electronic energy, kcal/mol, calculated at b3-lyp/TZVP//b3-lyp/SV(P)).

For CoCl₂, the energy ranges for geometry changes from ideal TBP to SP are within 5.5 kcal/mol for ligands 1-5. For FeCl₂, the range of energies is slightly higher (~ 6.5kcal/mol). For complexes with unsubstituted DIP (1: Ar = Ph), TBP is preferred for both metals with a very flat PES (the changing of ω from 0 up to 0.75 only requires 3 kcal/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 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 kcal/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 ω distributions in Figure 3.10 and the X-ray analysis results in Table 3.2 suggests that experimentally, $(DIP)MCl_2$ 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.^{XIX} but a

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 92

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 H4 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 ω 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 4-coordinate complexes, low-spin d⁸ electronic configurations lead to square planar geometries while d¹⁰ configurations favor tetrahedral coordination.^{125b,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)MCl₂ (M: first row transition metal) in their high-spin states.



Figure 3.16. Deformation curves for (**3**)MCl₂ complexes. (M: first row transition metal, electronic energy, kcal/mol, calculated at b3-lyp/TZVP//b3-lyp/SV(P))

As the PES in Figure 3.16 indicate, all metals except $CuCl_2$ prefer TBP or intermediate geometries. It is best to start with zinc, for its 3d 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 ω of 0.4, and it costs only 1 kcal/mol for ω 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. Mn²⁺, with a half-filled 3d shell, shows a similar trend. The Cr²⁺, Fe²⁺, Co²⁺ and Ni²⁺ curves are close to each other, with SP around 1 kcal/mol

higher than TBP. However, Cu^{2+} shows a completely opposite trend,^{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 Cu-Cl = 2.326 Å, equatorial Cu-Cl = 2.206 Å), which is expected for d⁹ metal centers due to the distortion^{XXI} that is similar to the idea behind Jahn-Teller distortion.

3.6 Extension to (DIP)FeR₂ complexes

As we know, DIP metal alkyl complexes are possible intermediates in the activation of (DIP)FeCl₂ and (DIP)CoCl₂ complexes in ethylene polymerization reactions.¹⁵⁰ 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 $(DIP)Fe(CH_2SiMe_3)_2$ complexes (DIP: ligands **3**, **5**, **13**, **14** in Figure 3.17) can be found and were extracted from CSD. One additional complex $(Pybox)Fe(CH_2SiMe_3)_2$ (Pybox: ligand **15** in Figure 3.17), was prepared by me according to a procedure for the

^{XX} Cr^{2+} was expected to have the same geometry preference as Cu^{2+} . The reason why it does not show SP preference as Cu^{2+} does here is not so clear. One possible reason is that, as Figure 4.11 indicates, the π -basicity of Cr^{2+} is not negligible; as a result, a significant amount of electron might transfer from Cr^{2+} to the DIP ligand, which might lead to the unexpected geometry preference here.

^{XXI} Although there are no degenerate orbitals in these systems, two orbitals, of which energies are close, are to be distorted.

preparation of (3)Fe(CH₂SiMe₃)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).



Figure 3.17. Structures of DIP ligands in FeR₂ complexes

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

Name ^a	ω	Metal dev (Å)	Catalytic activity ^b
(5)FeR ₂	0.36	0.54	Highly active
(14)FeR ₂	0.34	0.43	active
(3)FeR ₂	0.32	0.50	active
(13)FeR ₂	0.00	0.01	No data ^c
(15)FeR ₂	0.02 (0.05)	0.00 (0.05)	Not active

a: $R = CH_2SiMe_3$. b: ethylene polymerization. c: active in acrylate polymerization.¹⁵³

Compared with the FeCl₂ complexes, Fe(CH₂SiMe₃)₂ complexes have a higher tendency to adopt TBP geometries while the metal deviation from the N₃ plane is same as that in the dichlorides. As the Fe-C bond is shorter than the Fe-Cl bond, the alkyl is closer to the N₃ 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**, 14^{152} are active in ethylene polymerization, while there is no activity for ligand **15** complex, although (13)FeCl₂¹⁵³ showed some activity in acrylate polymerization. Table 3.3 shows that the most active ethylene polymerization catalyst (5)Fe(CH₂SiMe₃)₂ has the largest metal deviation from N₃ 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 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 97

ligands is probably due to the fact that steric bulk can protect the metal center against side reactions (e.g. disproportionation to L_2M complexes)⁶⁶ and prevent β -hydrogen transfer (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 ω 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 FeCl₂ and CoCl₂. 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 CuCl₂. Extension to metal dialkyl complexes shows that precursors to the catalysts active in ethylene polymerization tend to have a larger metal deviation from N₃ 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 (χ)¹⁵⁸ and one steric parameter (θ , cone angle). For the electronic parameter χ , Tolman and coworkers took the difference between the A₁ carbonyl stretching frequency of LNi(CO)₃ in CH₂Cl₂ and 2056.1 cm⁻¹ (the frequency when L = tri-*t*-butylphosphine). The steric parameter θ 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.



(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 $LNi(CO)_3$ complexes.

4.2 Linear free energy relation

A linear free energy relation is intended to quantitatively correlate equilibrium or reactivity with structure.^{159a} 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.^{159b-c} Parameters σ_p (to describe para substituent effects) and σ_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.(K_H is the ionization constant for benzoic acid and K_X is the ionization constant for substituted benzoic acid).

4.3 QALE

As an extension of Tolman parameters (electronic (χ) and steric (θ) effects), quantitative analysis of ligand effects (QALE)¹⁵⁷ developed by Giering¹⁶⁰ 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 χ of Tolman was decomposed into three main components:

1) χ_d is used to describe the σ -donor ability of phosphine ligands (a small value means a good σ -donor);

- π_p is a measure of the π-acceptor property (a large value means a strong πacceptor);
- 3) E_{ar} is used to evaluate the "E_{ar} 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 PCl₃ ligands.

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

Property =
$$a(\chi_d) + b(\theta - \theta_{st})\lambda + c(E_{ar}) + d(\pi_p) + f$$
 Eq. 4.1

Where,

$$\lambda = 1 \text{ when } \theta > \theta \text{st. Property} = a(\chi_d) + b(\theta - \theta_{st}) + c(E_{ar}) + d(\pi_p) + f$$
$$= 0 \text{ when } \theta < \theta \text{st. Property} = a(\chi_d) + c(E_{ar}) + d(\pi_p) + f^{161}$$

However, when $PZ_{3-i}H_i$ 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:

Property =
$$a(\chi_d) + b(\theta - \theta_{st})\lambda + c(E_{ar}) + d(\pi_p) + ei + f$$
 Eq. 4.2

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 104

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 χ_d used in Eq. 4.1 is different from the original definition of Tolman for χ :

1) for common trialkyl phosphines and triaryl phosphines, it is same as the Tolman χ parameter using the following equation reported by Bartik:¹⁶²

$$\chi_{PX3} = v(CO)(A_1) - 2056.1 \text{ cm}^{-1}$$

where, $v(CO)(A_1)$ is the A1 carbonyl stretching frequency for LNi(CO)₃

2) for mixed alkyl-aryl phosphine ligands, χ_d is obtained by studying E^o/T of the following reaction:

$$Cp(CO)(L)Fe(COMe)^+ + e \implies Cp(CO)(L)Fe(COMe)$$

From the plot of E^o/T versus 1/T, ΔH^o (the slope) and ΔS^o (the intercept) can be obtained. With all these data, χ_d can be generated by projecting ΔH^o onto the calibration curve of ΔH^o versus z_3 (a linear combination of χ and θ) calibrated by two ligands (PMe₃ and PPh₃).¹⁶³

For both above two types of phosphines, χ_d can also be obtained by linear regression from the pK_a value:¹⁶¹

$$\chi_{\rm d} = 1.47 \rm p K_a - 0.069\theta + 27.8$$

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3) for phosphite ligands, χ_d was generated by linear regression on five properties: pKa values, ionization potentials (IP) for PZ₃, v_{co} for η -Cp(CO)(PZ₃)Fe(COMe)⁰ and E^o (229K) and ΔH^o for the η -Cp(CO)(PZ₃)Fe(COMe)^{+/0} couple. Together with the generation of the χ_d value, this also generates E_{ar} and π_p parameters for this type of ligand.

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

Thirdly, π_p was introduced to describe phosphite ligands since there is a significant π effect in phosphites compared to that in trialkylphosphine ligands.¹⁶⁴

Finally, the parameter E_{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 E_{ar} of phosphines containing zero, one, two and three aryl groups, respectively. Later on, it was found that better fits for PCl₃ and phosphites were obtained by assigning their ligands non-zero E_{ar} values. E_{ar} can be generated as the co-products of regression for generating the χ_d for phosphite ligands. Normally, it is included in situations where χ and θ 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 106

complexes, the enthalpy of the ligand-displacement reaction, ¹³C NMR shifts etc. When the property can not be expressed well by existing parameters, a new parameter can be introduced^{XXII}. These parameters, especially χ and π , can be scaled to apply to donor groups in such as sulphides,¹⁶⁶ silyls,¹⁶⁷ nitriles,¹⁶⁸ amines, arsines, carbenes¹⁶⁸ 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 σ -donor ability and π -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 σ -donor, π acceptor and steric properties of monophosphines,¹⁷¹ the application of QALE to diiminepyridine ligands is problematic. First, in order to generate the σ -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: θ , E_{ar}, π_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 γ parameter (v_{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)Ni(CO)₃ reference complexes anyway.^{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 σ donor and π -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 LNi(CO)₃ complexes.

The alternative method of separating metal-ligand interaction energies for each complex into σ - and π -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' in its lowest energy state can be defined as the overall change in electronic energy of the following Eq. 4.3.

$$L + L'F \rightarrow LF + L' \qquad \Delta E_{bind}(F,L) \qquad Eq.4.3$$

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°) is the pre-organized conformation for coordination to metal centers, while the extended geometry (NCCN torsion angles close to 180°) 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 energy¹⁷³ of the ligand, denoted as $\Delta E_{reorg}(L)$ relative to that of reference ligand L' (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.

$$\Delta E_{\text{bind}}(F,L) = \Delta E_{\text{reorg}}(L) + \Delta E_{\text{stab}}(F,L) \qquad \text{Eq. 4.4}$$

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

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Stabilization energy

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

$$\Delta E_{stab}(F,L) = \alpha_F \sigma_L + \beta_F \pi_L \qquad \qquad Eq. 4.5$$

- α_F depends on the metal fragment F, measuring its Lewis acidity (the ability to accept electrons from a ligand through σ-interactions)
- β_F depends on the metal fragment F, measuring its π-basicity (the ability to donate electrons to a ligand through π-interactions)
- σ_L depends on the ligand L, representing its σ -donation ability
- π_L depends on the ligand L, representing its π -acceptor ability

With this definition, the more negative $\Delta E_{stab}(F,L)$, the more stable the corresponding complex of the ligand relative to the reference ligand L'.

4.5.2 Generation of parameters

As Eq. 4.5 shows, there is only one ΔE_{stab} for any combination of F and L but four parameters (α_F , β_F , σ_L , π_L). 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 F (F₁ and F₂) and their α_F and β_F values were chosen, σ_L and π_L for all other ligands referenced to the standard ligand (L') will be completely determined by calculating their ΔE_{stab} with F₁ and F₂ and fitting to Eq. 4.5. Thus, parameters for any new ligand can be generated simply by calculating its ΔE_{stab} for two reference metals.

4.6 Results and Discussion

4.6.1 Choice of metal fragments

The choice of reference fragments and their α_F and β_F values is, in a sense, arbitrary. However, we wish to choose them such that the resulting σ_L and π_L parameters represent σ -donation and π -back donation. Ideally we want one "pure σ -acid" fragment F, for which we set $\alpha(F) = 1$, $\beta(F) = 0$, and one "pure π -base" fragment F, which has $\alpha(F) = 0$ and $\beta(F) = 1$. In practice, it does not quite work like that.

As for probing the σ -donation interaction, the fragment ZnCl₂ is a good choice due to the d¹⁰ character of Zn²⁺ (which means donation of d electrons from Zn²⁺ 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 MgCl₂ fragment (where one could never have back-donation) is shown in Figure 4.3. The high correlation further supports the eligibility of the ZnCl₂ fragment as the probe for σ -donation interactions.



Figure 4.3. $\Delta E_{stab}(MgCl_2)$ vs $\Delta E_{stab}(ZndCl_2)$ with 10 selected ligands. (for structures of ligands, see Figure 4.7; linear correlation coefficient: $\rho = 0.989$)

However, as for probing the π -acceptor interaction, it is hard to find suitable metal fragments which show *only* π -basicity *without* Lewis acidity. Thus, we are forced to select a fragment with strong π -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 ZnCl₂ and CoMe change as a function of the substituents to see whether these two metal fragments can probe σ -donation and π -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 σ_p and σ_p^- parameters.¹⁷⁵ As the Figure shows, the substituent effects on the stability of ZnCl₂ and CoMe are quite different. For ZnCl₂, the presence of electron-donating groups increases the complex stability while electron-withdrawing 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, σ -donation is more important for ZnCl₂ fragments, and π back-donation provides the dominant contribution to the metal-ligand binding for the CoMe fragment.^{XXIV}

^{XXIV} The information here will be used to estimate the α (CoMe) later.



Figure 4.4. Effect of pyridine 4-substituent on stabilization energies of the complexes of ZnCl₂ (\bullet , $\rho = 0.988$,) and CoMe (\diamond , $\rho = -0.983$) fragment, plotted against Taft σ_p and σ_p^- parameters¹⁷⁵

Secondly, Figure 4.5 (ligands 8-13 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 kcal/mol in Figure 4.4 and 6 kcal/mol in Figure 4.5) and electron-withdrawing groups induce destabilization for both ZnCl₂ and CoMe fragments (Figure 4.4). Although π -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 π -system (pyridine + imine arms). In addition, the coefficients of the ligand π^* 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 σ -donation to the metal center.



Figure 4.5. Effect of N-aryl 4-substituent on ZnCl_2 (\blacksquare , $\rho = 0.971$) and CoMe (\blacklozenge , $\rho = 0.981$) fragment stabilization energies, plotted against Taft σ_p parameters¹⁷⁵

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, σ_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 $ZnCl_2$ (**a**) and CoMe (**A**) fragment stabilization energies, plotted against Taft σ_p parameters¹⁷⁵

Therefore, it seems that $ZnCl_2$ (d¹⁰, Lewis acid with negligible π -basicity) and CoMe (good π -basicity, but Lewis acidity cannot be ignored) are reasonable choices for our two reference metal fragments to probe σ -donor and π -acceptor properties of the DIP-type ligands. Now two equations (Eq. 4.6 and Eq. 4.7) can be generated from Eq.4.5.

$$\Delta E_{\text{stab}}(\text{ZnCl}_2, L) = \alpha(\text{ZnCl}_2) \sigma_L + \beta(\text{ZnCl}_2) \pi_L \qquad \text{Eq. 4.6}$$

$$\Delta E_{stab}(CoMe, L) = \alpha(CoMe) \sigma_L + \beta(CoMe) \pi_L$$
 Eq. 4.7

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4.6.2 Solving ligand parameters

Based on the properties of the two metal fragments above, it is reasonable to set $\beta(\text{ZnCl}_2) = 0$ and $\beta(\text{CoMe}) = 1$ to define the π -basicity scale and $\alpha(\text{ZnCl}_2) = 1$, $\alpha(\text{CoMe}) \neq 0$ to define the Lewis acidity scale. Unfortunately, there is no unique way to assign a value to $\alpha(\text{CoMe})$. Thus we derive a "reasonable" value by requiring orthogonality of variations in σ_L and π_L parameters over our test set of ligands (33 ligands, for structures, see Figure 4.7):

$$\sum_{L} (\sigma_{L} - \overline{\sigma})(\pi_{L} - \overline{\pi}) = 0$$

$$\overline{\sigma} = \frac{1}{n(L)} \sum_{L} \sigma_{L} \quad \overline{\pi} = \frac{1}{n(L)} \sum_{L} \pi_{L}$$

Eq. 4.8

By satisfying the above equation 4.8,¹⁷⁶ α (CoMe) was calculated to be 0.25, which seems reasonable as long as there is no systematic correlation between σ -donation and π 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 σ_L and π_L parameters. As α_F and β_F are dimensionless, σ_L and π_L will have units of energy.

$$\sigma_{\rm L} = \Delta E_{\rm stab}({\rm ZnCl}_2, {\rm L})$$
 Eq. 4.9

$$\pi_{\rm L} = \Delta E_{\rm stab}({\rm CoMe,\,L}) - 0.25 \ \Delta E_{\rm stab}({\rm ZnCl}_2,\,{\rm L}) \qquad {\rm Eq.} \ 4.10$$

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.



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 $ZnCl_2$ and CoMe complexes are shown in Figure 4.8.



Figure 4.8. Calculated structures of (1)ZnCl₂ and (1)CoMe

As expected, the ZnCl₂ complex has a strongly distorted square-pyramidal (SP) geometry with two inequivalent chlorine atoms. The geometries of CoMe complexes of DIP-type 121

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 σ_L and π_L parameters

By using the above models and optimizing structures of the DIP ligands and the corresponding $ZnCl_2$ 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, σ_L/π_L parameters, and ligand reorganization energies (kcal/mol)

Ligand	$\Delta E_{stab}(ZnCl_2), \sigma_L$	$\Delta E_{stab}(CoMe)$	$\pi_{ m L}$	ΔE_{reorg}
Type I				
1	(0)	(0)	(0)	(0)
2	3.46	-7.33	-8.19	-0.84
3	3.05	-4.17	-4.93	-0.23
4	2.40	-2.27	-2.87	-0.28
5	1.02	-3.76	-4.01	-0.96

Ligand	$\Delta E_{stab}(ZnCl_2), \sigma_L$	$\Delta E_{stab}(CoMe)$	$\pi_{ m L}$	ΔE_{reorg}
6	-1.26	2.73	3.05	0.46
7	-3.49	4.09	4.96	0.91
Type II				
8	3.50	2.76	1.88	-1.12
9	2.77	2.15	1.45	-0.77
10	0.09	0.23	0.21	-0.06
11	1.09	0.10	-0.17	-0.02
12	-0.40	-0.42	-0.32	-0.31
13	-1.55	-1.26	-0.87	0.26
Type III				
14	9.92	-5.37	-7.85	-7.43
15	10.67	1.60	-1.07	-7.03
16	2.13	-0.09	-0.63	-5.30
17	6.76	6.09	4.40	-1.94
18	3.45	13.78	12.91	-9.95
19	7.95	15.08	13.09	-4.80
Type II				
20	8.46	-0.09	-2.21	0.49
21	1.41	0.96	0.61	-0.26
22	-10.16	-6.84	-4.30	1.79
23	11.39	-2.36	-5.21	-11.33
Type IV				
24	4.31	18.80	17.73	-3.70
25	-15.16	2.16	5.95	-0.08
26	1.93	7.28	6.80	-2.41
27	3.10	8.45	7.67	0.67
28	-6.01	-1.65	-0.15	2.36
29	-6.48	26.43	28.05	-6.09
30	-17.54	-17.42	-13.03	5.40
Type I				
31	3.06	-1.10	-1.87	-1.51
32	2.50	0.47	-0.15	-5.80
33	5.50	2.80	1.42	-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 σ -donor (from -17.54 kcal/mol to 3.10 kcal/mol) and π -acceptor properties (from 28.05 kcal/mol to -13.03 kcal/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 σ -donor parameters, substituents at the N-aryl ring have relatively smaller effects on π -acceptor properties of DIP ligands. Taking the cyano group as an example, at the imine carbon position (ligand 14), σ -donor ability decreases significantly with the σ parameter changing from 0 (for ligand 1) to 9.92 kcal/mol (for ligand 14); at the same time, the π -acceptor ability increases with π -parameter changing to -7.85 (for ligand 14) kcal/mol. Introduction of CN at the 4-position of the N-aryl ring results in a much smaller reduction of π -acceptor ability as indicated by the change of π parameter from 0 (for ligand 1) to 1.88 (for ligand 8) kcal/mol.

4.6.5 Transferability of σ_L and π_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 Fe(I)Me and FeN₂ 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 σ and π properties. For each fragment F, α_F and β_F parameters were obtained by fitting to Eq. 4.5 using ligand σ_L and π_L parameters in Table 4.1; therefore, α_F obtained will be the value relative to ZnCl₂ (α (ZnCl₂) = 1) and β_F will be the value relative to CoMe (β (CoMe) = 1). As the fitting is performed on two variables, the quality of the fitting is 124 graphically shown in Figure 4.9 (for Fe(I)Me) and Figure 4.10 (for FeN₂) by plotting calculated $\Delta E_{stab}(F,L)$ against predicted $\Delta E'_{stab}(F,L)$ (using the best fit to Eq. 4.5).^{XXV}

As we can see from Figure 4.9 and Figure 4.10, the fits for both FeMe and FeN₂ are very good, with linear correlation coefficients ρ of 0.975 for FeMe and 0.994 for FeN₂. For both metal fragments, Lewis acidity parameters are close to zero while the π -basicity parameter for FeN₂ ($\beta_{FeN2} = 1.23$) is larger than that of FeMe ($\beta_{FeMe} = 0.99$), indicating that FeN₂ is more π -basic than both CoMe and FeMe.

^{XXV} If it can be expressed as a linear combination (e.g. in the form of Eq. 4.5) of the two ligand parameters (σ_L and π_L), the calculated $\Delta E_{stab}(F,L)$ will have a high correlation with any value ($\Delta E'_{stab}(F,L)$) that comes from this linear combination. If the correlation coefficient equals 1, $\Delta E_{stab}(F,L)$ will equal $\Delta E'_{stab}(F,L)$.



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



Figure 4.10. Comparison of calculated $\Delta E_{stab}(FeN_2)$ values with those predicted $\Delta E'_{stab}(FeN_2)$ using the best fit to Eq. 4.5($\alpha_{FeN2} = -0.07 \pm 0.07$, $\beta_{FeN2} = 1.23 \pm 0.05$; $\rho = 0.994$; The solid line represents the ideal $\Delta E_{stab}(FeN_2) = \Delta E'_{stab}(FeN_2)$ 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 MCl_2 fragments (M = Sc-Zn) in 127 their high spin states in the same manner. The fitted data and the corresponding α_F and π_F values are summarized in Table 4.2 and plotted in Figure 4.11.

Table 4.2. α_F and β_F parameters of MCl₂ fragments for first-row transition metals

and the linear-correlation coefficients ρ between calculated $\Delta E_{stab}(F)$ and predicted $\Delta E'_{stab}(F)$ by fitting to Eq. 4.5

MCl ₂	$lpha_{ m F}$	β_{F}	ρ
$ScCl_2$	0.11 ± 0.16	0.65 ± 0.10	0.911
TiCl ₂	0.35 ± 0.09	0.59 ± 0.06	0.972
VCl ₂	0.81 ± 0.05	0.41 ± 0.03	0.993
CrCl ₂	1.00 ± 0.06	0.23 ± 0.04	0.990
MnCl ₂	1.00 ± 0.04	0.02 ± 0.03	0.992
FeCl ₂	0.98 ± 0.06	0.16 ± 0.04	0.987
CoCl ₂	1.11 ± 0.05	-0.01 ± 0.03	0.993
NiCl ₂	1.27 ± 0.06	0.03 ± 0.04	0.995
CuCl ₂	1.33 ± 0.13	0.03 ± 0.08	0.972
ZnCl ₂	(1)	(0)	(1)

The ScCl₂ fragment gives a poor fit and larger errors in the parameters, but the other metals generally produce good fits ($\rho = 0.970-1.0$)^{XXVI}.

^{XXVI} ScCl₂ differs from the other MCl₂ 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 $ScCl_2^+$ and DIP⁻ fragments. Secondly, Sc, is significantly larger than the other first-row transition metals. Finally, for $ScCl_2$ 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. α_F (**•**) and β_F (**•**) values fitted for fragments ScCl₂-ZnCl₂ and a set of 10 test ligands using Eq 4.5.Error bars indicate $\pm 1\sigma$

As Figure 4.11 shows, Lewis acidity (α_F) increases monotonically from d¹ to d⁹. In contrast, π -basicity (β_F) decreases to zero as the number of d electrons increases from 1 to 5 (from ScCl₂ to MnCl₂). After the number of d electrons was further increased to 6 (FeCl₂), β_F becomes significant again. For the remaining metal fragments, β_F is not important. This trend of π -basicity (β_F) 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 π -basicity (β) and the amount of imine bond elongation was obtained.



Figure 4.12. Correlation between β_F parameter and calculated C=N bond length in (DIP)MCl₂ complexes (correlation coefficient $\rho = 0.964$)

4.6.7 Issues addressed

The choice of α_{CoMe}

As we reconsider our model to generate σ_L and π_L for DIP type ligands and α_F and β_F values for metal fragments, the absolute values of these parameters depend on the choices of the α and β values for the two reference fragments ZnCl₂ and CoMe. As for the β -

scale, the choice of the setting ($\beta_{ZnCl2} = 0$, $\beta_{CoMe} = 1$) is OK due to the safe assumption that back-donation from ZnCl₂ is negligible. However, for the α -scale, while the assignment of 1 to α_{ZnCl2} is acceptable, the choice of α_{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 α_{CoMe} affects only the π_L values. For ligands where $\Delta E_{stab}(ZnCl_2)$ is large relative to $\Delta E_{stab}(CoMe)$, the π_L value will change significantly if α_{CoMe} is changed. Among the reasonable range of values for α_{CoMe} (estimated as 0.15-0.50)^{XXVII}, π_L values would be significantly affected for ligands **15**, **17**, **20**, **22**, **29** and **30**. Taking ligand **30** as an example, it was predicted to be a strong σ donor and a strong π -acceptor when α_{CoMe} equals 0.25. However, whether it is a good π acceptor is still a matter of debate. If it were a weak π -acceptor, then a more positive π_L would be preferred. Thus, in order to reduce π_{30} value to zero (making it only as strong a π -acceptor as ligand **1**), α_{CoMe} needs to be set to around 1.0, which means that the Lewis acidity of CoMe would be as large as that of ZnCl₂. This clearly does not make chemical sense because CoCl₂ has similar Lewis acidity to ZnCl₂ and the Lewis acidity of CoMe is expected to be much smaller than that of CoCl₂.

On the other hand, the choice of the α_{CoMe} value can also affect the parameters of the other metal fragments. Values for the π -basicity (β_F) remain unchanged, but the α_F

^{XXVII} According to Figure 4.4, the strength of π -basicity of CoMe is similar to that of Lewis acidity of ZnCl₂, thus I think α (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 α (CoMe) can be reasonably regarded as higher than 0.15.

parameters vary roughly in parallel with α_{CoMe} . For example, for the fragment Fe(N₂), α_F is calculated to be close to zero; however, it would be negative when $\alpha_{CoMe} < 0.25$, which indicates repulsive σ -interactions compensated by stronger attractive π -interactions. Although possible, this still does not seem very reasonable. Therefore, the margins for choosing different α_{CoMe} values (and hence obtaining significantly different ligand parameters) are quite limited.

In summary, any choice of α_F/β_F for the reference fragments will produce scales for σ_L/π_L for ligands and α_F/β_F for other metal fragments. As long as linear dependencies are avoided, any choice will produce the same predicted ΔE_{stab} (Eq. 4.5) and ΔE_{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 σ -effects and π -effects are concerned, the choice of α_{CoMe} will matter a lot.

Steric effects

Our procedure does not produce a separate steric parameter. Thus σ_L and π_L represent the interactions that include the contributions by steric effects of the ligand. In addition, steric effects can also affect the reorganization energy ΔE_{reorg} . Thus, the parameters developed here also contain a steric contribution.

4.7 Conclusions

Ligand parameters σ_L and π_L for DIP-type ligands have been devised through DFT calculations and represent the overall σ -donation and π -accepting ability of the ligands. Although there is some uncertainty about the choice of α_{CoMe} , the results make chemical sense. DIP was shown to be a strong π -acceptor, although bis(carbene)pyridine (ligand **30** in Figure 4.7) is even better. Bis(phosphinimine)pyridine ligands are acceptable σ -donors but very poor π -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, α_F (representing Lewis acidity relative to ZnCl₂) and β_F (representing π -basicity relative to CoMe). Our study of MCl₂ fragments (M = Sc-Zn) showed that Lewis acidity increases monotonically from ScCl₂ to CuCl₂ while π -basicity first goes to zero from ScCl₂ to MnCl₂, then increases again for FeCl₂, 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 σ_L and π_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)FeCl₂ when reacted with FeCl₂. By contrast, the less hindered phDIP-ligand (2,6-(phenylimino)ethylpyridine) is good at oligomerization¹³⁷ and prefers to form the bis-ligand coordinated complex [L₂Fe]²⁺ [FeCl₄]²⁻ when reacted with FeCl₂.¹⁷⁸ 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, (Py)₂FeR₂,¹⁷⁹ (TMEDA)NiMe₂,¹⁸⁰ (Py)₂MnR₂¹⁸¹ 135 (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 ligands¹⁴² 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 $[Co(2,4,6-Me_3C_6H_2)_2]$ 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 $Co[2,6-(2,4,6-Me_3C_6H_2)_2-C_6H_3]_2$ from $CoCl_2$ 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 coworkers¹⁸⁴ used MeMgBr to alkylate (Py)₂CoCl₂ to generate a very unstable product formulated as (Py)₂CoMe₂. 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 coworkers¹⁸⁵ found that

(TMEDA)Co(CH₂SiMe₃)₂ can be made by reducing anhydrous CoCl₂ with 4.0 eq. LiCH₂SiMe₃ 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 Cámpora¹⁵¹ 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 (Py)₂CoR₂ (R = CH₂SiMe₃)

Anhydrous $(Py)_4CoCl_2$ was treated with 2.0 eq. of LiCH₂SiMe₃ in hexane at -70 °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 $(Py)_2Co(CH_2SiMe_3)_2$. The ¹H NMR spectrum of this green oil is shown in Figure 5.1A.



Figure 5.1. ¹H NMR spectra of (A) $(Py)_2Co(CH_2SiMe_3)_2$ and (B) (TMEDA)Co(CH_2SiMe_3)_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 $(Py)_2Fe(CH_2SiMe_3)_2$ was also prepared¹⁵¹ and the comparison of their ¹H NMR data are summarized in Table 5.1.

	$(Py)_2Co(CH_2SiMe_3)_2$		$(Py)_2Fe(C)$	$CH_2SiMe_3)_2^{151}$
	δ (ppm)	$\Delta v_{1/2}$ (Hz)	δ (ppm)	$\Delta v_{1/2}$ (Hz)
SiMe ₃	10.3	80	11.2	318
Ру Н2	114	1600	129 ^a	1614 ^a
Ру <i>Н</i> 3	38.4	500	35.5	657
Ру <i>Н</i> 4	-8.5	190	17.4	348

Table 5.1. Comparison of ¹H NMR shifts (ppm) for $(Py)_2M(CH_2SiMe_3)_2$ complexes (M = Co, Fe)

^a This chemical shift was not reported by Cámpora.¹⁵¹ Co CH_2 and Fe CH_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 $(Py)_2Co(CH_2SiMe_3)_2$ 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 ppm.^{XXVIII} The broadness of the peaks in Figure 5.1A 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): $\delta^{obs} = \delta^{orb} + \delta^{FC} + \delta^{PC}$

The δ^{orb} for high-spin iron(II) and cobalt(II) complexes of the same ligand should be very similar. As the δ^{PC} contributions to the chemical shifts of both cobalt(II) and iron(II) are usually negligible, δ^{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 Co(II), three unpaired electrons will be located in the d_{xy} , d_{xz} , and d_{yz} orbitals, while for iron(II), four unpaired electrons are in d_{xy} , d_{xz} , d_{yz} and d_{x2-y2} orbitals. The contributions of the d_{xy} , d_{xz} , and d_{yz} electrons will be very similar for the two metals, and 139

the compound; integration of the peaks strongly supports the formulation as $(Py)_2Co(CH_2SiMe_3)_2$. In addition, this compound is stable at -35 °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 LiCH₂SiMe₃ used plays a key role in obtaining high yield and high purity. Different batches of the LiCH₂SiMe₃ 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, LiCH₂SiMe₃ was crystallized from the freshly received solution by cooling it to -35 °C and the crystalline solid obtained was stored in a glove box at low temperature to maintain its quality.
- 2) Pink (Py)₄CoCl₂ used was prepared from anhydrous CoCl₂ and dry pyridine, rather than from the commonly used hydrated cobalt dichloride, to avoid potential problems in the reaction with LiCH₂SiMe₃. 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_{x2-y2} 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 d_{x2-y2} orbital will be affected significantly. This is might be the case for the pyridine H4 proton of $(Py)_2Co(CH_2SiMe_3)_2$ and $(Py)_2Fe(CH_2SiMe_3)_2$.

suspended in pentane or hexane in the synthesis of $(Py)_2Co(CH_2SiMe_3)_2$, but this dissociation did not affect the outcome of the reaction.

3) Chirik and coworkers¹⁸⁷ reported that the mono alkyl complex $(Py)_2Fe(CH_2SiMe_3)Cl$ can be prepared from the reaction of $(Py)_4FeCl_2$ with only 1.0 equivalent of LiCH₂SiMe₃. However, for the Co case studied here, we found that $(Py)_2Co(CH_2SiMe_3)Cl$ could not be detected when 1.0 equivalent of RLi was used. Instead, only $(Py)_2Co(CH_2SiMe_3)_2$ was generated together with a blue solid suspected to be unreacted $(Py)_nCoCl_2^{XXIX}$.

The main characterization of this compound is by ¹H NMR as reported above. The oily nature of the product prevented the determination of a crystal structure. In order to further characterize (Py)₂Co(CH₂SiMe₃)₂, an internal standard (hexamethylbenzene) was used to quantify the amount of (Py)₂Co(CH₂SiMe₃)₂ and its hydrolysis products. The purity of the product was estimated to be 91% from the ¹H 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 method⁹⁸ to be 4.8(3) μ_B which falls in the commonly observed range of high spin cobalt(II) (4.3-5.2 μ_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 $LiCH_2SiMe_3$ converted this blue solid into $(Py)_2Co(CH_2SiMe_3)_2$.

5.3 Synthesis of (TMEDA)CoR₂ (R = CH₂SiMe₃)

By adding 10 eq. of dry TMEDA to freshly prepared green (Py)₂Co(CH₂SiMe₃)₂ in hexane or diethyl ether at -20 °C, a brown solution was obtained. As (TMEDA)Co(CH₂SiMe₃)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)Co(CH₂SiMe₃)₂ was obtained by crystallization from a hexane solution containing one drop of TMEDA at -35 °C. The total yield over two steps from the starting material (Py)₄CoCl₂ was 57%. The simplicity of the whole procedure and the high yield will make this method preferable to the procedure reported by Hay-Motherwell¹⁸⁵ and wide application can be expected in the future. The ¹H NMR spectrum of (TMEDA)Co(CH₂SiMe₃)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(CH_2SiMe_3)₂ is shown in Table 5.2.

	(TMEDA)Co(CH ₂ SiMe ₃) ₂		(TMEDA)Fe	$e(CH_2SiMe_3)_2^{179c}$
	δ (ppm)	$\Delta v_{1/2}$ (Hz)	δ (ppm)	$\Delta v_{1/2}$ (Hz)
Si <i>Me</i> ₃	9.6	70	12.14	180
NCH_3	78	350	86.8	1100
CH_2N	80	600	72.6	890

Table 5.2. Comparison of ¹H NMR shifts (ppm) for (TMEDA)M(CH₂SiMe₃)₂ complexes $(M = Co, Fe)^{a}$

^a CoC H_2 and FeC H_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)Co(CH₂SiMe₃)₂ (Figure 5.2).



Figure 5.2. Thermal ellipsoid plot for (TMEDA)Co(CH₂SiMe₃)₂. (30% probability, hydrogens omitted for clarity). Selected bond distances (Å) and angles (deg):Co(1)-N(1): 2.186(2); Co(1)-N(2): 2.179(2); Co(1)-C(7): 2.035(2); Co(1)-C(8): 2.035(2); C(7)-Co(1)-N(1): 115.55(10); C(8)-Co(1)-N(2): 113.40(11); C(7)-Co(1)-N(2): 106.80(9); C(7)-Co(1)-C(8): 122.91(11).

(TMEDA)Co(CH₂SiMe₃)₂ prepared according to our method has the same unit cell and the same structure that previously reported¹⁸⁵ with the cobalt center having tetrahedral coordination geometry. This clearly confirms the identity of (TMEDA)Co(CH₂SiMe₃)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 $(Py)_2CoR'_2$ ($R' = CH_2CMe_2Ph$)

Because the X-ray structure of $(Py)_2Co(CH_2SiMe_3)_2$ 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.^{XXX} For iron, Cámpora¹⁵¹ found that $(Py)_2Fe(CH_2SiMe_3)_2$ did not form a crystal, but $(Py)_2Fe(CH_2CMe_2Ph)_2$ crystallized well. Thus, we decided to prepare $(Py)_2CoR'_2$ (R' = CH₂CMe₂Ph)₂), hoping it would generate X-ray quality crystals. However, the reaction turned out to be not as simple as for $(Py)_2Co(CH_2SiMe_3)_2$. As R'Li is not commercially available, R'MgCl was used to react with $(Py)_4CoCl_2$ in diethyl ether at -50 °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 °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.

^{XXX} The synthesis of $(Py)_2CoPh_2$ and $(Py)_2CoMe_2$ using the same synthesis procedure for $(Py)_2Co(CH_2SiMe_3)_2$ was not successful. For experimental details, see Section 9.3 in Chapter 9.



Figure 5.3. X-ray structure of $(Py)_2CoR'_2$ (thermal ellipsoids drawn at 30% probability, hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Co(1)-C(1): 2.066(3); Co(1)-C(31): 2.075(4); Co(1)-N(1): 2.117(3); Co(1)-N(2): 2.108(3); N(1)-Co(1)-N(2): 127.32(15); C(11)-Co(1)-C(31): 96.20(11).

	(Py) ₂ CoR' ₂	$(Py)_2FeR'_2^{151}$
a (Å)	11.8183(11)	11.6538(12)
b (Å)	11.8294(12)	11.8197(12)
c (Å)	12.1892(12)	12.0936(13)
α (deg)	105.652(2)	108.971(2)
β (deg)	109.119(2)	105.834(2)
γ (deg)	108.825(2)	108.571(2)
Average M-C (Å)	2.071	2.091
Average M-N (Å)	2.112	2.149
Average N-M-C(deg)	104.76 and 109.74	104.08 and 109.31
N-M-N(deg)	96.20(11)	91.70
C-M-C(deg)	127.32(15)	131.31

Table 5.3. X-ray structures: comparison of (Py)₂CoR'₂ and (Py)₂FeR'₂

As Table 5.3 shows, the two structures are very similar except that the angle NMN is around 5° larger and the angle CMC is around 5° smaller for Co. Unfortunately, $(Py)_2CoR'_2$ 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 $(Py)_2CoR_2$ and $(Py)_2CoR'_2$ 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 CH_2SiMe_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.

R″•	·CH ₂ SiMe ₃	·CH ₂ CMe ₃	·CH ₂ CMe ₂ Ph
DFT	$\Delta E (\Delta G)^{a}$, kcal/mol	$\Delta E (\Delta G)^{a}$, kcal/mol	$\Delta E (\Delta G)^{a}$, kcal/mol
b3-lyp(SVP)	0.0(0)	-7.3(-7.1)	-2.9 (-2.9)
b3-lyp(TZVP)	0.0(0)	-7.7(-7.4)	-3.1(-3.1)

 \cdot CH₂SiMe₃ + R"Li \longrightarrow LiCH₂SiMe₃ + \cdot R"

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

During the preparation of $(Py)_2CoR'_2$, the use of the magnesium reagent is problematic due to the formation of $(Py)_2MgR'_2$. The similar solubility of the Mg and Co analogs makes purification difficult. In order to verify the identity of the impurity $(Py)_2MgR'_2$, it was prepared separately by adding pure pyridine to an ether solution of ClMgCH₂CMe₂Ph followed by crystallization from a pentane solution at -35 °C; its identity was confirmed by ¹H NMR, ¹³C NMR and 2D Gradient HSQC. Later, we found that the change from Et₂O 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 ¹H NMR (Figure 5.4), although the yield was only 20 %. The chemical shifts of pyridine in $(Py)_2CoR'_2$ are similar to those in $(Py)_2CoR_2$ and the comparison with the iron analog is shown in Table 5.5.



Figure 5.4. ¹H NMR spectrum of (Py)₂CoR'₂ in C₆D₆

-		(Py) ₂ CoR' ₂			$(Py)_2FeR'_2^{151}$
		δ (ppm)	$\Delta v_{1/2}$ (Hz)	δ (ppm)	$\Delta v_{1/2}$ (Hz)
-	Py H2	108	5300	No data.	No data.
	Ру НЗ	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 ^b	1350 ^b
	Ph Hm	7.4	27	5.42	48
	Ph Hp	3.9	17	11.77	330

Table 5.5. Comparison of ¹H NMR shifts (ppm) for $(Py)_2MR'_2$ complexes $(M = Co, Fe)^a$

^a CoC H_2 and FeC H_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 report¹⁵¹ 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 CMe₂ group. Also, one would expect for (Py)₂FeR'₂ chemical shifts of coordinate pyridines similar to those observed for (Py)₂Fe(CH₂SiMe₃)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 ¹H 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 ¹H NMR

The theory of the paramagnetic chemical shifts has been discussed in detail in Chapter 2. Here, the details on how we^{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}

$$\delta^{\text{obs}} = \delta^{\text{orb}} + \delta^{\text{FC}} + \delta^{\text{PC}}$$
 Eq. 5.1

In this equation, δ^{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 δ^{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 δ^{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

^{XXXI} The calculation of DFT was done by Peter H.M. Budzelaar and me.

$$\delta^{FC} = A_{iso} \frac{g_e \beta_e S(S+1)}{g_N \beta_N 3kT}$$
 Eq. 5.2

where,

- A_{iso} is the isotropic hyperfine coupling constant, calculated using ORCA (B3LYP/TZVP).¹¹⁹
- g_e is the rotationally averaged electronic g-value.
- g_N is the nuclear g-value.
- β_e and β_N are the Bohr and nuclear magnetons, respectively.
- S is the total spin quantum number (multiplicity = 2S+1)
- κT is the thermal energy.

 δ^{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)CoR₂ ($R = CH_2SiMe_3$) (Table B.2 in the Appendix B) and (Py)₂CoR'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 ¹H 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 ¹H NMR chemical shifts of $(Py)_2CoR_2$, $(Py)_2CoR'_2$ 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).

System	Н	$A_{iso}\left(MHz ight)$	$\delta_{orb} \left(ppm \right)^{a,b}$	$\delta_{pred} \left(ppm \right)^{b}$	δ _{obs} (ppm)
$(Py)_2CoR_2$	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
	CoCH ₂	2.756	1.360	364.3	n.o.
	SiMe ₃	0.063	-0.492	7.8	10.3
(TMEDA)CoR ₂	NCH ₂	0.543	2.545	74.1	80
	NMe ₂	0.580	2.067	78.4	78
	CoCH ₂	2.797	1.203	369.5	n.o.
	SiMe ₃	0.079	-0.209	10.1	9.6
$(Py)_2CoR'_2$	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
	CoCH ₂	3.339	3.812	443.4	n.o.
	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

Table 5.6. B3LYP calculation of paramagnetic ¹H shifts for Co complexes^a

^a Geometry was optimized at b3-lyp/TZVP. R: -CH₂SiMe₃; R':-CH₂C(Me₂)Ph;

^b correction to the published data.

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 154

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 ¹H NMR chemical shifts for cobalt(II) complexes in Chapter 6.



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

5.6 Conclusions

A new complex $(Py)_2CoR_2$ was easily prepared from $(Py)_4CoCl_2$ in high yield and high purity. Although its oily nature prevented full characterization, ¹H NMR, magnetic moment measurements (Evans method) and hydrolysis experiments clearly support the constitution of the complex. In addition, the "CoR₂" fragment of (Py)₂CoR₂ can be transferred to TMEDA to form (TMEDA)CoR₂ in high yield. The identification of (TMEDA)CoR₂ 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)₂CoR'₂ was determined by single-crystal X-ray diffraction; it is similar to the iron analog. However, it is much less stable than (Py)₂CoR₂ and will not be as useful as a source of CoR'₂. The ¹H 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 ¹H NMR spectrum.

Chapter 6. Experimental and computational study on the generation of Co(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)CoCl₂ into the active species in ethylene polymerization.⁸¹ The standard method to make (DIP)cobalt(I) alkyl complex is to use a Grignard or organo-lithium reagent to reduce and alkylate the corresponding (DIP)cobalt(II) dihalides. However, for less hindered DIP ligands, reaction of RLi compounds with (DIP)CoCl₂ 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 single-electron 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.^{81b}

^{XXXII} Figures, part of tables, part of schemes and part of the texts of the corresponding experimental part in Chapter 9 are copied directly from the published paper.

However, whether (DIP)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. succeeded synthesizing $(Py)_2Co(CH_2SiMe_3)_2$ we in (TMEDA)Co(CH₂SiMe₃)₂ and (Py)₂Co(CH₂CMe₂Ph)₂ in a convenient way. The further application of these labile cobalt alkyl precursors will be explored in this chapter. Because (Py)₂Co(CH₂CMe₂Ph)₂ is not stable at room temperature, only stable (Py)₂Co(CH₂SiMe₃)₂ and (TMEDA)Co(CH₂SiMe₃)₂ were applied to ligand-exchange reaction with DIP-type ligands to generate (DIP)CoCH₂SiMe₃ or (DIP)Co(CH₂SiMe₃)₂ in the following content of this chapter, $R = CH_2SiMe_3$).

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 σ -donor and π -acceptor abilities (see also Chapter 4) were explored.



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)CoCl₂ precursor with the organo-lithium reagent.⁸¹ Although iron dihalide complexes of ligands **3**, **4**, and **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 **10** was reported to be highly active in ethylene oligomerization, but showed no activity in ethylene polymerization.^{61b}

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 5 is a stronger π -acceptor, but weaker σ -donor while ligand 6 is a much weaker π -acceptor than ligand 7

but a comparable σ -donor. Among the remaining two variations, ligand **8** is a weaker σ donor and weaker π -acceptor than ligand **7**, while ligand **9** is a combination of imine and phosphinimine characters. Ligand **10** is a stronger σ -donor and stronger π -acceptor.

6.2.2 Ligand Exchange Study

Both (Py)₂CoR₂ and (TMEDA)CoR₂ (R: CH₂SiMe₃) react rapidly with ligands 1 and 2 to cleanly generate purple diamagnetic cobalt(I) trimethylsilylmethyl complexes which can be easily identified by their characteristic ¹H NMR peaks^{XXXIII}: one is a triplet at $\delta = 10.1$ ppm (Py H4), the other one is a singlet at $\delta = -1.2$ ppm (N=CMe). The product from the reaction between ligand 2 and (Py)₂CoR₂ 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: Co(1)-N(1), C(1)-N(2), and C(1)-C(2) bond lengths are virtually identical, indicating a similar amount of electron transfer from the cobalt center to the conjugated π system of DIP. In both cases, the alkyl groups are bent out of the CoN_3 plane (defined by the central pyridine, cobalt and two imine bonds) by a similar amount (the *trans* NCoC angle is around 165°), 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° smaller and the torsion angle between the N-aryl ring and the imine bond is also around 5-10° smaller

^{XXXIII} The products from the \cdot CH₂SiMe₃ released end up as TMS and (CH₂SiMe₃)₂ detected by ¹H NMR.

than that in (7)CoR, which is probably due to the smaller repulsion between the bulky SiMe₃ 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 (Å) and angles (deg): Co(1)-N(1): 1.834(2); Co(1)-N(2): 1.9165(15); C(1)-N(2): 1.330(2); C(1)-C(2): 1.434(3); Co(1)-C(14): 1.964(3); N(1)-Co(1)-N(2): 80.63(5); Si-C(14)-Co(1): 128.55(15); N(1)-Co(1)-C(14): 165.07(10).

Table 6.1. Comparison of the X-ray structures of (7)CoCH₂SiMe₃ and (1)CoCH₂SiMe₃.

(labelling of the atoms as in Figure 6.2; distances in Å; angles in deg)

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

Steric shielding (relative to ligand 7) is further reduced in ligands 3 and 4. Although the reaction with both $(Py)_2CoR_2$ and $(TMEDA)CoR_2$ seems to generate the cobalt(I) monoalkyl complexes, the results are complicated. On the one hand, both ligand 3 and 4 reacted with excess $(Py)_2CoR_2$ to generate diamagnetic cobalt(I) monoalkyl complexes, but the Py H4 resonances of these products were found at "atypical" chemical shifts 162

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 ¹H NMR). After 30 mins, an unknown purple precipitate started to form, and further identification was not successful.^{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)CoR₂ 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 ¹H NMR spectra of products generated from the reaction with $(Py)_2CoR_2$ and from (TMEDA)CoR₂. A further experiment was carried out by adding free pyridine to the product generated from (TMEDA)CoR₂ and ligand **4** (Figure 6.4D). The pyridine H4 resonance in the resulting ¹H NMR spectrum is much closer to that obtained from direct reaction between the ligands and excess $(Py)_2CoR_2$. Therefore, the difference between the reactions with $(Py)_2CoR_2$ 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)CoCH₂SiMe₃ might also lead to the generation of cobalt(0).⁶⁷ (3)CoCH₂SiMe₃ might have similar decomposition routes.

hindrance and no significant π -acceptor character, and will not coordinate to the cobalt(I) center.

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



Figure 6.3. Tentative assignment of ¹H NMR resonances for the reaction in C_6D_6 of ligand **3** with (A) an equimolar amount of (TMEDA)CoR₂; (B,C) excess (Py)₂CoR₂ at two different concentrations. (* denotes (CH₂SiMe₃)₂; the assignment of "h" peak is corrected from the published one)



Figure 6.4. Tentative assignment of ¹H NMR resonances for the reaction in C_6D_6 of ligand **4** with (A) excess (TMEDA)CoR₂; (B,C) excess (Py)₂CoR₂ at two different concentrations; (D) mixture (A) with added Py. (* denotes (CH₂SiMe₃)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 π -acceptor than standard ligand **2**. The procedure for the synthesis of ligand **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 CF₃ 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 (Å) and torsion angles (deg): C(2)-C(5): 1.492(3); C(5)-N(7): 1.267(3); N(1)-C(2)-C(5)-N(7): 134.98.

When this better π -acceptor ligand **5** reacted with labile cobalt dialkyl complexes, the ¹H NMR spectrum of the immediate mixture of ligand **5** and (Py)₂CoR₂ 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, ¹⁹F 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, ¹⁹F NMR showed that there is no reaction between (TMEDA)CoR₂ and ligand **5** after immediate mixing; longer standing resulted in decomposition.



Figure 6.6. ¹H NMR spectra for reaction in C_6D_6 of ligand **5** with excess $(Py)_2CoR_2$: (A) pure **5**; (B) after addition of $(Py)_2CoR_2$, showing a few tentative assignments. (* denotes $(CH_2SiMe_3)_2$; assignment of h peak is corrected from the published one)



Figure 6.7. ¹⁹F NMR spectra for the reaction of ligand **5** with excess $(Py)_2CoR_2$ in C₆D₆: (A) pure **5**; (B) after addition of $(Py)_2CoR_2$; (C) 2h after mixing; (D) after hydrolysis

As the above results indicate, the ligand-exchange reactions with ligands **1-5** involve a change in oxidation state of cobalt from II to I. Thus it is not a simple ligand-displacement reaction but involves the reduction of the cobalt center. The strong π -acceptor property of the DIP ligand accounts for the ease of this reduction. Thus we suspected that a ligand with weaker π -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 π -acceptor but a comparable σ -donor,¹⁹⁵ see Chapter 4) was used for this purpose. Indeed,

when it was reacted with $(Py)_2CoR_2$ 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 ¹H NMR spectrum. Unfortunately, the reaction was not clean enough to allow isolation of the product. When Pybox **6** reacted with (TMEDA)CoR₂, 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)CoR₂. This mixture decomposed in hours at room temperature, but was stable for longer times at -35 °C.



Figure 6.8. ¹H NMR spectrum of "(6)CoR₂", still containing some (TMEDA)CoR₂

When poor π -acceptor properties were maintained but the σ -donor properties were further reduced by using ligands **8** and **9**, no reaction with (TMEDA)CoR₂ was detected by ¹H NMR. This clearly showed that a certain σ -donor strength is required for successful ligand exchange.

The biscarbene **10** with better σ -donor and better π -acceptor properties reacted with both (Py)₂CoR₂ and (TMEDA)CoR₂. 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)NiMe₂ or (TMEDA)PdMe₂¹⁹⁶ 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 ¹H NMR of (6)CoR₂

The ¹H NMR assignments for (6)CoR₂ (Figure 6.8) are based on integration and comparison with (6)FeR₂ (Table 6.2). The arrangement of peak positions of Si*Me*₃, Py *H3*, C*H*₂O and C*Me*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 ¹H NMR spectra of CoCl₂, FeCl₂, CoR₂ and FeR₂ complexes of ligands in Figure 6.1; results are summarized in Table 6.3.

	(6)C	oR ₂	(6)]	FeR ₂ ^b
	δ (ppm)	$\Delta v_{1/2}$ (Hz)	δ (ppm)	$\Delta v_{1/2}$ (Hz)
SiMe ₃	21.8	120	9.3	277
Ру <i>H</i> ₃	44.4	80	25.1	224
Ру <i>Н</i> ₄	-66.5	34	337	1074
CH ₂ O	-5.6	36	-0.46	432
CMe ₂	-16.9	110	-6.4	222

Table 6.2. Comparison of ¹H NMR shifts (ppm) for (6)MR₂ complexes (M = Co, Fe)^a

^a CoC H_2 and FeC H_2 were not observed, probably due to the broadness of the peaks and the large chemical shift induced directly by iron and cobalt. ^b (6)FeR₂ was studied in Chapter 3.

Entry	Complexes	Ру <i>H</i> ₃	Ру <i>Н</i> 4
1	$(1)CoCl_2^{197}$	N.R.	N.R.
2	(1) FeCl_2^{197}	86.2	39.6
3	(1)FeR ₂ ¹⁵¹	58.12	279.42
4	(2)CoCl ₂ ¹⁹⁷	111.4	36.14
5	(2) $FeCl_2^{197}$	83.7	40.1
6	(2)FeR ₂ ¹⁵¹	57.55	283.07
7	(5)CoCl ₂ ^c	113.7	33.4
8	(5)FeCl ₂ ^c	83.7	85.7
9	(6)CoCl ₂ ^b	78.4	11.7
10	(6)FeCl ₂ ^b	61.5	-7.65
11	(6)FeR ₂ ^c	25.1	337
12	$(7)CoCl_2^{197}$	117.1	49.91
13	(7)FeCl ₂ ¹⁹⁷	81.7	81.1
14	(7)FeR ₂ ¹⁵¹	52.39	306.41
15	(9)CoCl ₂ ^c	106	26.0
16	(9)FeCl ₂ ^c	86.6	39.9

Table 6.3. Summary of ¹H NMR shifts (ppm) of the central pyridine ring protons in

DIP ir	on and	cobalt	comp	lexes ^a

^{a 1}H NMR was measured in CD_2Cl_2 . ^b prepared by me (see experimental part) and ¹H NMR was performed in CD_2Cl_2 . ^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 *H4* chemical shift in their cobalt or iron dialkyl complexes. Thus Py *H4* chemical shifts of (**6**)CoR₂ in its high spin state and with tridentate coordination mode of ligand **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 π -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 *H4* 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)CoR₂ would be expected to be much larger than 11.7 ppm if the coordination mode of the ligand **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 ¹H NMR spectrum we observed, the Py H4 peak in (6)CoR₂ moves significantly to higher field. Thus, a bidentate coordination of ligand **6** and/or a low-spin state of the cobalt center seem likely.

6.2.4 Low temperature NMR study

The reactions of ligand **1** with both $(Py)_2CoR_2$ and $(TMEDA)CoR_2$ were further studied by low-temperature NMR, aiming at detecting a hypothetical (**1**)CoR₂ intermediate. The ¹H NMR spectrum for the reaction of $(Py)_2CoR_2$ with ligand **1** at low temperature showed broad peaks which could not be interpreted. However, reaction with $(TMEDA)_2CoR_2$ gave an interpretable ¹H NMR (Figure 6.9). At -35 °C, there is no reaction (Figure 6.9(1)). At 0 °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.



3) 0 °C; 4) 25 °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 L_2CoR_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).



Scheme 6.1. Illustration of L_2CoR_2 with ligand 1 or 6

First, the structure of the (6)CoR₂ complex ($R = CH_2SiMe_3$) was explored by DFT. The ¹H NMR spectrum showed that the complex has effective C_{2v} 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 ¹H NMR spectrum of cobalt and iron complexes, (6)CoR₂ 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 (6)CoR₂, the geometries of (6)CoR₂ and (1)CoR₂ 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 (6)CoR₂ to be 10 kcal/mol lower than high-spin state while b3-lyp predicted the high-spin state to be 10 kcal/mol lower in energy. Thus which functional can best describe the spin state of (6)CoR₂ needs to be further explored. A

good way to decide this issue is to compare the property prediction with experimental results. For (6)CoR₂, two pieces of experimental data are available: the chemical shifts in the 1 H NMR spectrum and the equilibrium constant between (6)CoR₂ and (TMEDA)CoR₂.

Both functionals were firstly used to predict the equilibrium constant of the reaction between (TMEDA)CoR₂ and ligand **6**: b3-lyp predicts the free energy for this reaction to be 2.8 kcal/mol while b-p predicts it to be -12.97 kcal/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 ($\Delta G = 0.04$ kcal/mol).^{XXXV} In contrast, the exchange equilibrium for **1** is predicted to be less favourable than for **6** (free energy is calculated to be 10 kcal/mol larger than for **6**; see Table C.2 in the Appendix C), which agrees with the observation that no paramagnetic intermediate for the reaction of (TMEDA)CoR₂ with ligand **1** was detected by low temperature NMR (see Section 6.2.4). As the prediction of paramagnetic ¹H NMR shifts worked quite well for (Py)₂CoR₂ and (TMEDA)CoR₂, we decided to apply it also to (**6**)CoR₂. As mentioned in Chapter 5, the B3LYP functional works better than BP86 in predicting the ¹H NMR chemical shifts of cobalt(II) dialkyl complexes in high-spin states. Therefore, B3LYP was used for the

^{XXXV} 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 ¹H NMR has itself a certain experimental error margin (normally ~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.

prediction of ¹H NMR chemical shifts of (6)CoR₂, but BP86 calculations were still done at the same time for comparison. The ¹H NMR chemical shifts for both high-spin and low-spin states of (6)CoR₂ were calculated and compared with experimental data (Table 7.1). For B3LYP, the calculated ¹H NMR shifts of high-spin (6)CoR₂ are more consistent with the experimentally observed values, particularly the Py H4 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 C_{2v} symmetry in solution can be explained by rapid exchange between two alternative κ^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)CoR₂ as being high spin with a κ^2 -bound ligand. Structure labelling of various (6)CoR₂ conformations is shown in Figure 6.10.

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

Table 6.4. Paramagnetic ¹H NMR shifts for Co complexes calculated at B3LYP ^a

^a For Co complexes of **6**, the Gaussian 03 SCF calculations needed for calculating δ^{orb} did not converge, therefore we used the values calculated for the free ligand and for the CH₂SiMe₃ group in (TMEDA)CoR₂. The errors this introduces should be of the order of 1-2 ppm, which is small relative to the δ^{FC} contribution.



Figure 6.10. Structures and different names of $(6)CoR_2$ complexes depending on the coordination mode of the ligand (in parenthesis is the relative electronic energy (kcal/mol) of $(6)CoR_2$ the high-spin state calculated at b3-lyp/TZVP)

Based on ligand-exchange results with **1** and **6**, the following mechanism for the reaction of $(Py)_2CoR_2$ with DIP-type ligands is proposed (Scheme 6.2). First, the DIP-ligand exchanges with pyridine in $(Py)_2CoR_2$ to generate the high spin κ^2 intermediate, which can be easily converted to the low spin κ^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 (Py)₂CoR₂.

Because we are mainly concerned with how easily Co(II) dialkyl is converted to the Co(I) alkyl complex, the energy profiles for (6)CoMe₂, (1)CoMe₂, (6)CoR₂ and (1)CoR₂ from the high-spin κ^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 κ^2 to low-spin κ^3 . Both possibilities were examined. The minimum-energy crossing point (MECP) (for basic theory see the Appendix C) approach¹⁹⁸ was used to locate the crossing points between the S = 3/2 and S = 1/2 states starting from points closer to the κ^2 and κ^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 CoMe₂ and Co(CH₂SiMe₃)₂ fragments bound to ligands **1** and **6** (Δ E, b3-lyp/TZVP, kcal/mol). Points marked × 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 κ^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 CoMe₂ and Co(CH₂SiMe₃)₂ fragments bound to ligands **1** and **6** (Δ G, b3-lyp/TZVP, kcal/mol). Points marked × 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 κ^2 or κ^{2*} and to adjacent low-spin κ^2 or κ^{2*} minima.

As Figure 6.12 indicates, to form the low-spin κ^2 complex, Pybox 6 needs around 5 kcal/mol more than 1 for CoMe₂, and only 2 kcal/mol more than 1 for CoR₂. The subsequent coordination of the second imine arm to form the low-spin κ^3 structure is different in different cases. As for CoMe₂, the formation of low spin κ^3 structure is more favourable for ligand 1, but is around 12 kcal/mol uphill for ligand 6, probably due to the larger steric hindrance in 6. For CoR₂, the formation of low-spin κ^3 states from low-spin κ^2 state is unfavourable for both ligand 1 and ligand 6, and requires 4 kcal/mol more in energy for ligand 6 than ligand 1. Apparently, the observation of (6)CoR₂ can be partly explained by the greater reluctance of the second imine arm to approach the cobalt center in (6)CoR₂. Once the low spin κ^3 intermediate formed, loss of a CH₂SiMe₃ radical is favourable for both 1 and 6 in the CoR₂ case (although loss of Me is not).

In all, as Figure 6.12 indicated, loss of the alkyl radical from high-spin (6)CoR₂ requires 6 kcal/mol more than from (1)CoR₂, which is believed to be consistent with the fact that between them only (6)CoR₂ was detected by ¹H NMR.

6.4 Conclusions

The "CoR₂" fragment in (Py)₂CoR₂ and (TMEDA)CoR₂ can be transferred to DIP-type ligands as long as the ligand has certain steric protection and certain strength of σ -donor ability. Strong π -acceptors favour the formation of a cobalt(I) alkyl complex. The proposed mechanism for the formation of (DIP)CoR from (Py)₂CoR₂ involves the exchange of the ligand to form the high-spin κ^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.



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
1	2,6-Me ₂ -C ₆ H ₃
2	2,4,6-Me ₃ -C ₆ H ₂
3	2,6-Et ₂ -C ₆ H ₃
4	$2,6-^{i}Pr_{2}-C_{6}H_{3}$
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 Cr, Fe and (low-spin) Co centers.

Recently,^{199b} Chirik and coworkers have done extensive studies on the chemistry of diiminepyridine (DIP) iron complexes. (4)Fe(N₂)₂ was found to be efficient at breaking alkyl-bromine or vinyl bromine bonds (Scheme 7.2).^{199a} 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 N-N bond of diazoalkanes.^{199b}



Scheme 7.2. Reaction of $(4)Fe(N_2)_2$ with EtBr

Similar to complexes of DIP-type ligands, transition metal complexes with β diketiminate ligands have also attracted a lot of attention; its strong σ -donor ability makes the β -diketiminate ligand special. Smith and coworkers used β -diketiminato chromium(II) complexes for single-electron oxidative addition of CH₃I to generate the corresponding Cr(III) iodide and Cr(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 Cr(II) complex with CH₃I

Low-spin cobalt(II) complexes were explored systematically by Halpern and coworkers decades $ago.^{202}$ Examples include $Co(CN)_5^{3-}$, Co(saloph)B (saloph = N,N'-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 Co(III)R and Co(III)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 Co(CN)_{5}^{3-} (Scheme 7.4) was proposed to go through an atom-transfer mechanism.^{202a}

$$2 \operatorname{Co}(\operatorname{CN})_5^{3-}$$
 + $\left[\operatorname{Co}(\operatorname{CN})_5 I\right]^{3-}$ + $\left[\operatorname{Co}(\operatorname{CN})_5^{3-}\right]^{3-}$

Scheme 7.4. Reaction of $Co(CN)_5^{3-}$ 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(N₂) (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 (1)Co(N₂)

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 C_{sp3} - C_{sp3} 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 transfer²⁰⁹ (in carbon-heteroatom coupling reactions) and iodine atom transfers²⁰⁹ (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 C_{sp2} - C_{sp2} bond formation efficiently, but the more interesting aspect of the cobalt catalyst is its ability to accommodate alkyl halide substrates and form C_{sp3} - C_{sp3} bonds. Although mechanisms similar to those of palladium centers were proposed, evidence for the involvement of radicals was also obtained.²¹¹ 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 (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**)CoCl₂, reported first by the group of Brookhart and the group of Gibson in 1998,^{16,17} 194

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^{55,81a,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 Gibson²¹² 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 C-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)Co(I) complexes.²¹³ In the present chapter, I focus on the even less-hindered ligand **1**.

7.4 Cobalt(0) intermediates

When purple (1)CoR ($R = CH_2SiMe_3$) 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 ¹H NMR (broad peaks at around 5 ppm and 17 ppm) together with around 5-10% diamagnetic impurities^{XXXVII} (Figure 7.2).



Figure 7.2. ¹H NMR spectrum of the green solution generated by adding 2.0 mL of $H_2(g)$ to (1)CoCH₂SiMe₃ in benzene-*d*₆ under a nitrogen atmosphere (* denotes diamagnetic impurities)

 $^{^{\}rm XXXVII}$ For possible approaches to identify these unknown side products, see the Outlook section in Chapter 8

As the ¹H 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 77K) reveals a rhombic g-tensor ($g_x = 1.967$, $g_y = 2.019$, $g_z = 2.130$) with resolved cobalt hyperfine couplings along g_x (77 MHz) and g_z (60 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)Co(N₂) and has a ligand-centered radical character which agrees with (DIP)Co(N₂) complexes reported by Chirik.²¹⁵



Figure 7.3. Experimental and simulated X-band EPR spectrum of $(1)Co(N_2)$ in frozen toluene at 70 K (generated by reacting $(1)CoCH_2SiMe_3$ with 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)Co(N₂) was also prepared according to the procedure reported by Chirik.²¹⁵ The crude product showed the same ¹H 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 ((1)CoCl and (1)CoPh, see section 7.5) as the green solution derived from (1)CoR + H₂. In addition, (1)Co(N₂) synthesized by these two methods showed the same NN stretching frequency (v_{NN} 2084 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_{NN} in toluene was reported to be 2093 cm⁻¹ reported by Chirik²¹⁵)^{XXXVIII}. Therefore, We assume the green solution generated by hydrogenolysis of (1)CoR contains (1)Co(N₂)^{XXXIX}. Because the hydrogenation of (1)CoR to generate (1)Co(N₂) is much more convenient than the sodium amalgam method, I stick to this method in the following reactions. As (1)Co(N₂) was generated in situ (no separate isolation is done), the amount of (1)Co(N₂) will be assumed to be equal to that of (1)CoR used.

The generation of $(1)Co(N_2)$ 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

^{XXXVIII} The error margin is $\pm 4 \text{ cm}^{-1}$ 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 (1)Co(N₂) made from hydrogenolysis or Na-amalgam are considered to be same.

^{XXXIX} The eelectronic structure of (1)Co(N₂) is describes as the low-spin cobalt(I) bound to the ligand anion.

presence of diphenylacetylene resulted in the generation of the corresponding (1)CoC(Ph)=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 (1)CoC(Ph)=CHPh. In contrast, the reaction of (1)CoR in the presence of excess phenylacetylene generated a different cobalt(I) complex through insertion of the intermediate (1)CoC=CPh into another molecule of PhC=CH,^{XL} and the ¹H NMR spectrum strongly indicates the structure as (1)CoC(Ph)=C(H)C=CPh by comparison with (4)CoBz.²¹⁶

^{XL} The ¹H NMR spectrum of an immediate mixture of (1)CoR and PhC=CH (1:1 ratio) showed that two products ((1)CoC=CPh and (1)CoC(Ph)=C(H)C=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 (1)CoC(Ph)=C(H)C=CPh. The further increase in the amount of PhC=CH did not affect the product.



Figure 7.4. ¹H NMR spectra for the reaction of (1)CoCH₂SiMe₃ under nitrogen in the presence of Ph_2C_2 , with a) 1.5 mL of H_2 (g); b) 3.6 mL of H_2 (g),

Additional convincing evidence was obtained from the trapping reaction using *p*-chlorobenzonitrile, which cleanly furnished the corresponding (1)CoN=CHPh-4-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 (Å) and angles (deg): Co(1)-N(1): 1.804(4); Co(1)-N(2): 1.896(4); Co(1)-N(3): 1.899(4); Co(1)-N(4): 1.726(4); C(12)-N(2): 1.336(6); C(12)-C(13): 1.423(7); C(18)-N(3): 1.330(6); C(17)-C(18): 1.453(7); N(1)-Co(1)-N(2): 81.46(17); N(4)-Co(1)-N(2): 98.79(19); N(4)-Co(1)-N(1): 178.1 (2); C(41)-N(4)-Co(1): 169.9(5); N(4)-C(41)-C(42): 124.3(6); N(2)-Co(1)-N(3): 162.9(17); C(18)-N(3)-Co(1): 116.8(3); C(12)-N(2)-Co(1): 116.2 (3).

In Figure 7.5, the angle of C(41)-N(4)-Co(1) is close to 180° , which indicates significant ionic bonding between the cobalt center and the imine nitrogen atom. The imine bond length (1.33Å) 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)CoCl.²¹⁶ ¹H 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^{XLI} (Figure 7.6).⁸³



Figure 7.6. ¹H NMR spectra of (1)Co(N=CH)PhCl (2, black) vs free ligand (1, red) in C_6D_6

XLI See also Section 2.4.4 in Chapter 2.

7.5 Oxidative addition of organic halides

7.5.1 Model reaction

When (1)Co(N₂) reacted with one equivalent of 4-chlorotoluene, the solution color changed from green to purple and the ¹H 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. ¹H NMR spectrum of product mixture from the reaction between (1)Co(N_2) 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)CoCl₂ with Na amalgam.²¹⁵ (1)CoPhMe-4 was prepared by reacting (1)CoCl₂ 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 complex²¹⁷ with the cobalt center having a distorted square-planar geometry. The tolyl ring is not perpendicular to the N₃ plane but makes an angle of 67.94° 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 (Å) and angles (deg): Co(1)-N(1): 1.829(2); Co(1)-N(2): 1.905(2); Co(1)-N(3): 1.910(2); Co(1)-C(1):

1.945(3); N(2)-C(14): 1.329(4); N(3)-C(13): 1.330(4); N(1)-Co(1)-N(2): 80.84(11); N(1)-Co(1)-N(3): 80.97(11); N(1)-Co(1)-C(1): 172.45(12).

The identification of each complex in the mixture was done by comparing peaks of the corresponding ¹H 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: (1)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 (CF₃PhCl) as the aryl halide substrate. The advantage of this substrate is that it has a clear ¹⁹F 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 ((1)CoAr and (1)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%, ^{XLII} while the conversion of the aryl halides decreased dramatically from 96% to 28%. With the ratio of two reactants kept at

^{XLII} Error margin probably ~5%. The ratio of (1)CoAr to (1)CoCl in the ¹H NMR spectrum is used to determine the amount of cobalt products and the ratio of CF₃PhCl to (1)CoAr in the ¹⁹F NMR spectrum is used to determine the total amount of remaining aryl halide. The amount of CF₃PhCl 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)Co(N₂) with CF₃PhCl generated only a small amount of cobalt(I) aryl product, together with a trace amount of (4)CoH ((4)CoAr:(4)CoCl:(4)CoH = 0.14:1.00:0.11). Thus it seems that ligand 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 ¹H NMR spectrum indicated no reaction even after one week. In contrast, when (1)CoCH₂SiMe₃ reacted with excess methyl iodide, trimethylethylsilane was detected by ¹H 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. ¹H NMR spectrum from the reaction between (1)CoCH₂SiMe₃ with MeI in benzene-d6

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 $(1)Co(N_2)$ with excess ArX, but for reactions with alkyl halides, a ratio of RX:(1)Co(N₂) = 0.5 was used to avoid further reactions.

7.5.3 Scope of reactions

As (1)Co(N₂) 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 ((1)CoAr and (1)CoCl) was determined from the ¹H spectra of the reaction mixtures, in particular from the characteristic ¹H resonances for Py H4 (triplets around 10 ppm) and imine Me (singlet around -1 ppm),⁸³ and results are shown in Table 7.2; all the ¹H 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 Cl < Br < 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 (1)CoAr/(1)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.

Entry	Organic halides (ArX or RX)	[(1)CoAr]:[(1)CoX] ^c	Rxn time ^d
1	PhI	0.24	seconds
2	PhBr	0.25	1 minute
3	PhCl	0.59	hours
4	$2,4,6-(Me)_3C_6H_2Br$	~0	seconds
5	$2,4,6-(^{t}Bu)_{3}C_{6}H_{2}Br$	0.27 ^e	seconds
6	$2,6-(Me)_2C_6H_3Cl$	~0	days
7	<i>p</i> -(MeCO)C ₆ H ₄ Cl	0.91	30 minutes
8	<i>p</i> -(MeOOC)-C ₆ H ₄ Cl	0.83	seconds
9	<i>p</i> -(CF ₃)C ₆ H ₄ Cl	0.77	seconds
10	<i>p</i> -FC ₆ H ₄ Cl	0.40	seconds
11	$3,5-(MeO)_2C_6H_3Cl$	0.59	seconds
12	$1,4-(Cl)_2C_6H_4$	0.59	seconds
13	<i>p</i> -MeC ₆ H ₄ Cl	0.59	hours
14	<i>p</i> -(MeO)C ₆ H ₄ Cl	0.50	hours
15	MeI	0.71 ^b	seconds
16	<i>n</i> -butyl chloride	0.13	seconds
17	<i>n</i> -Hexyl bromide	0.30 ^b	seconds
18	Benzyl bromide	0.14 ^b	seconds
19	Benzyl chloride	0.45 ^b	minutes
20	2,6-dichloropyridine	1.00	seconds
21	$(C_5F_{11})(CH=CH_2)CF-F$	0.59	minutes
22	<i>n</i> -Octanyl fluoride	N.R.	
23	Allyl chloride	1.0	seconds
24	Cyclopropylmethyl chloride	0.5	seconds

Table 7.2. Reaction with organic halides^a

a: Reaction conditions: (1)CoCH₂SiMe₃ (0.0140 g, 0.027 mmol), H₂ (2.0 mL) ArX (0.027 mmol, 1.0 eq.), 0.4 mL C₆D₆ as solvent. b: RX (0.014 mmol, 0.5 eq.) was used. The product ratio was determined according to the relative area ratio of the imine methyl peaks. c: From ¹H NMR; estimated error margin \approx 5%. d: qualitative indication. e: the identity of the cobalt aryl product was corrected as (1)CoCH₂CMe₂(3,5-di(tert-butyl)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



coefficient $\rho = 0.91$)

The sensitivity of these reactions to steric hindrance was not very high: even BrC_6H_2 -2,4,6-^{*t*}Bu₃ gave a significant amount of (1)CoCH₂CMeC₆H₃-3,5-^{*t*}Bu₂ (entry 5), which will be discussed later. However, 2,6-di*methyl* 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 RX (X = Cl, Br, 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 β -H elimination. Unexpectedly, methyl iodide produced a high yield of (1)CoMe. Unactivated C(sp³)-F bonds are not active (*n*-C₈H₁₇F, 210

entry 22), but the allylic fluoride $n-C_6F_{13}CH=CH_2$ (entry 21) produced a reasonable amount of an alkyl complex, tentatively identified as $(1)Co(\sigma-CH_2CH=CFC_5F_{11})$ (¹H NMR spectrum, see Figure D.2 in the Appendix D). The reaction of $(1)Co(N_2)$ with an allyl chloride produced (1)Co(η^3 -allyl) instead of (1)Co(η^1 -allyl) and a 1:1 ratio of (1)Co(η^3 -allyl) to (1)CoCl was obtained (entry 23). One exceptional character of this cobalt(I) allyl complex is its ¹H NMR spectrum (for ¹H NMR spectrum of this reaction, see Figure D.5 in the Appendix D): the ¹H NMR spectrum of (1)Co(η^3 -allyl) does not show the characteristic triplet around 10 ppm and singlet around -1 ppm. Instead, a "normal" diamagnetic spectrum with the ¹H chemical shifts of the coordinate DIP ligand similar to that of a free ligand was observed. The reaction of $(1)Co(N_2)$ with cyclopropylmethyl chloride generated the ring-opening product (1)Co(η^3 -crotyl) complex; this complex showed a similar ¹H NMR spectrum to that of (1)Co(η^3 -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 ¹H 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 $(1)Co(N_2)$ 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(*tert*butyl)phenyl bromide clearly indicates that mononuclear oxidative addition of the aryl halide, followed by transfer of the aryl radical or its isomer to (1)Co(N₂), is unlikely because the required "side-on" C-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 ($k_{RBr}/k_{RCI} \sim 10^3$), whereas for electron-transfer-mediated reactions, the rate difference is much smaller ($k_{RBr}/k_{RCI} \sim 2$).^{202e} Our results show rate differences k_{RI}/k_{RBr} and k_{RBr}/k_{RCI} 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 Pd(0) center. Bond length is in Å. (coordinates are taken from ref. 220a).

Atom transfer at a low-spin cobalt(II) complex has been proposed by Halpern.^{5d} Halide abstraction by a Co(III) complex bearing redox-active ligands has also been reported,²⁸ and generation of free radical through irradiating cobalt(III) alkyls has been observed²²¹. 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 ((1)CoCl) and a phenyl radical (Ph•). This phenyl radical may meet another cobalt(0) center to generate a cobalt(I) phenyl product ((1)CoPh). The observed product ratio ((1)CoAr:(1)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 Gibson²¹² and Budzelaar⁸⁵ and this step is fast at room temperature in our system, only the breaking of the aryl carbon-halogen bond with the (1)Co(N₂) 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 ClC_6H_5 at two Co(0) centers according to Scheme 7.6. Bond lengths (for the TS) in Å

The displacement of N_2 from (1)Co(N_2) by ClC₆H₅ to form a terminally Cl-bound chlorobenzene complex (1)Co(ClC₆H₅) is endergonic by about 10 kcal/mol (Figure 7.12) and the homolytic breaking of the C-Cl bond costs another 10 kcal/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 kcal/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(tert-butyl)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 (1)CoCl and (1)CoPh generated by reaction of (1)Co(N₂) with 1.0 eq. PhCl was further reacted with benzyl chloride (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: Bn-Bn, PhBn and PhPh. Calibration for these three products showed that the ratio BnBn:PhBn: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 ¹H NMR. Thus, the generation of three products (BnBn, 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.

Entry	(1)CoAr	RX	Products ^a
1	(1)Co-CF ₃	CI	$-CF_3 + F_3C - CF_3$
			major minor
2	(1)Co	CI	✓ → ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓
			major minor
3	(1)Co-OMe	CI	
			major minor
4	(1)Co-Cl	BnCl	Bn-Cl + Bn-Bn
			major minor
5	(1)Co-CF ₃	BuCl	N.R.
6	(1)Co-CF ₃	BnBr	Bn-CF ₃ + Bn-Bn
			major minor
7	(1)Co	n-C ₆ H ₁₃ Br	N.R.
8	(1)Co	BnBr	Bn + Bn-Bn + Ph-Ph

Table 7.3. Reaction of a mixture of (1)CoAr + (1)CoCl with alkyl halides^d:

Entry	(1)CoAr	RX	Products ^a
9	(1)Co	BnCl	Bn + Bn-Bn + Ph-Ph 3.5 : 1.0 : 0.03
10	(1)C- CH SiM- ^f	M-I	
10	(1)Co-CH ₂ SIMe ₃	Mei	EtSIMe ₃
11	(1)CoPh ^e	PhI	N.R.
12 ^b	(1)Co F	BnBr	C_5F_{11} F C_5F_{11} F C_5F_{11} F C_5F_{11} b
13	(1)Co	CI	No cross-coupled product was detected
14	(1)Co-N-CI	BnCl	N.R. ^g
15	(1)Co-N-CI	BnBr ^c	CI N + Bn-Bn major major
16	(1)Co COOMe	BnCl	N.R.
17	(1)CoMe	BnCl	$\sum_{h,}$
18	(1)Co	BnCl	or

a: Product was detected by GC/MS and the regiochemistry of the CC-coupling product is assumed.^{XLIII} 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 (1)Co(N₂) d: mixture of (1)CoAr + (1)CoCl generated from (1)CoN₂ 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)CoCH₂SiMe₃ and 1.8 equiv. of CH₃I; 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 Ar₂)

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)Co(Py-6-Cl) showed similar low activity (entry 14). Replacing benzyl chloride by more reactive

^{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.

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 (1)Co(Py-6-Cl) and (1)CoCl (1:1) generated by reacting of (1)Co(N₂) 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-Cl):(1)CoBr^{XLIV}: (1)CoCl = 1.0 : 0.67 : 0.44; for the ¹H 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 ¹H 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 (1)CoCl with BnCl clearly showed that the coupling reaction most likely occur through a radical mechanism.^{XLV}

^{XLIV} The generation of (1)CoBr is probably through the exchange of chlorine in (1)CoCl by bromine facilitated by benzyl radical.

^{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

 $Co^{(0)}$ 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)CoR₂ 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 (1)CoCl is problematic for the coupling of (1)Co-Py-6-Cl with benzyl bromide and a larger amount of BnBr is needed.

7.9 Extension to C-O bond-cleavage reactions

(1)Co(N₂) 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 ¹H NMR spectrum. The reaction with ethyl benzoate showed similar results but required even longer time. Compared with the (4)Fe(N₂)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)Fe $(N_2)_2$ with ethyl benzoate



Scheme 7.11. Reaction of $(1)Co(N_2)$ with diphenyl carbonate.

However, when hydrogen gas was injected *after* the addition of diphenyl carbonate, the reaction was immediate and ¹H NMR indicated two triplets (one at 9.2 ppm, indicating the presence of (1)CoOPh; the other at 8.8 ppm; the ratio of these two peaks is 2:1). When more $H_2(g)$ 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)Co(OCH₃) (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 (1)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 $(1)Co(N_2)$ complexes generated in situ by hydrogenation of $(1)CoCH_2SiMe_3$ in the presence of dinitrogen. The reaction with a variety of aryl halides 225
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 (1)Co(N₂) 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:

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-di*iso*propylphenyliminylpyridine, 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 σ -donors and good π -acceptors.

An optimum combination of σ -donor and π -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)CoCl₂ precatalyst by MAO. Although they are diamagnetic, the ¹H NMR spectra are somewhat unusual, especially the position of the pyridine H4 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 admixture²⁴⁵ 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 σ_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-di*iso*propylphenylimino)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 H4 resonance is affected:

- 1) Three labile cobalt(II) dialkyl complexes $((Py)_2Co(CH_2SiMe_3)_2, (TMEDA)Co(CH_2SiMe_3)_2$ and $(Py)_2Co(CH_2CMe_2Ph)_2)$ have been successfully prepared. Reactions with DIP-type ligands showed that for ligands with stronger π -acceptor ability, cobalt (I) alkyl complexes are the only observable product while for a ligand with comparable σ -donor but worse π -acceptor properties (Pybox), only a cobalt(II) dialkyl was detected. Thus a good π -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 (Py)₂Co(CH₂SiMe₃)₂ and with (TMEDA)Co(CH₂SiMe₃)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 229

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 H4 shifts: a) the replacement of a cobalt-bound alkyl by a cobalt-bound aryl shifts the pyridine H4 peak from 10.0 ppm downfield to 10.26 ppm; b) the ¹H NMR spectrum of (DIP)CoN=C(H)PhCl-4 showed the pyridine H4 peak at 7.9 ppm; c) a (DIP)Co(η^3 -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 H4 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 ¹H 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(N₂) 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 GC/MS results. The ability for C_{sp3} - C_{sp3} 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 complexes²⁴⁶ (Scheme 8.1).



Scheme 8.1. Active species for (DIP)FeCl₂ complex in ethylene polymerization by MAO 231

For cobalt, I would expect a similar mechanism. In other words, a cobalt(II) monoalkyl cation might be the active species, although a Co(III) center was suspected to be the active species by the group of Gibson.⁸¹ As there was no report on the (DIP)CoR₂ complexes before the current work, the observation of a (Pybox)CoR₂ complex in this thesis might provide some insight into the activation of cobalt catalysts.

Firstly, the lower stability of $(Pybox)CoR_2$ relative to $(Pybox)FeR_2$ might be the reason why (DIP)CoCl₂ 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]⁺, M: Fe, 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)FeX₂ has been accepted as [(DIP)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:

 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 approach²⁴⁷ 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 volume²⁴⁸ 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 "CoR₂" sources

As illustrated in Chapter 5 and Chapter 6, two convenient sources of "CoR₂" 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 media⁵⁵ can be meaningful in terms of recycling the complex. Bidentate ligands with strong non-innocent character such as bisimine¹³ or imine-pyridine²⁴⁹ ligands can be interesting to explore. In addition, these "CoR₂" 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 (Py)₂Co(CH₂SiMe₃)₂ and (Py)₂Co(CH₂Me₂Ph)₂. As neither compound contains βhydrogens, a weaker ability to stabilize the cobalt center in the latter case is suspected. In addition, attempted synthesis of (Py)₂CoPh₂ using the same procedure as (Py)₂Co(CH₂SiMe₃)₂ was unsuccessful, which might be due to easy C-C coupling (see footnote in Section 5.4). Further exploration of the stability of (Py)₂CoR₂ (R: any alkyl group) or the decay of (Py)₂CoAr₂ (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 (Py)₂CoR₂ 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 Co-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)Co(N₂) 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 H₂ 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 H₂ 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 $(DIP)Co(N_2)$.

Obtaining experimental evidence for the mechanism of conversion of (DIP)CoH into $(DIP)Co(N_2)$ 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 D₂ instead of H₂ 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. ²D 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 ¹H NMR. Obtaining their crystal structures will not be easy, but knowledge of their structures might result in ideas about the reaction mechanism.

4B) 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)CoN₂ by a suitable 1-e reducing reagent (e.g. Na-Hg), or it can be converted by a suitable hydride source into (DIP)CoH which will automatically decay into (DIP)Co(N₂). 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, NaBHEt₃ not only reacted with (DIP)CoCl, but also with (DIP)CoAr.

4C) The formation of (iPrDIP)CoH from the reaction of (iPrDIP)Co(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)Co(N₂), so C-H bond activation (of an aryl halide or the THF solvent) or β -hydrogen elimination from an unknown cobalt(I) alkyl intermediate are suspected. Labelling experiments might be performed and ²D NMR might be able to verify this idea. However, the broadness of the H(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 C-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)CoCl₂ 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 ¹H 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 (XANES²⁵¹) 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 ¹H 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 voltammetry²⁵²), 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 C, N, O, Cl, P atoms of lower scattering ability, data tended to be weak at higher 2 θ angles. Thus the intensity of the scattered X-ray decreases rapidly as the 2 θ 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 θ . 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, 2,6-diacetylpyridine, sodium, anilines and anhydrous FeCl₂ and CoCl₂ 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-di*iso*propylphenylimino]-6-bromopyridine,¹⁴⁶ 6-Bis[4',4'-dimethyloxazolin-2'-yl]pyridine **15**,²²² 2,4,6-trimethylphenylazide, 2,6-diisopropylphenylazide and phenylazide,²²³ ligand

 $7^{224}_{,,2}$ CoCl₂(THF)_{1.5}²²⁵ and FeCl₂(THF)_{1.5}²²⁶ were prepared according to literature methods.

¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All data were collected at room temperature; chemical shifts (δ) are reported in ppm. ¹H and ¹³C chemical shifts were referenced to residual proton solvent signals (CDCl₃: ¹H 7.26, ¹³C 77.0; CD₂Cl₂: ¹H 5.33, ¹³C 54.2). Listing assignments: Ms = 2,4,6-Me₃C₆H₂, Ar = 2,6-^{*i*}Pr₂C₆H₃.

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

Synthesis of ligands

2-[2,6-^{*i*}**Pr₂C₆H₃N=CMe]-6-Ph₂P-C₅H₃N¹⁴²:** 1.3 g (0.056 mol) Na was added in small pieces to 200 mL of liquid ammonia. To the deep-blue solution was added 6.13g (0.023 mol) triphenylphosphine in small portions. The resulting solution was stirred for 2h, during which time it turned dark red. Then 1.25g (0.023 mol) dry ammonium chloride was added to the solution, which turned a lighter orange. After 30 min, 7.8 g 2-[2,6-di*iso*propylphenylimino]-6-bromopyridine (0.022 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°C for 2h, and then cooled again to room temperature. 80 mL water and 50 ml CH₂Cl₂ were added, the organic layer was separated and the water layer extracted with two more portions of CH₂Cl₂. The combined organic layers were dried over Na₂SO₄, filtered and evaporated using a rotary evaporator to give a 242

red residue. Crystallization from toluene/ether/CH₃OH gave 8.0 g (80%) of the product as a yellow powder.

¹H NMR (300.1 MHz, CDCl₃): δ 8.27 (d, 1 H, *J* 7.9 Hz, Py *H*3), 7.71 (t, 1 H, *J*_{av} 7.5 Hz, Py *H*4), 7.48-7.57 (m, 4 H, Ph *o*), 7.36-7.45 (m, 6 H, Ph *m*,*p*), 7.29 (d, 1 H, *J* 6.9 Hz, Py *H*5), 7.08-7.22 (AB₂ m, 3 H, Ar *m*,*p*), 2.77 (sept, 2 H, *J* 6.9 Hz, C*H*Me₂), 2.13 (s, 3 H, N=C*Me*), 1.18 and 1.19 (2 d, 6H each, *J* 6.9 Hz, CH*Me*₂).

¹³C NMR (75.5 MHz, CDCl₃): δ 167.4 (*C*=N), 162.3 (d, *J*_P 3 Hz, Py C6), 156.5 (d, *J*_P 11 Hz, Py C6), 146.4 (Ar *i*), 136.4 (d, *J*_P 10 Hz, Ph *i*), 136.0 (d, *J*_P 3 Hz, Py C4), 135.7 (d, *J*_P 20 Hz, Ph *o*), 129.1 (d, *J*_P 20 Hz, Py C5), 129.0 (Ph *p*), 128.4 (d, *J*_P 7 Hz, Ph *m*), 123.5 (Ar *p*), 122.9 (Ar *m*), 119.6 (Py C3), 28.2 (CHMe₂), 23.2, 22.8 (CH*Me*₂), 17.2 (N=C*Me*). ³¹P NMR (121.5 MHz, CDCl₃): -2.2.

Anal. Calcd for C₃₁H₃₃N₂P (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-^{*i*}Pr₂C₆H₃N=CMe]-6-[2,4,6-Me₃C₆H₂N=PPh₂]-C₅H₃N (8)¹⁴²: To a solution of 2.73 g (5.8 mmol) of 2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-Ph₂P-C₅H₃N in 20 ml of dry toluene was added 3 g of 2,4,6-trimethylphenylazide, resulting in vigorous evolution of dinitrogen. After stirring for 2h at room temperature, the solution was heated at 60°C for 2h. 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.

¹H NMR (300.1 MHz, CDCl₃): δ 8.38 (d, 1H, *J* 7.7 Hz, Py *H*3), 8.18 (t, 1H, *J*_{av} 6.4 Hz, Py *H*4), 7.91 (dd, 1H, *J* 7.9 Hz, *J*_P 4.0 Hz, Py *H*5), 7.78-7.88 (m, 4H, Ph *o*), 7.35-7.54 (m, 243 6H, Ph *m*,*p*), 7.06-7.19 (AB₂ m, 3H, Ar *mp*), 6.75 (s, 2H, Ms *m*), 2.69 (sept, 2H, *J* 6.8 Hz, C*H*Me₂), 2.20 (s, 3H, Ms *p*), 2.04 (s, 6H, Ms *o*), 1.94 (s, 3H, N=C*Me*), 1.13, 1.15 (2 d, 6H each, *J* 6.9 Hz, CH*Me*₂).

¹³C NMR (75.5 MHz, CDCl₃): δ 166.7 (*C*=N), 156.2 (d, *J*_P 129 Hz, Py C6), 155.9 (d, *J*_P 18 Hz, Py C2), 146.2 (Ar *i*), 144.1 (Ms *i*), 136.5 (d, *J*_P 9 Hz, Py C4), 135.6 (Ar *o*), 133.6 (d, *J*_P 101 Hz, Ph *i*), 132.5 (d, *J*_P 9 Hz, Ph *o*), 132.1 (d, *J*_P 7 Hz, Ms *o*), 131.1 (d, *J*_P 2 Hz, Ph *p*), 129.4 (d, *J*_P 20 Hz, Py C5), 128.4 (Ms *m*), 128.0 (d, *J*_P 12 Hz, Ph *m*), 127.5 (Ms *p*), 123.7 (Ar *p*), 123.0 (Ar *m*), 121.9 (d, *J*_P 3 Hz, Py C3), 28.2 (CHMe₂), 23.2, 22.8 (CH*M*e₂), 21.3 (Ms *o*), 20.5 (Ms *p*), 17.0 (N=C*Me*).

³¹P NMR (121.5 MHz, CDCl₃): -12.5.

Anal. Calcd for C₄₀H₄₄N₃P (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-^{*i*}**Pr₂C₆H₃N=CMe]-6-[2,6-iPr₂C₆H₃N=PPh₂]-C₅H₃N (9)**: This was prepared like ligand **8**, but using 1.02 g (2.2 mmol) of 2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-Ph₂P-C₅H₃N in 3mL dry toluene and 2.5 g of 2,6-di*iso*propylphenylazide. 1.15 g (82%) of a yellow powder was obtained.

¹H NMR (300.1 MHz, CDCl₃): δ 8.39 (d, 1H, *J* 7.7 Hz, Py *H*3), 7.96 (t, 1H, *J*_{av} 6.2 Hz, Py *H*4), 7.85-7.90 (m, 1H, Py *H*5), 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, PN*Ar m*), 6.81 (t, 1H, *J*_{av} 7.5 Hz, PN*Ar p*), 3.34 (sept, 2H, *J* 6.8 Hz, PN*Ar* C*H*Me₂), 2.67 (sept, 2H, *J* 6.9 Hz, C*H*Me₂), 1.86 (s, 3H, N=C*Me*), 1.13 (t, 12H, *J*_{av} 6.3 Hz, CH*Me*₂), 0.88 (d, 12H, *J* 6.8 Hz, PN*Ar* CH*Me*₂). ¹³C NMR (75.5 MHz, CDCl₃): δ 166.8 (*C*=N), 155.7(d, *J*_P 128 Hz, Py C6), 156.03 (d, *J*_P 18 Hz, Py C2), 146.2 (Ar *i*), 143.9 (PNAr *i*), 142.6 (d, *J*_P 7 Hz, PNAr *o*), 136.4 (d, *J*_P 9 Hz, Py C4), 135.6 (Ar *o*), 132.8 (d, *J*_P 103 Hz, Ph *i*), 132.6 (d, *J*_P 9 Hz, Ph *o*), 131.2 (Ph *p*), 129.0 (d, *J*_P 20 Hz, Py C5), 128.0 (d, *J*_P 12 Hz, Ph *m*), 123.6 (Ar *p*), 122.9 (Ar *m*), 122.5 (d, *J*_P 3 Hz, Py C3), 121.9 (PNAr *m*), 119.2 (PNAr *p*), 28.5 (PNAr CHMe₂), 28.2 (CHMe₂), 23.5 (PNAr CH*Me*₂), 23.1, 22.8 (CH*Me*₂), 16.9 (N=C*Me*).

³¹P NMR (121.5 MHz, CDCl₃): -11.1.

Anal. Calcd for C₄₃H₅₀N₃P (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-^{*i*}**Pr**₂**C**₆**H**₃**N=CMe]-6-[C**₆**H**₅**N=PPh**₂]-**C**₅**H**₃**N (10)**: This was prepared like ligand **8**, but using 2.04 g (4.39 mmol) of 2-[2,6-^{*i*}**Pr**₂**C**₆**H**₃**N=CMe]-6-Ph**₂**P**-**C**₅**H**₃**N and 2.52 g of** phenylazide. 2.37 g (97%) of a yellow powder was obtained.

¹H NMR (300.1 MHz, CDCl₃): δ 8.45 (d, 1H, *J* 7.9 Hz, Py *H*3), 8.36 (t, 1H, *J*_{av} 6.4 Hz, Py *H*4), 7.92 (dt, 1H, *J* 7.9 Hz, *J*_P 4.0 Hz, Py *H*5), 8.00-8.06 (m, 4H, Ph *o*), 7.44-7.58 (m, 6H, Ph *m*,*p*), 7.09 (t, 2H, *J* 7.4 Hz, NPh *m*), 6.94 (d, 2H, *J* 7.9 Hz, NPh *o*), 6.72 (t, 1H, *J* 7.3 Hz, NPh *p*), 2.73 (sept, 2H, *J* 6.9 Hz, C*H*Me₂), 2.12 (s, 3H, N=C*Me*), 1.18, 1.17 (2 d, 6H each, *J* 6.9 Hz, CH*Me*₂).

¹³C NMR (75.5 MHz, CDCl₃): δ 166.3 (*C*=N), 156.5 (d, *J*_P 18 Hz, Py *C*2), 153.9 (d, *J*_P 129 Hz, Py *C*6), 151.0 (d, *J*_P 2.4 Hz, NPh *i*), 146.1 (Ar *i*), 136.7 (d, *J*_P 9 Hz, Py *C*4), 135.6 (Ar *o*), 132.9 (d, *J*_P 9 Hz, Ph *o*), 131.6 (d, *J*_P 3 Hz, NPh *m*), 130.3 (d, *J*_P 98 Hz, Ph *i*), 130.0 (d, *J*_P 20 Hz, Py *C*5), 128.6 (d, *J*_P 2 Hz, Ph *p*), 128.3 (d, *J*_P 12 Hz, Ph *m*), 123.7

(d, *J*_P 8Hz, NPh *o*), 123.4 (Ar *p*), 123.0 (Ar *m*), 122.5 (d, *J*_P 3 Hz, Py C3), 117.4 (NPh *p*) 28.2 (CHMe₂), 23.2, 22.8 (CH*M*e₂), 17.2 (N=C*M*e).

³¹P NMR (121.5 MHz, CDCl₃, 25°C): δ -2.0.

Anal. Calcd for C₃₇H₃₈N₃P (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

Synthesis of {2,6-bis[2,4,6-Me₃C₆H₂N=CMe]-C₅H₃N}CoCl₂^{XLVI}: (3)CoCl₂^{141,227}

1.1 g of $CoCl_2 \cdot 6H_2O$ was dissolved in 20 mL *iso*propanol. A solution of 2.0 g of **3** in 15 mL of toluene was added dropwise. The resulting reaction mixture was heated at 80°C for 1 h. The green precipitate was filtered over a glass frit to give 2.76 g (89%) of a green powder.

¹H NMR(300.1 MHz, CD₂Cl₂, all signals broad singlets): 35.5(1H, Py *H*4), 16.7 (6H, Ms p-*Me*), 6.4 (4H, Ms *m*), -0.6 (6H, N=CC*H*₃), -26.2(12H, Ms o-*Me*).

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

/* Synthesis of {2,6-bis[2,4,6-Me₃C₆H₂N=CCF₃]-C₅H₃N}CoCl₂: (7)CoCl₂

To 0.1 g of $CoCl_2(THF)_{1.5}$ was added a solution of 0.23 g 7 in 10 mL of CH_2Cl_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

 $^{^{}XLVI}$ As (3)CoCl₂ 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)CoCl₂·CH₂Cl₂. The yield is not determined

¹H NMR (300.1 MHz, CDCl₃, all signals broad singlets): 113.7 (2H, Py H3), 33.4 (1H,

Py H4), 15.8 (6H, Ar p-Me), 3.7 (4H, Ar Hm), -31.9 (12H, Ar o-Me).

¹⁹F NMR (282.4 MHz, CDCl₃): -74.1.

Synthesis of {2,6-bis[2,4,6-Me₃C₆H₂N=CCF₃]-C₅H₃N}FeCl₂ :(7)FeCl₂

This was prepared following the same procedure as for (7)CoCl₂. The solution is deepgreen and toluene layering produces large dark-green needles of (7)FeCl₂·(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.

¹H NMR (300.1 MHz, CDCl₃, all signals broad singlets): δ 85.7 (1H, Py *H*4), 83.7 (2H, Py *H*3), 28.5 (6H, Ms p-*Me*), 13.4 (4H, Ms *m*), 12.0 (12H, Ms o-*Me*).

¹⁹F NMR (282.4 MHz, CDCl₃): -256.0.*\

Synthesis of {2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[C₆H₅N=PPh₂]-C₅H₃N}CoCl₂:(10)CoCl₂

Ligand **10** (0.54 g, 0.97 mmol) and CoCl₂ (0.13 g, 0.97 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 CH₂Cl₂ and layered with pentane at room temperature for two days, giving 0.35g (56%) of the brown crystalline product, suitable for the X-ray diffraction.

¹H NMR (300.1 MHz, CD₂Cl₂, all signals broad singlets): 94.6 (1H, Py *H*3), 66.7 (1H, Py *H*5), 27.5 (2H, N-Ar *m*) 19.2 (1H, Py *H*4), 16.6 (3H, N=C*Me*), 5.2 (2H, NPh *m*), 4.5 (4H, PPh *m*), 0.3 (1H, NPh *p*), 0.0 (2H, PPh *p*), -4.9 (6H, CH*Me*₂), -10.2 (4H, PPh *o*), -11.3 (1H, NAr *p*), -14.1 (2H, NPh *o*), -17.3 (6H, CH*Me*₂), -30.5 (2H, C*H*Me₂).

Anal. Calcd for C₃₇H₃₈Cl₂CoN₃P (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 {2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[C₆H₅N=PPh₂]-C₅H₃N}FeCl₂:(10)FeCl₂

This was prepared like (9)FeCl₂, but using 0.10g (0.79 mmol) of anhydrous FeCl₂ and 0.50 g of 10. Purification was done by layering with a mixture of diethylether and pentane instead of pure pentane, and gave 0.38 g (62%) of the deep blue crystalline product.

¹H NMR (300.1 MHz, CD₂Cl₂, all signals broad singlets): 87.4 (1H, Py H3), 58.9 (1H,

Py H5), 46.4 (1H, Py H4), 22.7 (2H, NAr m), 16.7 (4H, br, PPh o), 13.3 (4H, PPh m),

11.9 (2H, NPh m), 6.1 (8H, suspected as CHMe₂ and PPh p), 0.1 (1H, NAr p), -3.8 (6H,

CHMe₂), -8.0 (2H, br, NPh o), -21.1 (1H, NPh p), -42.2 (2H, CHMe₂), -79.1 (3H,

N=C*Me*). The peaks in region between 0-9 ppm cannot be unambiguously assigned due to the solvent peaks overlapping.

Anal. Calcd for C₃₇H₃₈Cl₂FeN₃P (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 {2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[2,4,6-Me₃C₆H₂N=PPh₂]-

C₅H₃N}CoCl₂:(8)CoCl₂

Ligand 8 (0.66g, 0.97 mmol) was dissolved in 20 mL THF and added into a suspension of $CoCl_2$ (0.13g, 0.97 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 CH_2Cl_2 solution and layering with pentane at room temperature.

Tentive assignments:

¹H NMR (300.1 MHz, CD₂Cl₂, all signals broad singlets): 106.6 (1H, Py H3), 71.3

(1H, Py H5), 37.0 (3H, Ms p-Me), 35.3 (2H, N-Ar m), 27.0 (3H, N=CMe), 25.9 (1H, Py

H4), -0.5 (3H), -0.9 (6H, Ms o-Me), -5.7 (6H, CHMe₂), -12.2 (1H, NAr p), -16.5 (4H,

PPh *o*), -21.4 (br, 6H, CHMe₂), -42.2(br, 1H, CHMe₂).

Anal. Calcd for C₄₀H₄₄Cl₂CoN₃P (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 {2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[2,6-*i*Pr₂C₆H₃N=PPh₂]-

C₅H₃N}CoCl₂:(9)CoCl₂

Ligand 9 (0.95g, 1.48 mmol) was dissolved in CH_2Cl_2 (40 mL) and added into a blue suspension of CoCl₂ (0.19 g, 1.46 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 CH_2Cl_2 and layered with pentane at room temperature. The green needles were obtained and the yield was not determined. Tentative assignments:

¹H NMR (300.1 MHz, CD₂Cl₂, all signals broad singlets): 111.9 (1H, Py *H*3), 69.7 (1H, Py *H*5), 37.9 (2H, N-Ar *m*), 30.4 (1H, Py *H*4), 27.1 (3H, N=C*Me*), -1.4 (2H, PPh *p*), -7.4 (6H, CH*Me*₂), -9.9 (6H, CH*Me*₂), -14.6 (1H, NAr *p*), -21.5 (4H, PPh *o*), -23.0 (6H, CH*Me*₂), -60.3 (1H, C*H*Me₂).

A satisfactory elemental analysis could not be obtained. The X-ray structure determination shows the presence of CH_2Cl_2 of crystallization; partial loss of this cocrystallized solvent is probably responsible for the analysis issues.

Synthesis of {2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[2,4,6-Me₃C₆H₂N=PPh₂]-

C₅H₃N}FeCl₂:(8)FeCl₂

This was prepared like (9)FeCl₂, but using 0.13g anhydrous $FeCl_2$ (1.0 mmol) and 8 (1.0 mmol). Crystals of the deep-blue crystalline product were obtained by layering the corresponding dichloromethane solution with pentane.

Tentative assignments:

¹H NMR (300.1 MHz, CD₂Cl₂, all signals broad singlets): 86.6 (1H, Py *H*3), 56.4 (1H, Py *H*5), 39.9 (1H, Py *H*4), 27.4 (4H, PPh *m*), 22.2 (2H, NAr *m*), 16.5 (4H, br, PPh *o*), 15.7 (3H, Ms p-*Me*), 13.6 (12H, Ms o-*Me* and NAr CH*Me*₂), -2.2 (6H, CH*Me*₂), -84.3 (3H, N=C*Me*₃).

A satisfactory elemental analysis could not be obtained. The X-ray structure determination shows the presence of $1.5 \text{ CH}_2\text{Cl}_2$ of crystallization; partial loss of this co-crystallized solvent is probably responsible for the analysis issues.

Synthesis of {2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[2,6-^{*i*}Pr₂C₆H₃N=PPh₂]-

C₅H₃N}FeCl₂:(9)FeCl₂

Under an argon atmosphere, 0.133 g (1.0 mmol) of anhydrous $FeCl_2$ and 0.66g (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 CH_2Cl_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.

¹H NMR (300.1 MHz, CD₂Cl₂, all signals broad singlets): 83.6 (1H, Py *H*3), 52.3 (1H, Py *H*5), 37.7 (1H, Py *H*4), 22.9 (2H, NAr *m*), 17.8 (4H, PPh *o*), 15.4 (2H, PNAr *m*), 13.1(4H, PPh *m*), -0.3 (6H, CH*Me*₂), -3.2 (6H, CH*Me*₂), -12.9 (4H, C*H*Me₂), -22.1 (1H, PNAr *p*), -79.2 (3H, N=C*Me*). Tentative assignment for rest peaks which might belong to the complex: 8.7 (6H, CH*Me*₂), 1.9 (2H, PPh), 0.1 (2H, NAr *p* and PNAr).

A satisfactory elemental analysis could not be obtained. The X-ray structure determination shows the presence of 3 CH_2Cl_2 of crystallization; partial loss of this cocrystallized solvent is probably responsible for the analysis issues.

Synthesis of (Py)₄FeCl₂

Under an argon atmosphere, anhydrous FeCl₂ (6.26g, 0.05 mol) was weighed into a 100 mL Schlenk tube and 80 mL dry pyridine was added. The resulting yellow suspension was stirred for 4h 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 {2,6-Bis[4',4'-dimethyloxazolin-2'-

yl)pyridine}Fe(CH₂SiMe₃):(15)Fe(CH₂SiMe₃)₂

Under argon atmosphere, $(Py)_4FeCl_2$ (0.48g, 1.1 mmol) was weighed into a 50 mL Schlenk tube and suspended in 20 mL dry Hexane. The resulting yellow suspension was cooled to -70 °C and kept at this temperature for 30 min. At -70 °C, 2.2 mL LiCH₂SiMe₃ (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 °C and kept at this temperature for 30 min. Ligand **15** (0.13g, 0.5 mmol) in 20 diethyl ether was added dropwisely. The resulting violet solution was continued to stir for another 1h 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 °C for overnight. A lot of deep violet crystals were generated. Yield was more than 23% based on the amount of ligand **15** used. The X-ray quality crystal was obtained by cooling Et₂O/hexane saturated solution at -35 °C.

¹H NMR (25°C, benzene-d6, 300 MHz): δ 337 (1H, br, Δν_½ 1074 Hz, Py *H*4), 25.1 (2H, br, Δν_½ 224 Hz, Py *H*3), 9.3 (18H, br, Δν_½ 277 Hz, Si*Me*₃), -0.46 (12H, br, Δν_½ 432 Hz, C*H*₂O), -6.4 (4H, br, Δν_½ 222 Hz). C*H*₂(Fe) was not observed.

Anal. Calcd for C₂₃H₄₁FeN₃O₂Si₂ (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 SADABS¹⁰² (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**)CoCl₂·H₂O, (**8**)FeCl₂ and (**10**)FeCl₂. 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)CoCl₂·H₂O: (Figure 9.1) Long needles of the compound were obtained by crystallization from a saturated CH₂Cl₂ solution cooled to -20°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°), 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 Å³ near a chloride contained the highest peak in the electron-density difference map. This was assumed to contain a partially occupied 253

water molecule (occupancy refined to ca 0.7). Its hydrogen atoms were not included in the refinement.



Figure 9.1. X-ray structure of (**3**)CoCl₂•H₂O. (thermal ellipsoids drawn at 30% probability, hydrogen atoms and co-crystallized water have been omitted for clarity). Selected bond distances (Å) and angles (deg): Co(1)-N(1): 2.244(15); Co(1)-N(2): 2.037(15); Co(1)-N(3): 2.214(16); Co(1)-Cl(1): 2.244(7); Co(1)-Cl(2): 2.258(6); C(2)-N(1): 1.27(2); C(2)-C(3): 1.49(2); C(3)-N(2): 1.35(2); C(7)-N(2): 1.37(2); C(7)-C(8): 1.41(2); N(3)-C(8): 1.27(2); N(2)-Co(1)-N(1): 76.4(6); N(2)-Co(1)-N(3): 75.0(6); N(3)-Co(1)-N(1): 151.4(6); N(2)-Co(1)-Cl(1): 120.5(4); N(2)-Co(1)-Cl(2): 124.5(4).

(7) $CoCl_2 \cdot CH_2Cl_2$: 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)FeCl₂·(toluene)_{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 Å, 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 Å, 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 (Å): N(3)-P(1): 1.533(7); C(2)-P(1): 1.828(8); N(1)-C(2): 1.348(8); N(1)-C(6): 1.340(10); C(6)-C(7): 1.495(9); N(2)-C(7): 1.265(9).

(10)CoCl₂·(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 Å³) which most likely contains dichloromethane; however, it cannot be modeled as disordered or discrete ordered CH₂Cl₂ molecules. Thus we use PLATON/SQUEEZE²²⁸ option to account for the solvent electron density.

(10)FeCl₂: (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)FeCl₂ (thermal ellipsoids drawn at 30% probability, hydrogen atoms and co-crystallized CH₂Cl₂ omitted for clarity). Selected bond distances (Å) and angles (deg): Fe(1)-N(1): 2.284(4); Fe(1)-N(2): 2.115(4); Fe(1)-N(3): 2.161(4); Fe(1)-Cl(1): 2.161(4); Fe(1)-Cl(2): 2.261(2); C(2)-N(1): 1.273(7) ; C(2)-C(3): 1.473(8); C(3)-N(2): 1.341(7); C(7)-N(2): 1.324(7); C(7)-P(1): 1.821(6); P(1)-N(3): 1.593(5); N(1)-Fe(1)-N(2): 73.3(2); N(2)-Fe(1)-N(3): 81.9(2); N(1)-Fe(1)-N(3): 154.3(2); N(2)-Fe(1)-Cl(1): 98.29(13); N(2)-Fe(1)-Cl(2): 137.68(13).

(8)FeCl₂: (Figure 9.4) Crystals were obtained by layering a dichloromethane solution with hexane. A long needle (0.7*0.2*0.1) 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 (8)FeCl₂ (thermal ellipsoids of one of the two molecules are drawn at 30% probability, hydrogen atoms and co-crystallized CH_2Cl_2 or other solvent have been omitted for clarity). Selected bond distances (Å) and angles (deg):

Fe(1)-N(3): 2.131(8); Fe(1)-N(5): 2.152(7); Fe(1)-N(4): 2.259(7); Fe(1)-Cl(5): 2.378(3); Fe(1)-Cl(4): 2.267(3); N(4)-C(25): 1.322(10); C(24)-C(25): 1.489(13); N(5)-C(24): 1.346(11);N(5)-C(10): 1.346(12); P(1)-C(10): 1.803(10); P(1)-N(3): 1.606(7); 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)-Cl(4): 151.8(2); N(5)-Fe(1)-Cl(5): 91.7(2).

(9)FeCl₂·3CH₂Cl₂: (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 CH₂Cl₂ molecules were found in the structure. PLATON indicated the presence of additional small voids (41 Å³), possibly containing water molecules. These voids were far away from the FeCl₂ fragment. I did not succeed in refining water molecules in these positions. For the three CH₂Cl₂ molecules, all C-Cl bond lengths were constrained to be same using the SADI option of SHELXL.¹⁰⁵ The intramolecular Cl-Cl distances were similarly constrained to enforce equal Cl-C-Cl angles. The most seriously disordered CH₂Cl₂ molecule was modeled as disordered over two orientations, Cl(13)-C(92)-Cl(14) (orientation 1) and Cl(84)-C(94)-Cl(83) (orientation 2); their occupancies were refined be to 0.300(5)/0.699(5).



Figure 9.5. X-ray structure of (9)FeCl₂ (thermal ellipsoids are drawn at 30% probability, hydrogen atoms and co-crystallized CH₂Cl₂ have been omitted for clarity). Selected bond distances (Å) and angles (deg): Fe(1)-N(2): 2.261(5); Fe(1)-N(3): 2.086(4); Fe(1)-N(4): 2.127(5); Fe(1)-Cl(8): 2.251(2); Fe(1)-Cl(9): 2.313(2); N(2)-C(6): 1.291(7); C(51)-C(6): 1.480(8); C(51)-N(3): 1.347(7); C(55)-N(3): 1.347(6); P(5)-C(55): 1.815(6); P(5)-N(4): 1.600(5); N(3)-Fe(1)-N(2): 73.85(17); N(3)-Fe(1)-N(4): 81.49(17); N(4)-Fe(1)-N(2): 149.10(18); N(3)-Fe(1)-Cl(8):154.22(14); N(3)-Fe(1)-Cl(9): 94.96(14).

(15)Fe(CH₂SiMe₃)₂: (Figure 9.6) Crystal was obtained by cooling the Et₂O/Hexane solution at -35 °C. A irregular fragment (approximate 0.25*0.30*0.40 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**)Fe(CH₂SiMe₃)₂ (thermal ellipsoids are drawn at 30% probability, one molecule and hydrogen atoms were omitted for clarity). Selected bond distances (Å) and angles (deg): N(8)-C(13): 1.279(3); C(8)-C(13): 1.432(3); N(7)-C(8): 1.370(3); N(7)-C(12): 1.371(3); C(12)-C(18): 1.443(3); N(10)-C(18): 1.272(3); Fe(1)-N(8): 2.2348(16); Fe(1)-N(7): 2.0089(16); Fe(1)-N(10): 2.2599(16); Fe(1)-C(25): 2.0794(19); Fe(1)-C(51): 2.0647(19); N(7)-Fe(1)-N(8): 75.12(6); N(7)-Fe(1)-N(10): 74.76(6); N(8)-Fe(1)-N(10): 149.88(6); N(7)-Fe(1)-C(25):120.50(7); N(7)-Fe(1)-C(51): 118.48(7); C(51)-Fe(1)-C(25): 121.02(8).

Computational methods

All geometries were optimized at the b3-lyp²²⁹/SV(P)²³⁰ level using the Turbomole package²³¹ in combination with an external optimizer: the standalone Baker optimizer²³² 261
for the local minima, and BOptimize¹⁴⁷ for the constrained optimizations used to explore the potential-energy surface using the two-angle criterion ω . The Turbomole b3-lyp functional is similar to the Gaussian B3LYP functional, but uses VWN(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 SV(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.

	8 ·0.5 toluene	(3)CoCl ₂ ·H ₂ O	(7)CoCl ₂ ·CH ₂ Cl ₂	(10)CoCl ₂ ·(solvent)
Formula	$\begin{array}{c} C_{40}H_{44}N_{3}P \\ \cdot 0.5 \ C_{7}H_{8} \end{array}$	$\begin{array}{c} C_{27}H_{31}Cl_2CoN_3\\ \cdot H_2O \end{array}$	$\begin{array}{c} C_{27}H_{25}Cl_2CoF_6N_3\\ \cdot CH_2Cl_2 \end{array}$	$C_{37}H_{38}Cl_2CoN_3P$ ·solvent
Mol wt	643.82	543.38	720.27	685.50
Cryst system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	11.6000(8)	7.986(3)	8.5975(4)	10.4731(4)
b/Å	14.0850(10)	13.707(4)	23.0136(11)	22.0957(9)
c/Å	14.3620(17)	25.479(8)	16.7577(8)	17.1785(7)
a/deg	118.2700(13)	90.00	90	90
ß/deg	110.2500(14)	95.414(5)	97.6641(12)	98.3666(9)
γ/deg	92.6000(13)	90.0	90	90
V/Å ³	1875.7(3)	2776.8(15)	3286.1(3)	3933.0(3)
Ζ	2	4	4	4
$D_{\rm c}/{\rm g~cm}^{-3}$	1.14	1.300	1.456	1.158
abs coef/mm ⁻¹	0.107	0.834	0.904	0.639
F ₀₀₀	690	1132	1460	1428
index ranges	$-14 \le h \le 14$	$-6 \le h \le 6$	$-10 \le h \le 10$	$-12 \le h \le 12$

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

	8 ·0.5 toluene	(3)CoCl ₂ ·H ₂ O	(7)CoCl ₂ ·CH ₂ Cl ₂	(10)CoCl ₂ ·(solvent)	
	$-17 \le k \le 17$	$-11 \le k \le 11$	$-27 \le k \le 26$	$-26 \le k \le 26$	
	$-17 \le l \le 17$	$-21 \le l \le 21$	$-20 \le l \le 20$	$-20 \le l \le 20$	
$2\theta_{max}/deg$	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	
$R (Fo>4\sigma(Fo))^{XLVII}$	0.1190	0.1065	0.1063	0.0420	
R (all data)	0.1305	0.1768	0.1427	0.0466	
wR2 (all data)	0.3162	0.2652	0.2121	0.1246	
largest peak,	1.363,	0.665,	0.733,	0.430,	
hole/e Å ⁻³	-1.182	-0.445	-0.376	-0.164	

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

	(7)FeCl ₂ ·1.5 toluene	(10)FeCl ₂ ·CH ₂ Cl ₂	(8)FeCl ₂ ·(solvent)	(9)FeCl ₂ ·3 CH ₂ Cl ₂	(Pybox)Fe(CH ₂ SiMe ₃) ₂
Formula	$\begin{array}{c} 2(C_{27}H_{25}Cl_2F_6N_3) \\ \cdot 3 \ C_7H_8 \end{array}$	$\begin{array}{c} C_{37}H_{38}Cl_2CoN_3P\\ \cdot CH_2Cl_2 \end{array}$	$C_{40}H_{44}Cl_2FeN_3P\cdot(CH_2Cl_2)$	$\begin{array}{c} C_{43}H_{50}Cl_2FeN_3P\\ \cdot 3\ CH_2Cl_2\end{array}$	$C_{23}H_{41}FeN_3O_2Si_2$
Mol wt	1540.90	767.35	759.95	1021.36	503.62
Cryst system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	Cc	$P2_1/n$
a/Å	12.7827(9)	10.4789(7)	12.9108(14)	13.2575(8)	10.8062(4)
$b/\text{\AA}$	17.3375(12)	22.0476(15)	20.122(2)	22.9960(12)	19.1223(8)
$c/\text{\AA}$	17.8208(13)	17.3356(12)	17.1707(19)	17.5282(10)	27.5846(12)
α/deg	90	90	95.669(4)	90	90
β/deg	107.0897(12)	98.285(2)	89.895(3)	95.2100(14)	94.7266(11)
γ/deg	90	90	95.449(3)	90	90
$V/Å^3$	3775.1	3963.3(5)	4418.8(8)	5321.7(5)	5680.7(4)
Ζ	2	4	4	4	8
$D_{\rm c}/{\rm g~cm}^{-3}$	1.356	1.286	1.151	1.275	1.178
abs coef/mm ⁻¹	0.601	0.720	0.587	0.748	0.637
F ₀₀₀	1588	1592	1600	2120	2160
index ranges	$-15 \le h \le 15$	$-12 \le h \le 12$	$-15 \le h \le 15$	$-16 \le h \le 16$	$-13 \le h \le 13$

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

	(7)FeCl ₂ ·1.5 toluene	(10)FeCl ₂ ·CH ₂ Cl ₂	(8)FeCl ₂ ·(solvent)	(9)FeCl ₂ ·3 CH ₂ Cl ₂	(Pybox)Fe(CH ₂ SiMe ₃) ₂
	$-21 \le k \le 21$	$-24 \le k \le 26$	$-24 \le k \le 24$	$-27 \le k \le 27$	$-23 \le k \le 23$
	$-21 \le l \le 21$	$-20 \le l \le 20$	$-20 \le l \le 20$	$-21 \le 1 \le 21$	$-33 \le l \le 33$
$2\theta_{max}/deg$	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
<i>R</i> (<i>F</i> o>4σ(<i>F</i> o))	0.0952	0.0962	0.1165	0.0777	0.0395
R (all data)	0.1399	0.1319	0.2364	0.0931	0.0491
wR2 (all data)	0.2738	0.2406	0.3437	0.1929	0.1075
largest peak,	0.822,	1.139	0.716,	0.917,	0.323,
hole/e Å ⁻³	-1.053	-0.645	-0.616	-0.703	-0.193

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, MgCl₂ and ZnCl₂ complexes were optimized at restricted b3-lyp²²⁹/SV(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/TZVP²³⁴//b3-lyp/SV(P). Thus all energies used in the text are pure electronic energies without zero-point 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*; $R = CH_2SiMe_3$; $R' = CH_2CMe_2Ph$)

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. LiCH2SiMe3 was purchased from Aldrich and crystallized -35°C. from pentane at Anhydrous CoCl₂, 2-methyl-2phenylpropylmagnesium chloride solution (0.5 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.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All NMR shifts (δ , ppm) were referenced to the solvent (benzene- d_6 , ¹H NMR: C₆D₅H δ 7.16 ppm; ¹³C NMR: C₆D₆ δ 128.0 ppm; CDCl₃, ¹H NMR: CHCl₃ δ 7.26 ppm; ¹³C NMR: CHCl₃ δ 77.0 ppm). 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.

 $(Py)_4CoCl_2$. Anhydrous CoCl₂ (1.36 g, 10.4 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 g (78%) of pink crude (Py)₄CoCl₂.

Anal. Calcd for C₂₀H₂₀Cl₂CoN₄ (446.24): C, 53.83; H, 4.52; N, 12.56; Cl, 15.89. Found: C, 53.67; H, 4.85; N, 12.81; Cl, 16.10.

(*Py*)₂*CoR*₂. Pink (Py)₄CoCl₂ (0.32 g, 0.72 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° C and kept at this temperature for 20 min. LiCH₂SiMe₃ (0.136g, 1.44mmol) 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° C. The color of the mixture changed to blue-green. It was kept at -70° C for another 20min, and was then allowed to slowly (3 h) warm to room temperature. During this, the color first changed to red (around -10° C), and then at around 0° 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 (Py)₂CoR₂ was prepared and used assuming this 75% yield.

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 114 (4H, br, Δν_{1/2} 1600 Hz, Py *H*2), 38.4 (4H, br, Δν_{1/2} 500 Hz, Py *H*3), 10.3 (18H, br, Δν_{1/2} 80 Hz, Si*Me*₃), -8.5 (2H, br, Δν_{1/2} 190 Hz, Py *H*4); C*H*₂(Co) not observed.

Evans method for determination of magnetic moment: in a dry-box, one drop of $(Py)_2CoR_2$ was dissolved in about 0.5 mL C_6D_6 in a small vial and 0.0253 g C_6Me_6 (reference and internal standard) was added. The resulting green solution was diluted to 3.1 mL by adding C_6D_6 . Integration of the ¹H NMR spectrum showed the concentration of $(Py)_2CoR_2$ to be 0.22 mol/L; the chemical-shift difference between C_6Me_6 in the paramagnetic solution and in pure C_6D_6 was 9.14 ppm, implying a magnetic moment of 4.9 μ_B . Two further experiments at different concentrations produced similar values (0.66 mol/L: 4.5 μ_B ; 0.052 mol/L: 5.0 μ_B); average 4.8(3) μ_B .

Hydrolysis: in a dry-box, 0.158g (Py)₂CoR₂ and 0.053g C₆Me₆ were weighed into a small vial. Part of this sample was used for a ¹H NMR (C₆D₆). From the observed molar ratio of (Py)₂CoR₂ and C₆Me₆ (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 ¹H 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 Py, Me₄Si and C₆Me₆ species in solution (1.97:2.12:1, by integration; expected 2.26:2.26:1) agreed reasonably well with the expected values for (Py)₂CoR₂, considering that some pyridine will remain coordinated to Co and/or stay in the water drop and some Me₄Si will evaporate during filtration.

 $(Py)_2CoPh_2$.(this paragraph is reported in paper in reference 217) Procedure A: Pink $(Py)_4CoCl_2$ (0.58 g, 1.3 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°C and kept at this temperature for 20 min. LiPh (1.4 mL, 1.8 M in dibutyl ether) was dropped into it to form a yellow suspension. After warming to room temperature over 4h, 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 (Py)₄CoCl₂ (0.45 g, 1.0 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°C and kept at this temperature for 20 min. LiPh (1.2 mL, 1.8 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.

 $(Py)_2CoMe_2$. (this paragraph is not reported in the paper in reference 217) Pink $(Py)_4CoCl_2$ (0.80 g, 1.79 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 mL, 1.6 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 °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 $(Py)_2Co(CH_2SiMe_3)_2$ in ¹H NMR spectrum were not observed.

(*TMEDA*)*CoR*₂ (the procedure here is slightly modified from the published procedure in reference 217) The *freshly prepared* (Py)₂CoR₂ (0.82 mmol assuming 75% yield from (Py)₄CoCl₂; see above) was dissolved in 5 mL pentane and the green solution was cooled to -30°C. TMEDA (10 eq. 1.25mL, 8.2 mmol) was slowly added at -30°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 1h. 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°C, depositing a dark solid. The cold liquid was pipetted off, and the solid was dried to give a purple-blue solid (0.2186 g, 57% yield based on (Py)₄CoCl₂ used or 76% yield based on the (Py)₂CoR₂). The deep bluish purple single crystal was grown by cooling the saturated pentane solution at -35 °C overnight.

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 80 (4H, br, Δν₂ 600 Hz, C*H*₂N), 78 (12H, br, Δν₂ 350 Hz, N*Me*), 9.6 (18H, br, Δν₂ 70 Hz, Si*Me*₃); C*H*₂(Co) not observed.

 $(Py)_2CoR'_2$: 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 $(Py)_2MgR'_2$ and $(Py)_2CoR'_2$ 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 (Py)₄CoCl₂ (1.24 g, 2.78 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°C. R'MgCl (11.8 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 °C, the filtrate deposited whitish crystals of (presumably) (Py)₂MgR'₂, dark-green blocks of (Py)₂CoR'₂, and some sticky dark oily droplets. A fragment of one of the darkgreen blocks was used for single-crystal X-ray structure determination. ¹H NMR of the deposited solids in C₆D₆ indicated the presence of (Py)₂MgR'₂ and (Py)₂CoR'₂ (see below).

Procedure (B): Pink (Py)₄CoCl₂ (0.69 g, 1.55 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 °C, during which pink solid precipitate formed. R'MgCl (2.8 mL of a 0.5 M solution in diethyl ether, 1.4 mmol) was added dropwise. The resulting mixture was warmed to around 0 °C in 1 h, during which it turned purplish and a white solid formed. The solution was again cooled to -50 °C, and R'MgCl (3.2 mL of a 0.5 M solution in

diethyl ether, 1.6 mmol) was added dropwise. The resulting suspension was stirred at -50 $^{\circ}$ C for 20 min and warmed to room temperature in 1h, during which it turned green. 0.6 mL of dry pyridine was added into it and the green mixture was cooled to -30 $^{\circ}$ 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 $^{\circ}$ C. Overnight, a dark and shiny solid crystallized; the mother liquid was pipetted off, leaving 0.15 g (20%) of reasonable pure (Py)₂CoR'₂. NMR samples always show some decomposition to diamagnetic compounds (pyridine, PhCMe₃), and within 4h all signals due to (Py)₂CoR'₂ disappear.

¹H NMR (25°C, benzene-*d*₆, 300 MHz; assignment tentative!): δ 108 (4H, Δ*ν*_{1/2} 5300 Hz, Py *H*2), 32.7 (4H, Δ*ν*_{1/2} 1700 Hz, Py *H*3), 21.6 (12H, Δ*ν*_{1/2} 270 Hz, C*Me*₂), 10.2 (4H, Δ*ν*_{1/2} 160 Hz, Ar *o*), 7.4 (4H, Δ*ν*_{1/2} 27 Hz, Ar *m*), 3.9 (2H, Δ*ν*_{1/2} 17 Hz, Ar *p*), -8.1 (2H, Δ*ν*_{1/2} 590 Hz, Py *H*4).

Synthesis of (Py)₂Mg(CH₂CMe₂Ph)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 °C overnight, forming a yellow crystalline solid (0.45g, 80% yield). ¹H NMR (25°C, benzene-*d*6, 300 MHz): δ 7.90 (d, 4H, *J* 4.0 Hz, Py *H*2), 7.78 (d, 4H, *J* 7.7 Hz, Ar *o*), 7.12 (t, 4H, *J* 7.7 Hz, Ar *m*), 6.99 (t, 2H, *J* 7.2 Hz, Ar *p*), 6.78 (t, 2H, *J* 7.4 Hz, Py *H*4), 6.41 (t, 4H, *J* 6.4Hz, Py *H*3), 1.83 (s, 12H, *Me*), 0.77 (s, 4H, *CH*₂). ¹³C NMR (25°C, benzene-*d*6, 75 MHz): δ 158.3 (Ar *i*), 148.82 (Py *C*2), 137.69 (Py *C*4), 127.80 (Ar *m*), 125.92 (Ar *o*), 124.21 (Py *C*4), 123.91 (Ar, *p*), 40.41 (*C*Me2), 36.62 (*CMe*2), 34.48 (*C*H2).

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

General. Refer to the single crystal X-ray diffraction in Chapter 2.

*(TMEDA)CoR*₂. A deep bluish-purple crystal fragment (ca. $0.5 \times 0.2 \times 0.15$ mm) was mounted in a thin-walled glass capillary. Data were collected at 293K on a Bruker 4-circle 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.

 $(Py)_2CoR'_2$. A large irregular crystal fragment (ca $0.6 \times 0.5 \times 0.4$ mm) was broken off an even larger block of green-black (Py)₂CoR'₂, 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° 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 SAINT¹⁰¹ with a decay correction, and an absorption correction was done using SADABS¹⁰². 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.

	(TMEDA)CoR ₂	(Py) ₂ CoR' ₂
Formula	$C_{14}H_{38}CoN_2Si_2$	C ₃₀ H ₃₆ CoN ₂
Mol wt	349.57	483.54
Cryst system	monoclinic	triclinic
Space group	C2/c	P-1

Table 9.3. Details of crystal structure determinations

	(TMEDA)CoR ₂	(Py) ₂ CoR' ₂
a/Å	25.565(3)	11.8183(11)
b/Å	10.1487(10)	11.8294(12)
c/Å	17.3758(18)	12.1892(12)
α/deg	90	105.652(2)
β/deg	100.104(6)	109.119(2)
γ/deg	90	108.825(2)
V/Å ³	4438.3(8)	1383.1(2)
Ζ	8	2
$D_{\rm c}/{\rm g~cm}^{-3}$	1.046	1.161
abs coef/mm ⁻¹	0.875	0.639
F ₀₀₀	1528	514
index ranges	$-30 \le h \le 30$	$-14 \le h \le 14$ $-14 \le k \le 14$
	$-12 \le k \le 12$	$-14 \le l \le 14$
	$-20 \le l \le 21$	
$2\theta_{max}/deg$	51	51

	(TMEDA)CoR ₂	(Py) ₂ CoR' ₂
# rflctns	13479	10195
# unique	4140	5166
$\# > 2\sigma$	3163	4314
GOF	1.054	1.088
# parameters	186	324
$R (Fo > 4 \sigma(Fo))$	0.0374	0.0685
R (all data)	0.0496	0.0772
wR2 (all data)	0.1090	0.2060
largest peak, hole/ <i>e</i> Å ⁻³	0.266, -0.171	0.555, -0.241

Computational methods

All geometry optimizations were done with Turbomole²³¹ using the SVP²³⁰ and TZVP²³⁴ basis sets and the functionals b3-lyp²²⁹ and b-p^{110,111} (the latter with the RI approximation) in combination with an external optimizer (PQS OPTIMIZE²³²). All calculations used the spin-unrestricted formalism with $S_z = \frac{3}{2}$ (Co^{II} 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 03¹¹⁸ (B3LYP and BP86 functionals, TZVP basis set, GIAO method²³⁶). EPR hyperfine couplings used to estimate Fermi contact shifts (Eq. 5.2) were calculated²³⁷ using the Orca¹¹⁹ 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*; $R = CH_2SiMe_3$; $R' = CH_2CMe_2Ph$)

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 1-3,²³⁸ 4²³⁹, 6²²², 8¹⁴² and 10²⁴⁰ in Chapter 6 were prepared according to published procedures. The procedure for synthesizing ligand 9 in this Chapter refers to the synthesis of 2-[2,6-^{*i*}Pr₂C₆H₃N=CMe]-6-[2,4,6-Me₃C₆H₂N=PPh₂]-C₅H₃N in the experimental part of Chapter 3.

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. All NMR shifts (δ , ppm) were referenced to the solvent (benzene- d_6 , ¹H NMR: C₆D₅H δ 7.16 ppm; ¹³C NMR: C₆D₆ δ 128.0 ppm; CDCl₃, ¹H NMR: CHCl₃ δ 7.26 ppm; ¹³C NMR: CHCl₃ δ 77.0 ppm). Data were collected at room temperature unless otherwise noted. Elemental analysis was done in Guelph Chemical laboratories LTD.

The following work between /* and *\ was done by Peter H.M. Budzelaar and Femke F.B.J. Janssen

/* 2,6-(*CF*₃*CO*)₂*C*₃*H*₃*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°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°C. 3 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°C resulted in dissolution of the precipitated dibromopyridine, giving a clear yellow solution. After 5 more minutes stirring at -90°C, the mixture was cooled to -100°C and 2.74 g (21.4 mmol) methyl trifluoroacetate was added over 10 minutes, keeping the temperature below -90°C. Some ether was used to rinse the funnel. The mixture was stirred for 20 minutes at -90°C, then cooled to -113°C, and 13.6 mL of 1.6 M *n*-BuLi was added while the

temperature was kept below -100°C. After 5 minutes of stirring, 2.8 g (21.8 mmol) methyl trifluoroacetate was added while keeping the temperature below -100°C.

The mixture was allowed to warm, and when it reached -60°C, a mixture of 7 mL 12M HCl and 5 mL water was added. The reaction mixture was then poured into a mixture of 25 mL 12M 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°C, small flask, short condensor) and then solidified on cooling. Short-path distillation (the product solidifies in the receiver) gave 4.47 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 **5**.

¹H NMR (300.1 MHz, CDCl₃, 25°C): δ 8.43 (2H, d, ³*J* 7.9 Hz, Py *H*3), 8.27 (1H, t, ³*J* 7.9 Hz, Py *H*4). ¹³C NMR (75.5 MHz, CDCl₃, 25°C): δ 179.7 (q, ²*J*_{CF} 35 Hz, *C*=O), 147.9 (Py *C*2), 139.2 (Py *C*4), 129.1 (Py *C*3), 116.4 (q, ¹*J*_{CF} 290 Hz, *C*F₃). ¹⁹F NMR (282.4 MHz, CDCl₃, 25°C): δ -73.1.

Before refluxing and distillation, the crude mixture contained only a small amount of $2,6-(CF_3CO)_2C_5H_3N$; 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 X-ray structure, see Figure C.2 in the Appendix C).

2,6-[2,4,6-Me₃C₆H₂N=C(CF₃)]₂C₅H₃N (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°C/RT) to give 6.23 g (78%) of yellow crystals. A crystal from this batch was used for X-ray structure determination.

¹H NMR (300.1 MHz, CDCl₃, 25°C): δ 7.42 (1H, t, ³*J* 7.9 Hz, Py *H*4), 6.93 (2H, d, ³*J* 7.9 Hz, Py *H*3), 6.75 (4H, s, Ar *m*), 2.22 (6H, s, Ar *p-Me*), 1.90 (12H, s, Ar *o-Me*).

¹³C NMR (75.5 MHz, CDCl₃, 25°C): δ 154.6 (q, ${}^{2}J_{CF}$ 33 Hz, *C*=N), 149.1 (Py *C*2), 142.3 (Ar *i*), 136.6 (Py *C*4), 134.1 (Ar *p*), 128.8 (Ar *m*), 124.8 (Ar *o*), 124.2 (Py *C*3), 119.2 (q, ${}^{1}J_{CF}$ 280 Hz, *C*F₃), 20.6 (Ar *p-Me*), 17.5 (Ar *o-Me*). ¹⁹F NMR (282.4 MHz, CDCl₃, 25°C): δ -68.6.

Anal. Calcd for $C_{27}H_{25}F_6N_3$ (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-Me₂C₆H₃N=CMe)-C₅H₃N]CoR ((1)CoR) from (Py)₂CoR₂. (Py)₂CoR₂ (1.14 mmol assuming 75% yield from (Py)₄CoCl₂; see experimental section of Chapter 5) was dissolved in 8 mL diethyl ether and the green solution was cooled to -30°C. Ligand 1 (0.39 g, 1.06 mmol) was dissolved in 20 mL diethyl ether and the clear yellow solution was slowly added to the above (Py)₂CoR₂ solution at -30°C. After the addition, the solution (which had turned red) was allowed to warm to room temperature (around 0°C the color changed to purple). After stirring for another hour, the deep purple 282 solution was filtered and the solvent was evaporated in vacuo. The residue was dissolved in 4mL 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 ° C overnight. The purple mother liquor was decanted and the residue was recrystallized from toluene (6 drops)/hexane (5 mL) to give shiny dark crystalline (1)CoR (0.23 g, 42%) suitable for X-ray diffraction.

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 10.08 (t, 1H, *J* 7.7 Hz, Py *H*4), 7.74 (d, 2H, *J* 7.7Hz, Py *H*3), 7.36 (t, 2H, *J* 7.4 Hz, Ar *p*), 7.27 (d, 4H, *J* 7.4 Hz, Ar *m*), 2.12 (s, 12H, Ar *Me*), 0.81 (s, 2H, CoC*H*₂), -0.62 (s, 9H, Si*Me*₃), -1.26 (s, 6H, N=C*Me*).

¹³C NMR (25°C, benzene-*d*₆, 75 MHz) δ 165.6 (ArN=*C*Me), 158.4 (*o*-*C*, Py), 156.0 (*i*-*C*, Ar), 130.2 (*o*-*C*, Ar), 129.1(*m*-*C*, Ar), 125.9 (*p*-*C*, Ar), 123.3 (*m*-*C*, Py), 116.7 (*p*-*C*, Py), 23.8 (N=*CMe*), 19.5 (o-*C*H₃, Ar), 3.8 (Si*Me*₃), -10.7 (br, Co*C*H₂).

Anal. Calcd for C₂₉H₃₈CoN₃Si (515.65): C, 67.55; H, 7.43; N, 8.15. Found: C, 67.32; H, 7.14; N, 7.70.

Synthesis of $[2,6-bis(2,6-Me_2C_6H_3N=CMe)-C_5H_3N]CoR$ ((1)CoR) from (TMEDA)Co(CH₂SiMe₃)₂. (A verbatim copy from the published: Zhu, D.; Budzelaar, P.H.M. Organometallics 2010, 29, 5759) In a dry-box, (TMEDA)Co(CH₂SiMe₃)₂ (0.31 g, 0.89 mmol) was weighed and dissolved in 10 mL hexane. The mixture was transferred to a Schlenk line and cooled to -20°C. At this temperature, ligand 1 (0.32 g, 0.87 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 283

evaporated to dryness and the residue was crystallized from diethyl ether (0.5 mL)/hexane (3 mL) at -35°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)CoR₂ (0.017g, 0.049 mmol) and ligand **1** (0.030g, 0.081 mmol) was weighed into an NMR tube and cooled to -80 °C, followed by adding 2 mL of toluene-*d*8 which is precooled to -70 °C to dissolve all the solids. The resulting mixture was slowly warmed to room temperature, during which ¹H NMR spectra were taken at -35 °C, -20 °C (Figure 9.7A), 0 °C (Figure 9.7B) and 25 °C(Figure 9.7C). Below 0 °C, peaks of paramagnetic compounds are too broad to be interpretable. At 0 °C, only (TMEDA)CoR₂, ligand **1**, (**1**)CoR₂ were observed. No other paramagnetic intermediate could be detected. The low-temperature reaction of ligand **1** with (Py)₂CoR₂ gave too broad peaks which cannot be interpreted.



Synthesis of [2,6-bis(2,4,6-Me₃C₆H₂N=CMe)-C₅H₃N]CoR ((2)CoR). This reaction was done as described for 1, using 0.9 mmol of (Py)₂CoR₂ and 0.35 g (0.88 mmol) of 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.

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 10.13 (t, 1H, *J* 7.0 Hz, Py *H*4), 7.79 (d, 2H, *J* 7.0 Hz, Py *H*3), 7.11 (s, 4H, Ar *m*), 2.37 (s, 6H, Ar *p-Me*), 2.16 (s, 12H, Ar *o-Me*), -0.60 (s, 9H, Si*Me*₃), -1.14 (s, 6H, N=C*Me*). The CoC*H*₂ signal could not be unambiguously assigned.

Reaction of (TMEDA) CoR_2 with 2,6-bis($C_6H_5N=CMe$)- C_5H_3N (3). In a dry-box, 0.0052g (0.0166 mmol) of 3 was dissolved in benzene- d_6 and transferred into an NMR tube, and a solution of 0.0062 g of (TMEDA)CoR₂ (0.0177 mmol, 1.1 equiv) in benzene- d_6 was added. For the ¹H NMR spectrum, see Figure 6.3A.

¹H NMR (25°C, benzene-d6, 300 MHz; tentative assignments): δ 9.79 (t, 1H, *J* 7.4 Hz, Py *H*4), 8.17 (d, 4H, *J* 6.6 Hz, Ar *o*), 7.76 (d, 2H, *J* 7.2 Hz, Py *H*3), 7.35-7.43 (m, 6H, Ar *m* and Ar *p*), 0.35 (s, 2H, CoC*H*₂), -0.64 (s, 9H, Si*Me*₃), -1.10 (s, 6H, N=C*Me*).

The part between following /* and *\ was not reported in the published paper in reference 217.

/* 1.3 μ L Pyridine was injected into this NMR sample and the immediate ¹H NMR spectrum showed that there were obvious changes in shifts of the ¹H NMR signals attributed to the Co^I alkyl in Figure 6.3C.*\

Reaction of $(Py)_2CoR_2$ with 3. In a dry-box, about 0.059 mmol of $(Py)_2CoR_2$ was dissolved in benzene- d_6 and 0.15 g (0.048 mmol; 0.81 equiv) of 3 was added. A ¹H NMR spectrum recorded immediately afterwards (Figure 6.3 B,C) showed peaks that we tentatively assign in terms of formation of 1 equiv of Me₄Si and 1 equiv of (3)CoR or (3)(Py)CoR.

¹H NMR (25°C, benzene-*d*₆, 300 MHz; tentative assignments): δ 8.71 (br, 1H, Py *H*4), 8.37 (br, Py *H*3), 7.00 (4H, Ph *o*), 6.91 (4H, Ph *m*), 6.82 (2H, Ph *p*), 0.85 (s, 6H, *Me*C=N), 0.45 (s, 2H, CoC*H*₂), 0.05 (s, 12H, *Me*₄Si), -0.50 (s, 9H, Si*Me*₃).

Reaction of (TMEDA)CoR₂ with 2,6-bis(C₆H₅CH₂N=CMe)-C₅H₃N (4). In a dry-box, 0.0068 g 4 (0.020 mmol) was weighed and dissolved in benzene-*d*6, followed by addition of around 0.0092g (TMEDA)CoR₂ (0.026 mmol, 1.3 equiv) in benzene-*d*₆. A ¹H NMR spectrum recorded immediately (Figure 6.4A) showed peaks that could be tentatively assigned to (4)CoR.

¹H NMR (25°C, benzene-*d*₆, 300 MHz; tentative partial assignments): δ 9.74 (t, 1H, *J* 7.4 Hz, Py *H*4), 7.40 (d, 2H, *J* 7.4 Hz, Py *H*3), 6.61 (s, 4H, PhC*H*2), -0.16 (s, 9H, Si*Me*₃), -0.64 (s, 6H, N=C*Me*).

Pyridine was added to this sample in small increments (1 μ L, 2.0 μ L); this resulted in changes in shifts of the ¹H NMR signals attributed to the Co^I alkyl. Figure 6.4D shows the spectrum after addition of 3 μ L Py.

*Reaction of (Py)*₂*CoR*₂ *with 4*. In a dry-box, into about 0.0068g (0.02 mmol) of 4 was added to a solution of about 0.04 mmol of (Py)₂*CoR*₂ in benzene- d_6 . A ¹H NMR spectrum

recorded immediately afterward (Figure 6.4C) showed peaks that could be interpreted in terms of formation of 1 equiv of Me₄Si and 1 equiv of (4)CoR or its Py.

¹H NMR (25°C, benzene-d6, 300 MHz; tentative assignments): δ 9.32 (t, 1H, *J* 6.6 Hz, Py *H*4), 7.54 (d, 2H, *J* 6.6 Hz, Py *H*3), 7.05-7.08 (br, Ar *o*), 6.90-6.93 (m, Ar p and Ar m), 6.32 (s, 4H, PhC*H*2), -0.15 (s, 6H, N=C*Me*), -0.24 (s, 9H, Si*Me*₃). CoC*H*2 cannot be unambiguously assigned.

Figure 6.4B shows the results of a similar experiment using different concentrations of 4 and (Py)₂CoR₂.

¹H NMR (25°C, benzene-*d*₆, 300 MHz; tentative assignments): δ 8.94 (br, 1H, Py *H*4), 7.63 (br, Py *H*3), 6.95, 6.89 (br, 10H, *Ph*), 6.08 (4H, NC*H*₂), 0.25 (s, 6H, *Me*C=N), 0.12 (s, 2H, CoC*H*₂), 0.02 (s, 12H, *Me*₄Si), -0.32 (s, 9H, Si*Me*₃).

*Reaction of (Py)*₂*CoR*₂ *with 5.* In a dry-box, 0.0069g (0.0174 mmol) 5 was weighed and dissolved in benzene- d_6 , followed by addition about 0.028 mmol (Py)₂CoR₂ in benzene- d_6 . ¹H and ¹⁹F NMR spectra were recorded immediately (Figure 6.6B, Figure 6.7B) and showed the formation of Me₄Si 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.

¹H NMR (25°C, benzene-*d*₆, 300 MHz; tentative assignments): δ 8.56 (d, 2H, *J* 7.9, Py *H*3), 2.36 (s, 6H), 0.34 (s, 2H, CoC*H*₂), -0.35 (s, 9H, Si*Me*₃). ¹⁹F NMR (282.4 MHz, benzene-*d*₆, 25°C): δ -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 (TMEDA)₂**CoR**₂ with 5. (This paragraph was not reported in the published paper in reference 217) In a dry-box, (TMEDA)Co(CH₂SiMe₃)₂ (0.0150 g, 0.043 mmol) was weighed into a small vial, followed by adding ligand 5 (0.0217g, 0.043 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)CoR² (0.082 g, 0.23 mmol) was dissolved in 2mL benzene and cooled to -35° C, and 0.06 g (0.23 mmol) of **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)CoR₂ and (TMEDA)CoR₂, see Figure 6.8) was characterized by ¹H NMR.

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 44.4 (2H, br, Δν₂ 80 Hz, Py *H*3), 21.8 (18H, br, Δν₂ 120 Hz, Si*Me*₃), -5.6 (4H, br, C*H*₂O), -16.9 (12H, br, Δν₂ 110 Hz, C*Me*₂), -66.5 (1H, br, Py *H*4).

*Synthesis of (6)CoCl*₂ *(6: 2,6-bis(4',4'-dimethyloxazolin-2-yl)pyridine)*^{159b-c}.(not published) Anhydrous CoCl₂ (0.45g, 3.5 mmol) was dissolved in 40 mL THF at refluxing temperature. At around 70 °C, ligand 6 (0.95g, 3.5 mmol) was dissolved in hot THF. 289

After the heater was turned off, the $CoCl_2$ solution in THF was added dropwise to the solution of ligand **6**. The resulting blue suspension was stirred for 1h. 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%).

¹H NMR (25°C, CD₂Cl₂, 300 MHz, all peaks are broad): δ 78.4 (2H, Py *H*3), 11.7 (1H, Py *H*4), -35.6 (12H, C*Me*₂). The peak at -12.4 ppm was tentatively assigned to be C*H*₂O.

*Synthesis of (6)FeCl*² *(6: 2,6-bis(4',4'-dimethyloxazolin-2-yl)pyridine).*^{159b-c} (not published) Anhydrous FeCl₂ (0.38g, 3.0 mmol) was suspended in 10 mL THF, followed by adding a THF solution of ligand **6** (0.84g, 3.0 mmol). The resulting blue suspension was stirred at room temperature overnight. After filtered over frit filter, the resulting blue solid was dissolved in dry CH_2Cl_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%).

¹H NMR (25°C, CD₂Cl₂, 300 MHz, all peaks are broad): δ 61.5 (2H, Py *H*3), 4.2 (12H, C*Me*₂), -7.6 (1H, Py *H*4). The peak at 16.7 ppm was tentatively assigned to be C*H*₂O.

*Reaction of (TMEDA)CoR*₂ with 8 (8: 2,6-bis(2,4,6-Me₃C₆H₂N=PC₆H₅)-C₅H₃N). (not published). In a dry-box, ligand 8 (0.0847g, 0.14 mmol) was weighed into 2 mL vial, followed by adding (TMEDA)CoR₂ (0.0495g, 0.14 mmol). The resulting mixture was

dissolved in 2 mL benzene-d6 at room temperature. The immediate ¹H 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 8. Ligand 9 (0.0977g, 0.136 mmol) and (TMEDA)CoR₂ (0.0478g, 0.136 mmol). The immediate ¹H 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-2ylidene]pyridine): (this paragraph is not reported in the published paper in reference 217) In a dry-box, ligand 10 (0.0113g, 0.136 mmol) and (TMEDA)CoR² (0.0090g, 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 ¹H NMR spectrum was messy and a lot of black solid precipitated out. The reaction with (Py)₂CoR₂ 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-[CF₃C(OH)₂]₂C₅H₃N. (this work was done by Peter H.M Budzelaar and Femke F.B.J. Janssen) A transparent regular platelet (approximately $0.3 \times 0.2 \times 0.1$ mm) was glued on a thin glass fiber. Data were collected at 208K on a Nonius KappaCCD diffractometer with area detector φ and ω scans. The structure was solved using CRUNCH.²⁴¹ There is some minor rotational disorder in the CF₃ 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-Me₃C₆H₂N=C(CF₃)]₂C₅H₃N (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 φ and ω scans. The structure was solved using CRUNCH.²⁴¹

(1)CoR. A deep purple crystal fragment (approx $0.6 \times 0.2 \times 0.1$ mm) was mounted in a thinwalled glass capillary. Data were collected at 293K 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

	2,6-[(HO) ₂ C(CF ₃)] ₂ C ₅ H ₃ N•THF	2,6-[(2,4,6-Me ₃ C ₆ H ₂ N=C(CF ₃)] ₂ C ₅ H ₃ N	(1)CoR
Formula	$C_9H_7NO_4F_6\bullet C_4H_8O$	$C_{27}H_{25}F_6N_3$	C ₂₉ H ₃₈ CoN ₃ Si
Mol wt	375.23	505.50	515.65
Cryst system	orthorhombic	tetragonal	monoclinic
Space group	Pcmn	$I4_1$	P2 ₁ /m (No.11)
a/Å	6.6689(3)	14.9916(10)	7.6802(3)
$b/{ m \AA}$	14.6578(8)	14.9916(10)	21.2770(10)
$c/\text{\AA}$	17.1651(12)	11.1077(5)	8.5207(4)
a/deg	90	90	90
β/deg	90	90	99.1876(11)
γ/deg	90	90	90
$V/\text{\AA}^3$	1677.91(17)	2496.4(3)	1374.52(11)
Ζ	4	4	2
$D_{\rm c}/{\rm g~cm}^{-3}$	1.485	1.345	1.246

Table 9.4. Details of crystal-structure determinations

	2,6-[(HO) ₂ C(CF ₃)] ₂ C ₅ H ₃ N•THF	2,6-[(2,4,6-Me ₃ C ₆ H ₂ N=C(CF ₃)] ₂ C ₅ H ₃ N	(1)CoR
abs coef/mm ⁻¹	0.154	0.111	0.689
F ₀₀₀	760	1048	548
index ranges	$-7 \le h \le 7$ -17 $\le k \le 17$ -20 $\le l \le 16$	$-17 \le h \le 17$ $-17 \le k \le 17$ $-13 \le l \le 13$	$-9 \le h \le 9$ $-25 \le k \le 25$ $-10 \le l \le 10$
$2\theta_{max}/deg$	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
$R (Fo > 4 \sigma(Fo))$	0.0649	0.0455	0.0379
R (all data)	0.0935	0.0358	0.0398
wR2 (all data)	0.1666	0.0853	0.1008
largest peak,	0.489,	0.111,	0.393,

	2,6-[(HO) ₂ C(CF ₃)] ₂ C ₅ H ₃ N•THF	2,6-[(2,4,6-Me ₃ C ₆ H ₂ N=C(CF ₃)] ₂ C ₅ H ₃ N	(1)CoR
hole/ e Å ⁻³	-0.344	-0.157	-0.174

Computational methods

All geometry optimizations were done with Turbomole²³¹ using the SVP²³⁰ and TZVP²³⁴ basis sets and the functionals b3-lyp²²⁹ and b-p^{110,111} (the latter with the RI approximation) in combination with an external optimizer (PQS OPTIMIZE²³² for minima, BOptimize¹⁴⁷ for MECP¹⁹⁸). All calculations used the spin-unrestricted formalism, with $S_z = 3/2$ (Co^{II} HS), 1/2 (Co^{II} LS) or 0 (Co⁽⁰⁾ LS). 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 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 SV(P) optimized geometries).

The σ and π parameters of ligand **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 *\ 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 received. 2,6-Bis[1-(2,6as dimethylphenylimino)ethyl]pyridine (1) and 2,6-Bis[1-(2,6di*iso*propylphenylimino)ethyl]pyridine (4) were prepared according to published procedures.²³⁸ (1)CoCH₂SiMe₃ was prepared according to the literature procedure in Chapter 7 using (TMEDA)Co(CH_2SiMe_3)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.

¹H NMR, ¹³C {H} NMR and ¹⁹F NMR spectra were recorded on a Bruker Avance 300 MHz or Bruker Avance 500 MHz spectrometer. All NMR shifts (δ , ppm) of ¹H NMR and ¹³C NMR spectra were referenced to the solvent (benzene-*d*₆, ¹H NMR: C₆D₅H δ 7.16 ppm; ¹³C NMR: C₆D₆ δ 128.0 ppm; CDCl₃, ¹H NMR: C*H*Cl₃ δ 7.26 ppm; ¹³C NMR: CHCl₃ δ 77.0 ppm; THF-*d*8, ¹H NMR: C*H*₂(2,5); δ 3.62 ppm; ¹³C NMR: CH₂(2,5); δ 68.03 ppm). ¹⁹F{H} NMR spectra were referenced to the internal benzotrifluoride in
benzene-*d*6 at δ -62.4 ppm. When necessary, COSY or HSQC NMR spectrum was also acquired in certain cases to assist the peak assignment in ¹³C NMR or ¹H 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 N₂-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).*\ (this work is done by Bas der Bruin in University of Amsterdam, the Netherland)

/*Synthesis of 4-methylphenyl lithium:

 LiC_6H_4 -4-Me.²⁴² BrC₆H₄-4-Me (1.40 g, 8.02 mmol) was dissolved in 16 mL diethyl ether and cooled to -70°C. At this temperature, *n*-butyl lithium (5.1 mL, 1.6 M in hexane, 8.16 mmol) was added dropwise to the stirred solution. The resulting clear solution was stirred for 4 h at -65°C. The solvent was removed *in vacuo* below -20°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)CoCl₂ complex¹⁶

Under argon atmosphere, anhydrous CoCl₂ (0.10g, 0.77 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 **1** (0.28g, 0.76 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 (0.38g, 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)CoC₆H₄-4-Me. (1)CoCl₂ (0.36 g, 0.72 mmol) was weighed and suspended in 12 mL dry toluene. At room temperature and high stirring speed, LiC_6H_4 -4-Me (0.1480g; assuming 95% purity: 1.44 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° C overnight. The mother liquid was pipetted off, leaving deep purple crystalline

(1)CoC₆H₄-4-Me (0.12 g, 32% yield). The crystal suitable for X-ray diffraction was obtained by layering a toluene solution with pentane at -35°C.

¹H NMR (benzene-*d*₆, 300 MHz): δ 10.36 (t, 1H, *J* 7.4 Hz, Py *H*4), 7.57 (d, 2H, *J* 7.4 Hz, Py *H*3), 7.11 (t, 2H, *J* 7.0 Hz, NAr *Hp*), 7.02 (d, 4H, *J* 7.0 Hz, NAr *Hm*), 6.38 (d, 2H, *J* 6.9 Hz, CoAr *Hm*), 4.68 (d, 2H, *J* 6.9 Hz, CoAr *Ho*), 2.05 (s, 12H, NAr *o*-CH₃), 2.00 (s, 3H, CoAr *p*-CH₃), -1.12 (s, 6H, N=CCH₃).

¹³C NMR (THF-*d*₈, 75 MHz): δ 168.8 (N=CCH₃), 159.5 (Py *C*2), 157.9 (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 *C*3), 124.6 (CoAr *C-m*), 123.8 (CoAr *C-p*), 119.7 (Py *C*4), 24.8 (N=CCH₃), 21.4 (CoAr *p*-CH₃), 20.1 (NAr *o*-CH₃). CoAr *C-i* was not observed, probably due to a large linewidth.

Anal. Calcd for C₃₂H₃₄CoN₃ (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)CoCl₂ (0.40 g, 0.80 mmol) was weighed and suspended in 12 mL toluene. At room temperature and at high stirring speed, LiC_6H_5 (0.90 mL, 1.8 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°C

overnight. The deep purple precipitate was re-dissolved in THF and layered with pentane at -35°C overnight, the mother liquor was pipetted away and the residue dried *in vacuo*, leaving deep purple crystalline (1)CoC₆H₅ (0.075 g, 19%). For unknown reasons, we were not able to obtain satisfactory elemental analysis for this compound.

¹H NMR (benzene-*d*₆, 300 MHz): δ 10.36 (t, 1H, *J* 7.6 Hz, Py *H*4), 7.56 (d, 2H, *J* 7.6 Hz, Py *H*3), 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, 6H, N=CC*H*₃).

¹³C NMR (benzene-*d*₆, 75 MHz): δ167.5 (N=CCH₃), 158.1(Py *C*-2), 156.4(NAr *C*-*i*),
137.7 (br, CoPh *C*-*i*), 131.9 (CoPh *C*-*o*), 129.4 (NAr *C*-*o*), 128.5 (NAr *C*-*m*), 125.4 (NAr *C*-*p*), 123.2 (Py *C*3), 122.3, 121.5 (CoPh *C*-*m* and *C*-*p*), 118.2 (Py *C*4), 23.8 (N=CCH₃),
19.4 (NAr *o*-CH₃).*\

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 mg, 0.68 mmol) was added; after addition of 20 mL dry toluene and violent stirring, all sodium dissolved into mercury within 30 min. (1)CoCl₂ (0.34 g, 0.68 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 301

to -35 °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.

/* ¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 9.49 (t, 1H, *J* 7.7 Hz, Py *H*4), 7.23 (t, 2H, *J* 7.3 Hz, Ar *Hp*), 7.12 (d, 4H, *J* 7.3 Hz, Ar *Hm*), 6.90 (d, 2H, *J* 7.7 Hz, Py *H*3), 2.15 (s, 12H, Ar *Me*), -0.09 (s, 6H, N=C*Me*).

¹³C NMR (25°C, benzene-*d*₆, 75 MHz) δ 166.9 (N=CCH₃), 154.3 (Py *C*2), 152.9 (Ar *C*-*i*), 130.2 (Ar *C*-*o*), 128.5 (Ar *C*-*m*), 126.1 (Ar *C*-*p*), 125.3 (Py *C*3), 115.1 (Py *C*4), 20.2 (N=CCH₃), 19.4 (Ar *o*-CH₃).

Reaction of (1)CoCH₂SiMe₃ with H₂ under nitrogen.

In a dry-box, (1)CoCH₂SiMe₃ (14 mg, 27 μ mol) was weighed and dissolved in around 0.4 mL benzene-*d6* in an NMR tube. Outside of the dry-box, 2 mL H₂ was injected into the tube; the solution turned green within one minute. The ¹H 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 cm⁻¹ indicated the coordination of dinitrogen to the cobalt center.

Reaction of (1)CoCH₂SiMe₃ with H₂ under nitrogen in the presence of Ph₂C₂.

In a dry-box, (1)CoCH₂SiMe₃ (28 mg, 55 μ mol) was weighed and dissolved in around 0.4 mL benzene-*d6* in an NMR tube, and diphenylacetylene (10 mg, 55 μ mol) was added. A ¹H 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 ¹H NMR

spectrum was taken immediately. This (Figure 7.4a) showed partial conversion of (1)CoCH₂SiMe₃ to one new Co(I) complex, tentatively identified as (1)CoC(Ph)=CHPh. After injection of another 2 mL hydrogen gas, the ¹H NMR spectrum (Figure 7.4b) showed mainly (1)CoC(Ph)=CHPh together with a small amount of another new Co(I) complex which could not be identified. After adding around 4 mL hydrogen gas, the sample turned blue. An ¹H NMR spectrum recorded at that time showed (1)CoC(Ph)=CHPh and the unidentified Co(I) complex as the main components. After hydrolysis of the mixture, GC/MS showed PhCH=CHPh and PhCH₂CH₂Ph but no unreacted diphenylacetylene.

(1)CoC(Ph)=CHPh, tentative assignment:

¹H NMR (benzene-*d*6, 300 MHz): δ 10.26 (t, 1H, *J* 7.6, Py *H*4), 7.46 (d, 2H, *J* 7.6, Py *H*3), 7.04-7.12 (br, 5H, =CHPh *H o,m,p*), 6.86 (t, 2H, 7.2, =CCoPh *Hm*), 6.78 and 6.71 (t, 2H, Ar *Hp*), 6.50-6.60 (m, 4H, Ar *Hm*), 5.49 (d, 2H, *J* 7.2, =CCo*Ph Ho*), 3.06 (s, 1H, =C*H*Ph), 2.21 (s, 6H, Ar *Me*), 1.88 (s, 6H, Ar *Me*), -1.08 (s, 6H, N=C*Me*). The =CCo*Ph Hp* resonance could not be unambiguously assigned and may overlap with the residual solvent peak. *\

Reaction of (1)CoCH₂SiMe₃ with PhCCH

In a N₂-filled dry box, (1)CoCH₂SiMe₃ (0.010g, 0.019mmol) 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 mL, 0.91 mmol), it turned purple immediately. After evaporating all solvent, the residue was dissolved in dry toluene and layered with pentane 303

at -35°C. After overnight, a dark snow-flake shaped solid precipitated out. The yield is not determined. The ¹H NMR spectrum is shown in Figure D.4 in the Appendix D. (1)CoC(Ph)=CHCCPh, tentative assignment:

¹H NMR (benzene-*d*6, 300 MHz): δ 10.15 (t, 1H, *J* 7.5, Py *H*4), 7.36 (d, 2H, *J* 7.5, Py *H*3), 6.91 (d, 2H, *J* 7.3), 6.70-6.78 (m, 4H), 6.58 (t, 2H, *J* 7.3), 6.16 (m, 2H), 5.47 (d, 2H, *J* 7.4, =CCo*Ph Ho*), 4.28 (1H, s, =C(*H*)), 2.85 (s, 6H, Ar *Me*), 1.58 (s, 6H, Ar *Me*), -0.76 (s, 6H, N=C*Me*). The CCPh peaks might be overlapped with benzene residue peaks.

Reaction of (1)CoCH₂SiMe₃ with H₂ under nitrogen in the presence of 4chlorophenylnitrile.

In a N₂ filled dry-box, (1)CoCH₂SiMe₃ (0.1031g, 0.20 mmol) was weighed in a small vial, followed by adding 4-chlorophenylnitrile (0.0278g, 0.20 mmol). 3 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 mL H₂ 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 mL Et₂O was added to dissolve it and cooled to -35 °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.

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 9.62 (s, 1H, N=C*H*), 7.92 (t, 1H, *J* 7.7, Py *H4*), 7.63 (d, 2H, *J* 7.7, Py *H3*), 7.01 (d, 2H, *J* 8.3, N=C*Ar H3*), 6.78-6.84 (br, 6H, N-Ar *m,p*), 6.77 (d, 2H, *J* 8.3, N=C*Ar H2*), 2.04 (s, 12H, NAr *Me*), 1.09 (s, 6H, N=C*Me*).

¹³C NMR (25 °C, benzene-*d*6, 75 MHz): δ: 156.7 (Py *C*-2), 152.0 (NAr *C*-*i*), 148.6 (br, CoN=*C*), 147.5 (N=CAr C-*o*), 138.7 (NAr *C*-*o*), 132.9 (CoN=CAr C-*p*), 130.0 (N=CAr C-*m*), 127.6 (N=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 (Py *C*4), 18.7 (N-Ar *o*-*C*H₃), 17.1 (N=CCH₃). N=CCH₃ was not observed, probably due to the low intensity.

Reaction of (4)Co(N₂) with 4-CF₃C₆H₄Cl.

In a N₂-filled dry-box, (4)Co(N₂) (11.8 mg, 20 μ mol) was weighed and dissolved in about 0.4 mL dry benzene-*d*6, and 4-CF₃C₆H₄Cl (2.45 μ L, 19.6 μ mol) was added. The mixture turned gray-blue. The immediately recorded ¹H NMR spectrum showed that the reaction was not complete (still (4)Co(N₂) visible) and three diamagnetic cobalt(I) complexes could be clearly observed: (4)CoH : (4)CoAr : (4)CoCl = 0.11 : 0.14 :1.00. After 4 h, the ¹H NMR spectrum showed that there was no (4)Co(N₂) left and the reaction was complete, with a product ratio (4)CoH : (4)CoAr : (4)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:

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 10.27 (1H, t, *J* 7.6 Hz, Py *H*4), 5.14 (2H, d, *J* 7.1Hz, CoAr *H*2), -0.65 (6H, s, C*H*₃C=N).

¹⁹F NMR (25°C, benzene-*d*₆, 282 MHz): δ -61.2.

Reaction of (1)CoCH₂SiMe₃ with CH₃I.

In a dry-box, (1)CoCH₂SiMe₃ (37.5 mg, 72 µmol) was dissolved in benzene-*d*6, followed by injecting 8 µL CH₃I (130 µmol, 1.8 eq.). The mixture immediately turned pink. ¹H 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 ¹H 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 ¹H NMR spectrum obtained in this way (Figure 7.9) had reasonable linewidths and showed a new quartet at δ 0.45 ppm (*J* 8.0 Hz). GC/MS analysis of this NMR sample clearly showed that EtSiMe₃ was the main compound and the ¹H-²⁹Si 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)Co(N₂) with aryl halides.

Procedure A: In a dry-box, (1)CoCH₂SiMe₃ (14 mg, 27 mmol) was weighed and dissolved in around 0.4 mL benzene- d_6 in an NMR tube. Outside of the dry-box, 2 mL H₂ 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 ¹H NMR (and ¹⁹F NMR 306

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 ¹H 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)CoCH₂SiMe₃ (14 mg, 27 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)CoCH₂SiMe₃ had disappeared according to the ¹H 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 (1)CoN₂ 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)Co(N₂) was made by hydrogenation of (1)CoCH₂SiMe₃ (0.0140g, 27 μ mol) and diphenyl carbonate (0.030, 14 μ mol) was added. Immediate ¹H NMR showed that there is no reaction happening. After two weeks, it turned pink and the ¹H NMR showed that only (1)Co(OPh) was present; no other cobalt(I) alkyl complex was observed.

(1)Co(OPh), partial tentative assignment:

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 9.11 (1H, t, *J* 7.3, Py *H*4), 6.71 (2H, t, *J* 7.2Hz, CoOPh *m*), 6.47 (1H, t, *J* 7.2, CoOPh *p*), 5.68 (2H, d, *J* 7.4, CoOPh *o*), 2.13 (12H, s, NAr *Me*), 0.05 (6H, s, C*H*₃C=N).

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 μ L, 14 μ mol). It takes three weeks for the sample to turn purple and only one complex ((1)CoOEt) can be identified from ¹H NMR.

Reaction of $(1)CoCH_2SiMe_3$ with PhOCOPh under H_2 gas

In a dry box, (1)CoCH₂SiMe₃ (0.0140g, 27 μ mol) and diphenyl carbonate (0.030, 14 μ mol) was dissolved in 0.4 benzene- d_6 and transferred into a NMR tube. After injection of 1.0 mL H₂ and violent shaking, ¹H NMR spectrum showed that there were two triplet 308

peaks (9.2 ppm and 8.8 ppm indicates cobalt(I) complexes) and some (1)CoN₂. The further addition of H₂ gas leads to near disappearance of the peak at 8.8 ppm.

Tentative assignment of the other complex at 8.8 ppm:

¹H NMR (25°C, benzene-*d*₆, 300 MHz): δ 8.80 (1H, t, *J* 7.3, Py *H*4), 7.41 (2H, d, *J* 7.4, Py *H*3), 3.82 (3H, s), 2.12 (12H, s, NAr *Me*), 0.16 (6H, s, C*H*₃C=N).

X-ray diffraction Determinants (see Table 9.5)

(1)CoC₆H₄-4-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 α radiation (0.71073 Å). 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 SHELXL97¹⁰⁵ (full-matrix least-squares refinement on F²); hydrogen atoms were placed at calculated positions and refined in riding mode. The structure was checked for solvent-accessible voids with PLATON.¹⁰⁶

(1)CoN=C(H)C₆H₄-Cl-4. A deep purple fragment (approximately 0.20*0.20*0.25 mm) broken from a large crystal cluster was mounted in a thin glass capillary. Data were 309 collected at 293 K in a Bruker 4-circle diffractometer with APEX detector using Mo-K α radiation (0.71073 Å). A sphere of data was collected with 0.2° 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 SHELXL97¹⁰⁵ (full-matrix least-squares refinement on F²); hydrogen atoms were placed at calculated positions and refined in riding mode. The structure was checked for solvent-accessible voids with PLATON.¹⁰⁶

	$(1)CoC_6H_4-4-Me$	(1)CoNCHC ₆ H ₄ -4-Cl
Formula	C ₃₂ H ₃₄ CoN ₃	C ₃₂ H ₃₂ ClCoN ₄
Mol wt	519.55	5677.00
Crystal system	Triclinic	Orthorhombic
Space group	P-1	P212121
<i>a</i> / Å	8.3015(4)	10.9905(8)
<i>b</i> / Å	10.6604(6)	14.5602(11)
<i>c</i> / Å	15.9805(9)	18.7056(15)
α/ deg	91.7982(10)	90
β/ deg	93.3207(14)	90
γ/ deg	103.7817(14)	90

Table 9.5. Details of crystal structure determination

	(1)CoC ₆ H ₄ -4-Me	(1)CoNCHC ₆ H ₄ -4-Cl
$V/\text{\AA}^3$	1369.72(13)	2993.3(4)
Ζ	2	4
$D_{\rm c}$ / g cm ⁻³	1.260	1.258
abs coef / mm ⁻¹	0.651	0.689
F ₀₀₀	548	1184
index ranges	$\begin{array}{l} -10 \leq h \leq 10 \\ -12 \leq k \leq 12 \end{array}$	$-13 \le h \le 13$ $-17 \le k \le 17$
$2\theta_{max}$ / deg	51	51
# rflctns	10154	19632
# unique	5096	5568
$\# > 2\sigma$	3961	3614
GOF	0.948	0.923
# parameters	345	349
$R (Fo > 4 \sigma(F))$	0.0556	0.0523
<i>R</i> (all data)	0.0738	0.0784
wR2 (all data)	0.1456	0.1443
largest peak, hole / $e \text{ Å}^{-3}$	0.472, -0.201	0.421, -0.350

Computational details

All geometries were optimized with Turbomole²³¹ using the TZVP basis set, the b3-lyp²²⁹ 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 Co(I) complexes preferred a broken-symmetry 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 K, 1 bar) using the standard formulae of statistical thermodynamics. Improved single-point energies were obtained using the TZVPP²³⁴ basis set at TZVP geometries, and combined with TZVP-level thermal corrections to generate the final free energies.

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 Spek, A.L.; Van Koten, G. *Organometallics* 1994, *13*, 2602. b) Nienkemper,
 K.; Kehr, G.; Kehr, S.; Fröhlich, R.; Erke, G. J. Organomet. Chem. 2008, 693, 1572.
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 2009, 42, 1995. b) Dempsey, J.L.; Winkler, J.R.; J.R.; Gray, H.B. J Am. Chem.

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Soc. 2010, 132, 1060. c) Dempsey, J.L.; Winkler, J.R.; J.R.; Gray, H.B. J Am. Chem. Soc. 2010, 132, 16774.

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Appendix

Appendix A: For Chapter 3

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

Reference	Refcodes
Small, B.L.; Carney, M.J.; Holman, D.M.; O'Rourke, C.E.; Halfen, J.A. <i>Macromolecules</i> 2004, <i>37</i> , 4375	JAPLUI
Vidyaratne, I.; Scott, J.; Gambarotta, S.; Duchateau, R. Organometallics 2007, 26, 3201	PIKGUM
Reardon, D.; Aharonian, G.; Gambarotta, S.; Yap, G.P.A. Organometallics 2002, 21, 786	ADOROA
Morale, F.; Date, R.W.; Guillon, D.; Bruce, D.W.; Finn, R.L.; Wilson, C.; Blake, A.J.; Schroder, M.; Donnio, B. <i>Chem. Eur. J.</i> 2003, 9, 2484	AHUQAV AHUPUO AHUPOI AHUQEZ
Gibson, V.C.; McTavish, S.; Redshaw, C.; Solan, G.A.; White, A.J.P.; Williams, D.J. <i>Dalton Trans.</i> 2003, 221	HURHOR HURHUX
Edwards, D.A.; Mahon, M.F.; Martin, W.R.; Molloy, K.C.; Fanwick, P.E.; Walton, R.A. J. Chem. Soc. Dalton Trans. 1990, 3161	JEXTUB JEXVAJ
Ren, CX.; Li, SY.; Yin, ZZ.; Lu, X.; Ding, YQ. Acta Crystallogr. Sect. E: Struct. Rep. Online 2009, 65, m572	LOSBIF
Guo, MP.; Guo, GQ.; Guo, HR.; Zhong, DC.; Zhou, WQ. Acta Crystallogr. Sect. E: Struct. Rep. Online 2007, 63, m3025	MIRBAR
Nakajima, K.; Kojima, M. Bull. Chem. Soc. Jpn. 1993, 66, 2109	PIGKAR
Li, JP.; Zhao, JS. Acta Crystallogr. Sect. E: Struct. Rep. Online 2006, 62, m810	REHDAK

Reference	Refcodes
Li, J.; Zhao, J. Struct. Chem. 2006, 17, 617	REHDAK01 QETSUE
Wang, S.; Zhu, Y.; Zhang, F.; Wang, Q.; Wang, L. <i>Polyhedron</i> 1992, <i>11</i> , 1909	VURZIR
Smit, T.M.; Tomov, A.K.; Gibson, V.C.; White, A.J.P.; Williams, D.J. <i>Inorg. Chem.</i> 2004, <i>43</i> , 6511	ACATII ACATEE
Campora, J.; Naz, A.M.; Palma, P.; Rodriguez-Delgado, A.; Alvarez, E.; Tritto, I.; Boggioni, L. <i>Eur. J. Inorg. Chem.</i> 2007, 1871	COBHOR COBHIL
Chen, Y.; Qian, C.; Sun, J. Organometallics 2003, 22, 1231	EKINAN EKINER
Chen, Y.; Chen, R.; Qian, C.; Dong, X.; Sun, J. Organometallics 2003, 22, 4312	EMEJEL EMEHOT EMEHUZ EMEJAH
Tellman, K.P.; Gibson, V.C.; White, A.J.P.; Williams, D.J. Organometallics 2005, 24, 280	FEQLUJ FEQLET FEQLOD FEQMAQ FEQLIX FERRIE
Liu, JY.; Zheng, Y.; Li, YG.; Pan, L.; Li, YS.; Hu, NH. J. Organomet. Chem. 2005, 690, 1233	GATNOF
Pelascini, F.; Wesolek, M.; Peruch, F.; Lutz, P.J. <i>Eur. J. Inorg. Chem.</i> 2006, 4309	GEQYAD GEQYEH
Sun, WH.; Hao, P.; Zhang, S.; Shi, Q.; Zuo, W.; Tang, X.; Lu, X. Organometallics 2007, 26, 2720	GIGHUA GIGHOU GIGJAI GIGHIO GIGJEM
Britovsek, G.J.P.; Bruce, M.; Gibson, V.C.; Kimberley, B.S.; Maddox, P.J.; Mastoianni, S.; McTavish, S.J.; Redshaw, C.; Solan, G.A.; Stromberg, S.; White, A.J.P.; Williams, D.J. <i>J. Am. Chem. Soc.</i>	PUGWIX02 GUCXIL GUCXUX

Reference	Refcodes
1999, 121, 8728	GUCXOR
Ionkin, A.S.; Marshall, W.J.; Adelman, D.J.; Fones, B.B.; Fish, B.M.; Schiffhauer, M.F.; Soper, P.D.; Waterland, R.L.; Spence, R.E.; Xie, T. J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 585	HOBPEU HOBQAR HOBQOF HOBQUL HOBQIZ QELJUN04 HOBPIY HOBPOE HOBQEV
Ionkin, A.S.; Marshall, W.J.; Adelman, D.J.; Fones, B.B.; Fish, B.M.; Schiffhauer, M.F. <i>Organometallics</i> 2008, <i>27</i> , 1902	JIYQIS JIYRAL QELJUN02 JIYQEO JIYQOY JIYQUE
Ionkin, A.S.; Marshall, W.J.; Adelman, D.J.; Fones, B.B.; Fish, B.M.; Schiffhauer, M.F.; Spence, R.E.; Xie, T. <i>Organometallics</i> 2008, <i>27</i> , 1147	JIZTUI QELJUN03 JIZTIW JIZTOC
Chen, Y.; Hao, P.; Zuo, W.; Gao, K.; Sun, WH. J. Organomet. Chem. 2008, 693, 1829	KIZZOJ KOBBEJ KIZZID KIZZUP KOBBAF
Wallenhorst, C.; Kehr, G.; Luftmann, H.; Frohlich, R.; Erker, G. Organometallics 2008, 27, 6547	LOPSUF LOPSEP LOPTAM LOPSOZ LOPSIT LOPTEQ
Britovsek, C.J.P.; Mastroianni, S.; Solan, G.A.; Baugh, S.P.D.; Redshaw, C.; Gibson, V.C.; White, A.J.P.; Williams, D.J.; Elsegood, M.R.J. <i>Chem. Eur. J.</i> 2000, <i>6</i> , 2221	MAZWEP MAZWOZ MAZWIT
Gibson, V.C.; Long, N.J.; Oxford, P.J.; White, A.J.P.; Williams, D.J.	NIGHOB

Reference	Refcodes
Organometallics 2006, 25, 1932	NIGHUH
Britovsek, G.J.P.; Gibson, V.C.; Kimberley, B.S.; Mastroianni, S.; Redshaw, C.; Solan, G.A.; White, A.J.P.; Williams, D.J. <i>J. Chem.</i> <i>Soc. Dalton Trans.</i> 2001, 1639	OBIGAH OBIGEL OBIFOU OBIFUA
Amort, C.; Malaun, M.; Krajete, A.; Kopacka, H.; Wurst, K.; Christ, M.; Lilge, D.; Kristen, M.O.; Bildstein, B. <i>Appl. Organomet. Chem.</i> 2002, <i>16</i> , 506	OGODIX
Kleigrewe, N.; Steffen, W.; Blomker, T.; Kehr, G.; Frohlich, R.; Wibbeling, B.; Erker, G.; Wasilke, JC.; Wu, G.; Bazan, G.C. <i>J. Am.</i> <i>Chem. Soc.</i> 2005, <i>127</i> , 13955	PAYTEP PAYSOY
Small, B.L.; Brookhart, M.; Bennett, A.M.A. J. Am. Chem. Soc. 1998, 120, 4049	PUGWIX PUGWET
Britovsek, G.J.P.; Gibson, V.C.; Kimberley, B.S.; Maddox, P.J.; McTavish, S.J.; Solan, G.A.; White, A.J.P.; Williams, D.J. <i>Chem.</i> <i>Commun.</i> 1998, 849	PUGWIX01
Ionkin, A.S.; Marshall, W.J.; Adelman, D.J.; Fones, B.B.; Fish, B.M.; Schiffhauer, M.F. <i>Organometallics</i> 2006, <i>25</i> , 2978	QELJOH QELJAT QELJIB QELJUN
Ionkin, A.S.; Marshall, W.J.; Adelman, D.J.; Shoe, A.L.; Spence, R.E.; Xie, T. J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 2615	VIFQEH VIFPUW QELJUN01 VIFQAD VIFPIK
Kaul, F.A.R.; Puchta, G.T.; Frey, G.D.; Herdtweck, E.; Herrmann, W.A. Organometallics 2007, 26, 988	VIBSOP
McTavish, S.; Britovsek, G.J.P.; Smit, T.M.; Gibson, V.C.; White, A.J.P.; Williams, D.J. J. Mol. Catal. A: Chem. 2007, 261, 293	VIFNAA VIFMON VIFMUT
Al-Benna, S.; Sarsfield, M.J.; Thornton-Pett, M.; Ormsby, D.L.; Maddox, P.J.; Bres, P.; Bochmann, M. J. Chem. Soc. Dalton Trans.	XEBDIR

Reference	Refcodes
2000, 4247	
Li, XG.; Zhong, DC.; He, R.; Guo, HR. Acta Crystallogr. Sect. E: Struct. Rep. Online 2008, 64, m786	BIZRAE
Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Zanobini, F.; Laschi, F.; Sommazzi, A. <i>Eur. J. Inorg. Chem.</i> 2003, 1620	JADMEH
Kooistra, T.M.; Hekking, K.F.W.; Knijnenburg, Q.; de Bruin, B.; Budzelaar, P.H.M.; de Gelder, R.; Smits, J.M.M.; Gal, A.W. <i>Eur. J.</i> <i>Inorg. Chem.</i> 2003, 648	LUXGUG
Davis, R.N.; Tanski, J.M.; Adrian Junior, J.C.; Tyler, L.A. Inorg. Chim. Acta 2007, 360, 3061	MIFCIO MIFCEK MIFCOU
Ozdemir, N.; Dincer, M.; Dayan, O.; Cetinkaya, B. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 2006, 62, m398	PELTUW
Dong, G.; Matthews, J.P.; Craig, D.C.; Baker, A.T. Inorg. Chim. Acta 1999, 284, 266	QINSUB QINSOV
Chen, J.; Huang, Y.; Li, Z.; Zhang, Z.; Wei, C.; Lan, T.; Zhang, W. J. Mol. Catal. A: Chem. 2006, 259, 133	RESLAD
Suhr, D.; Lotsher, D.; Stoeckli-Evans, H.; von Zelewsky, A. Inorg. Chim. Acta 2002, 341, 17	UKIVOZ
Barbaro, P.; Bianchini, C.; Giambastiani, G.; Rios, I.G.; Meli, A.; Oberhauser, W.; Segarra, A.M.; Sorace, L.; Toti, A. <i>Organometallics</i> 2007, <i>26</i> , 4639	VIKWES
Lappalainen, K.; Yliheikkila, K.; Abu-Surrah, A.S.; Polamo, M.; Leskela, M.; Repo, T. Z. Anorg. Allg. Chem. 2005, 631, 763	YAKRAE
Gao, R.; Zhang, M.; Liang, T.; Wang, F.; Sun, WH. Organometallics 2008, 27, 5641	BOKZEH BOKZIL
Fan, RQ.; Zhu, DS.; Mu, Y.; Li, GH.; Su, Q.; Ni, JG.; Feng, SH. Chem. Res. Chin. Univ. 2005, 21, 496	ECORIY ECOROE
Hao, P.; Zhang, S.; Sun, WH.; Shi, Q.; Adewuyi, S.; Lu, X.; Li, P. <i>Organometallics</i> 2007, <i>26</i> , 2439	GIFGIM GIFGEI

Reference	Refcodes
	GIFGAE
Baldovino-Pantaleon, O.; Hernandez-Ortega, S.; Morales-Morales, D. <i>Inorg. Chem. Commun.</i> 2005, <i>8</i> , 955	KAVVEJ
Suzuki, H.; Matsumura, S.; Satoh, Y.; Sogoh, K.; Yasuda, H. React. Funct. Polym. 2004, 58, 77	KECFOO KECFII
Baldovino-Pantaleon, O.; Hernandez-Ortega, S.; Morales-Morales, D. Adv. Synth. Catal. 2006, 348, 236	PEDGUB PEDGOV
Fan, RQ.; Fan, RJ.; Lv, ZW.; Yang, YL.; An, F.; Gu, DM. J. Coord. Chem. 2007, 60, 919	SIGCOB
Nicholson, G.A.; Petersen, J.L.; McCormick, B.J. Inorg. Chem. 1982, 21, 3274	BOBHEF BOBHAB
Ozdemir, N.; Dincer, M.; Dayan, O.; Cetinkaya, B. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 2006, 62, m315	CELGUW
Andjelkovic, K.; Tellgren, R.; Niketic, S.R.; Sladic, D.; Poleti, D. J. Chem. Cryst. 1999, 29, 575	DIQJAO
Katayama, T.; Ishida, T.; Nogami, T. Inorg. Chim. Acta 2002, 329, 31	FAGWEQ
Belicchi, M.F.; Fava, G.G.; Pelizzi, C. Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. 1981, 37, 924	IOHZCU
Abboud, K.A.; Palenik, R.C.; Palenik, G.J. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 1994, 50, 525	LEKDOU
Ozdemir, N.; Dincer, M.; Dayan, O.; Cetinkaya, B. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 2008, 64, m224	LOCGAM
Gamez, P.; Steensma, R.H.; Driessen, W.L.; Reedijk, J. Inorg. Chim. Acta 2002, 333, 51	MOLVIS MOLVEO
Trivedi, M.; Pandey, D.S.; Xu, Q. Inorg. Chim. Acta 2007, 360, 2492	QEZJIP
Bernardinelli, G.; Hopfgartner, G.; Williams, A.F. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 1990, 46, 1642	SICPUP

Reference	Refcodes
Balamurugan, R.; Palaniandavar, M.; Halcrow, M.A. <i>Polyhedron</i> 2006, <i>25</i> , 1077	TEHZEM
Li, X.; Zhu, D.; Gao, W.; Zhang, Y.; Mu, Y. J. Chem. Res. 2006, 371	BOMRAX
Oshio, H.; Yamamoto, M.; Ito, T.; Kawauchi, H.; Koga, N.; Ikoma, T.; Tero-Kubota, S. <i>Inorg. Chem.</i> 2001, <i>40</i> , 5518	ECIJEF
Oshio, H.; Yamamoto, M.; Kawauchi, H.; Koga, N.; Ito, T. J. Solid State Chem. 2001, 159, 455	ECIJEF01
Folmer-Andersen, J.F.; Lynch, V.M.; Anslyn, E.V. Chem. Eur. J. 2005, 11, 5319	HAWDOZ
Vance, A.L.; Alcock, N.W.; Heppert, J.A.; Busch, D.H. Inorg. Chem. 1998, 37, 6912	HEFQIS
Drew, M.G.B.; Hollis, S. J. Chem. Soc. Dalton Trans. 1978, 511	IMTPZN10
Fan, R.; Zhu, D.; Ding, H.; Mu, Y.; Su, Q.; Xia, H. Synth. Met. 2005, 149, 135	KALLIT KALLEP
Chen, TR. Acta Crystallogr. Sect. E: Struct. Rep. Online 2004, 60, m1544	MAHWIC
Liu, SG.; Zuo, JL.; Wang, Y.; Li, YZ.; You, XZ. J. Phys. Chem. Solids 2005, 66, 735	MAHWIC01
Panosyan, F.B.; Lough, A.J.; Chin, J. Acta Crystallogr. Sect. E: Struct. Rep. Online 2003, 59, m864	OLOLEG
Jiang, M.; Dalgarno, S.; Kilner, C.A.; Halcrow, M.A.; Kee, T.P. Polyhedron 2001, 20, 2151	QUPVEC
Zhao, B.; Shu, HM.; Hu, HM.; Qin, T.; Chen, XL. J. Coord. Chem. 2009, 62, 1025	FOPSEJ
Tondreau, A.M.; Lobkovsky, E.; Chirik, P.J. Org. Lett. 2008, 10, 2789	AFUTEB
Campora, J.; Naz, A.M.; Palma, P.; Alvarez, E.; Reyes, M.L. Organometallics 2005, 24, 4878	DAWKES

Pafaranca	Refeader	
Kelefellee	Refeores	
Bouwkamp, M.W.: Bart, S.C.: Hawrelak, E.J.: Trovitch, R.J.:	LAOJAP	
	C.	
Lobkovsky, E.: Chirik, P.J. Chem. Commun. 2005, 3406.		
Formandaz I: Trovitab P I: Labkovsky F: Chirik P I		
remanuez, I., Hovnen, R.J., Lookovsky, E., Chink, F.J.		
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Organometatiles 2008 27, 109		



Refcode	912	913	914	915	923	924	925	934	935	945
(DIP)CrCl ₂ co	mplexe	es								
JAPLUI	76.1	98.1	102.1	148.5	104.1	155.9	75.6	99.9	102.0	98.1
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 co	mplexe	es								
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	912	913	914	915	923	924	925	934	935	945
FEQLUJ	73.0	98.0	105.5	141.0	91.6	159.7	72.6	108.6	100.8	100.4
FEQMAQ	73.0	96.5	103.2	142.0	98.4	155.9	71.8	105.6	102.3	102.9
GATNOF	72.7	99.6	98.4	145.8	124.3	124.4	73.2	111.3	100.2	99.9
GEQYAD	73.7	100.0	100.8	139.2	89.3	151.1	72.9	119.5	102.5	97.2
GEQYEH	73.2	102.0	102.2	142.8	95.1	155.4	72.9	109.5	95.9	102.1
GEQYEH	73.7	97.9	103.2	144.5	91.8	153.4	73.0	114.7	95.1	101.0
GIGHIO	72.2	101.2	99.6	145.2	115.7	133.0	74.0	111.3	100.3	97.6
GIGHOU	71.6	102.8	95.8	142.4	97.9	147.6	74.2	114.2	97.0	104.9
GUCXIL	72.7	102.4	97.8	145.5	118.9	131.2	73.0	109.8	96.7	102.3
GUCXOR	72.8	102.5	98.2	145.4	118.6	132.3	72.8	109.1	97.0	102.0
HOBPEU	72.9	101.9	101.5	145.0	120.1	127.1	72.2	112.6	97.8	97.1
HOBPEU	72.2	103.0	101.9	146.1	118.3	132.1	73.8	109.4	93.7	100.0
HOBPIY	73.6	101.4	100.9	147.3	105.3	135.5	73.9	118.9	90.5	99.5
HOBPOE	73.1	98.9	103.0	146.7	115.8	127.9	73.5	116.1	95.1	97.6
HOBQAR	73.7	94.3	102.4	147.5	121.1	121.1	73.7	117.8	102.4	94.3
HOBQEV	73.5	98.9	103.8	145.7	110.7	134.9	72.5	114.1	96.6	97.3
HOBQIZ	73.2	100.2	104.7	147.1	107.4	133.8	74.0	118.2	92.1	95.9
HOBQOF	73.5	100.2	103.8	146.1	114.9	130.1	72.6	114.5	95.8	96.3
HOBQUL	73.4	98.8	103.3	146.0	109.6	136.6	72.9	113.6	96.7	97.8
JIYQEO	72.9	96.1	102.0	145.8	120.5	126.1	73.0	113.4	98.3	100.4
JIYQIS	73.5	102.7	101.1	145.8	121.8	126.3	72.4	111.6	94.9	99.2
JIYQOY	73.4	100.5	100.3	145.8	121.8	126.5	72.5	111.6	99.3	97.9
JIYQOY	73.3	97.6	99.9	147.5	115.5	126.7	74.2	117.8	97.2	98.4
JIYQUE	73.4	101.1	102.5	146.0	117.6	132.0	72.7	110.1	96.0	98.7
JIYRAL	72.4	99.3	102.9	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	912	913	914	915	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	142.3	91.1	150.7	73.1	118.2	97.0	100.3
PUGWIX	73.7	100.6	98.2	140.3	94.5	147.9	72.6	117.5	102.5	99.3
PUGWIX01	73.2	100.7	98.6	140.1	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)FeCl ₂ (a)	71.8	94.8	96.8	146.6	88.4	157.1	79.7	112.8	101.6	103.1
(8)FeCl ₂ (b)	80.7	100.3	103.8	148.0	91.7	151.9	72.1	114.2	97.2	93.0
(10)FeCl ₂	73.3	93.1	95.2	154.3	98.3	137.7	81.9	123.3	97.2	98.6

Refcode	912	913	914	915	923	924	925	934	935	945
(9)FeCl ₂	73.9	93.5	95.7	149.1	94.9	154.2	81.4	109.4	107.1	98.7
(7)FeCl ₂	72.8	101.7	100.2	145.2	116.4	136.0	72.9	107.6	98.4	100.4
(DIP)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	912	913	914	915	923	924	925	934	935	945
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
$(3)CoCl_2$	76.4	95.2	97.4	151.5	120.5	124.4	75.1	115.0	99.6	98.2
$(7)CoCl_2$	74.8	97.5	98.5	149.2	109.4	136.5	75.3	114.0	99.2	98.0
$(10)CoCl_2$	84.9	99.2	98.0	157.1	101.0	135.0	73.4	122.5	92.3	92.3
(DIP)NiCl ₂ co	mplexe	es								
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
$(DIP)CuCl_2 co$	mplex	es								
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	912	913	914	915	923	924	925	934	935	945
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)ZnCl ₂ c	omplex	es								
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	912	913	914	915	923	924	925	934	935	945
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(CH ₂ S	SiMe ₃) ₂	comple	exes							
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 anal	ysis		ω analysis	alysis			
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å)		
(DIP)CrCl ₂ com	plexes							
JAPLUI	0.772	0.451	SP	0.57	SP	0.33		
PIKGUM	0.891	0.393	SP	0.75	SP	0.42		
(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 ana	lysis		ω analys	sis	
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å)
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)FeCl ₂ co	omplexes					
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			ω analysis		
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å)
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			ω analysis	S		
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å)	
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)FeCl ₂ (a)	0.873	0.541	SP	0.76	SP	0.42	
(8)FeCl ₂ (b)	0.771	0.616	SP	0.67	SP	0.41	
(10)FeCl ₂	0.521	0.847	TBP	0.44	TBP	0.17	
(9)FeCl ₂	0.792	0.565	SP	0.66	SP	0.44	
(7)FeCl ₂	0.367	0.782	TBP	0.22	TBP	0.16	
(DIP)CoCl ₂ com	plexes						
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	

Refcode FAA analysis				<i>ω</i> analysis			
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å	
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	
$(3)CoCl_2$	0.137	0.991	TBP	0.04	TBP	0.01	
$(7)CoCl_2$	0.359	0.777	TBP	0.30	TBP	0.20	
(10)CoCl ₂	0.487	0.907	TBP	0.38	TBP	0.18	
(DIP)NiCl ₂ cc	omplexes						
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	

Refcode	FAA anal	lysis		ω analysi	S	
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å)
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
$(DIP)CuCl_2 con$	nplexes					
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 anal	ysis		ω analysis			
	σ(TBP)	σ(SP)	assign	ω	assign	M dev (Å)	
TEHZEM	0.884	0.425	SP	0.74	SP	0.40	
(DIP)ZnCl ₂ com	plexes						
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(CH ₂ SiN	$(1e_3)_2$						
LAQJAP	0.464	0.730	ТВР	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)FeR ₂	0.046	1.052	TBP	0.02	TBP	0.00	
(15)FeR ₂	0.070	1.006	TBP	0.05	TBP	0.05	



Figure A.1. Correlation between ω and out-of-plane deviation of the metal center for X-ray structure of (DIP)MX₂ 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 ω 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):
    c = atom.connections
    if len(c) == n1 and c.element_count(e2) == n2:
        yield atom, c
```

Given preordered metal center and its five connected atoms # the smallest distortion vector from ideal TBP was calculated by pertuting the labelling of the atoms

#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

=[[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] ,[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 = (s,a,change)
```

```
return best
```

```
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, 'N', 3):

mlist = []	#create a list that store chemically reasonable numbering
mlistN = []	#to store three nitrogen
mlistX = []	#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):
         mlist = [mlistN[0], mlistN[2]] + [mlistX[0]] + [mlistX[1]] + [mlistN[1]]
       else:
         mlist = [mlistN[0], mlistN[2]] + [mlistX[1]] + [mlistX[0]] + [mlistN[1]]
    elif angleMax == angle13:
       if angle(metal.coord, mlistX[0].coord, mlistN[1].coord) < angle(metal.coord,
mlistX[1].coord, mlistN[1].coord):
         mlist = [mlistN[0], mlistN[1]] + [mlistX[0]] + [mlistX[1]] + [mlistN[2]]
       else:
         mlist = [mlistN[0], mlistN[1]] + [mlistX[1]] + [mlistX[0]] + [mlistN[2]]
    else:
       if angle(metal.coord, mlistX[0].coord, mlistN[0].coord) < angle(metal.coord,
mlistX[1].coord, mlistN[0].coord):
         mlist = [mlistN[1],mlistN[0]] + [mlistX[0]] + [mlistX[1]] + [mlistN[2]]
       else:
         mlist = [mlistN[1],mlistN[0]] + [mlistX[1]] + [mlistX[0]] + [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"</pre>
```

#calculate the vector that is perpendicular to the N3 plane defined by three nitrogens norm_N = cross(mlist[1].coord, mlist[0].coord, mlist[4].coord)

```
#calculate all the angles around metal centers
angle 12 = degrees(angle(metal.coord, mlist[0].coord, mlist[1].coord))
angle 13 = 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 = [mlistX[0]] + mlistN + [mlistX[1]]
atoms = mlist2
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__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" ):
```

```
self.name = name
self.connections = {}
def __setitem__(self, key, value):
    al = 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 SERIAL = 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 )
    z = get field (SLICE ATOM Z, record )
    e = get field(SLICE ATOM ELEMENT, record)
    c = coordT(float(x), float(y), float(z))
    if e == None :
       i = 0
       while i < len(1) and l[i].isalpha(): i \neq 1
       e = 1[0:i]
    a = atom(a_id = aid,
          label = l.
          coord = c,
          element = 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.moleculea0 = 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( p0, p1, p2 ):
    """ Angle between vectors p0 -> p1 and p0 -> p2 """
    u = vector(p0,p1)
    v = vector(p0,p2)
    return acos(dot(u,v)/(length(u)*length(v)))
```

```
def length(v):
    """ Length of vector """
    return sqrt(dot(v,v))
```

```
def dot(v0, v1):
    """ 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 cross(p0, p1, p2):
    """generate the vectors"""
    u = vector(p0,p1)
    v = vector(p0,p2)
    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):
  a1 = dot(v1,v2)
  a2 = length(v2)
  if a_{2} = 0:
     p = a1 / a2
  else<sup>.</sup>
     p = 1000
  return sqrt(p * 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"""
  d12 = angle(p[0],p[1],p[2]) - radians(A ideal)
  d13 = angle(p[0],p[1],p[3]) - radians(B ideal)
  d14 = angle(p[0],p[1],p[4]) - radians(B ideal)
  d15 = angle(p[0],p[1],p[5]) - radians(2 * A ideal)
  d23 = angle(p[0], p[2], p[3]) - radians(120)
  d24 = angle(p[0],p[2],p[4]) - radians(120)
  d25 = angle(p[0],p[2],p[5]) - radians(A ideal)
  d34 = angle(p[0],p[3],p[4]) - radians(120)
  d35 = angle(p[0],p[3],p[5]) - radians(B ideal)
  d45 = angle(p[0],p[4],p[5]) - radians(B ideal)
  ""Get trigonal bipyramidal displacement vector given 7 co-ordinates"""
  s4 = sub(sum([d12,d13,d14]),sum([d25,d35,d45])) / sqrt(6)
  s6a = (2 * d24 - d34 - d23) / sqrt(6)
  s6b = (d34 - d23) / sqrt(2)
  s7a = (2 * d13 - d12 - d14 + 2 * d35 - d25 - d45) / sqrt(12)
```

```
s7b = (d12 - d14 + d25 - d45) / 2
```

s8a = (2 * d13 - d12 - d14 - 2 * d35 + d25 + d45) / sqrt(12)s8b = (d12 - d14 - d25 + d45) / 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"""

d12 = angle(p[0],p[1],p[2]) - radians(A_ideal)

d13 = angle(p[0],p[1],p[3]) - radians(B_ideal)

d14 = angle(p[0],p[1],p[4]) - radians(180 - A_ideal)

d15 = angle(p[0],p[2],p[3]) - radians(2 * A_ideal)

d23 = angle(p[0],p[2],p[3]) - radians(B_ideal)

d24 = angle(p[0],p[2],p[4]) - radians(C_ideal)

d25 = angle(p[0],p[2],p[5]) - radians(A_ideal)

d34 = angle(p[0],p[3],p[4]) - radians(B_ideal)

d35 = angle(p[0],p[3],p[5]) - radians(B_ideal)

d45 = angle(p[0],p[4],p[5]) - radians(180 - A_ideal)
```

```
"""calculate the displacement value in each coordinate"""

s_3 = (d_{15} + d_{24}) / sqrt(2)

s_5 = (d_{15} - d_{24}) / sqrt(2)

s_6 = (d_{12} + d_{45} - d_{14} - d_{25}) / 2

s_8a = (d_{13} - d_{35}) / sqrt(2)

s_8b = (d_{34} - d_{23}) / sqrt(2)

s_9a = (d_{12} - d_{45}) / sqrt(2)

s_9b = (d_{14} - d_{25}) / 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 (kcal/mol)^a

R:	Ме	CH ₂ SiMe ₃
$(Py)_2CoR_2 + TMEDA \rightarrow$	-3.5	-1.4
(TMEDA)CoR ₂ + 2 Py		

^a Electronic energies calculated using b3-lyp/TZVP; ZPE, enthalpy and entropy corrections for 298K, 1 bar, gas phase, taken from SV(P) calculations.

Table B.2. Observed (X-ray) and calculated average bond lengths (Å) for $(TMEDA)Co(CH_2SiMe_3)_2$

	Co-N	Co-CH ₂	CH ₂ -Si	Si-Me	N-Me	N-CH ₂	CH ₂ -CH 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 (Å) and angles (deg) for $(Py)_2CoR'_2$ (R' = CH₂CMe₂Ph).

	Co-I	N	Co-	С	N-Co-N	С-Со-С
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

~	**		2		
System	H	Aiso (MHz)	δ _{orb} (ppm)"	δ _{pred} (ppm)	δ _{obs} (ppm)
$(Py)_2CoR_2$	Py H2	1.198	8.379	166.1	114
	Ру НЗ	0.477	7.023	69.9	38.4
	Py H4	-0.422	7.173	-48.3	-8.5
	CoCH ₂	3.940	1.212	520.0	n.o.
	SiMe ₃	0.085	-0.293	10.9	10.3
	NCH.	0.710	2 624	06.1	80
(TMEDA)CoR ₂	INCH ₂	0.710	2.024	90.1	80
	NMe ₂	0.888	2.365	119.3	78
	CoCH ₂	3.423	1.177	451.9	n.o.
	SiMe ₃	0.100	-0.109	13.0	9.6
(Pv) ₂ CoR' ₂	Py H2	1.136	7.951	157.6	108
	Ру НЗ	0.473	11.673	73.9	32.7
	Py H4	-0.507	6.931	-59.8	-8.3
	CoCH ₂	4.665	2.982	617.3	n.o.
	CMe ₂	0.002	1.113	1.3	21.6
	Ph Ho	-0.037	7.455	2.6	10.2

Table B.4. Paramagnetic ¹H NMR shifts for Co complexes calculated at BP86^a

System	Η	Aiso (MHz)	δ _{orb} (ppm) ^a	δ _{pred} (ppm)	δ _{obs} (ppm)
	Ph Hm	0.034	7.111	11.6	7.4
	Ph Hp	-0.085	6.981	138.7	3.9

^a Geometry was optimized at b-p86/TZVP. R: -CH₂SiMe₃; R':-CH₂C(Me₂)Ph



Figure B.1. Comparison of calculated (BP86: $\delta^{orb} + \delta^{FC}$ only) and observed ¹H chemical shifts (correlation coefficient: 0.818). (The solid line represents the ideal $\delta_{obs} = \delta_{calc}$ 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

$$g = \alpha(V_1 - V_2)(g_1 - g_2) + g_1 - h(g_1 \cdot h)$$

where,

- α is an arbitrary constant
- V_1 and V_2 are potentials on the two PES
- g₁ and g₂ are corresponding gradients on the two PES
- h is a unit vector parallel to $(g_1 g_2)$

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 $2,6-[(HO)_2C(CF_3)]_2C_5H_3N$ (30% probability, hydrogens and THF of crystallization omitted for clarity) (this work was done by Peter Budzelaar)

Table C.1. Equilibrium between (TMEDA)CoR₂ and (6)CoR₂ ($R = CH_2SiMe_3$) as determined by ¹H NMR^a

[TMEDA]	[(TMEDA)CoR ₂]	[6]	[(6)CoR ₂]	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 (1σ) :	0.09

^a Relative concentrations from integrals.

Table C.2. Free energies (kcal/mol) of equilibrium between (TMEDA)CoR2 and (6)CoR2

or ($(1)CoR_2$	predicted	by DFT	using b3-ly	p and b-p ^a
			2	0 5	

Reactions	b3-lyp	b-p86
$(TMEDA)CoMe_2 + 6 \rightarrow (6)CoMe_2 + TMEDA$	-1.4	-18.6
$(TMEDA)Co(CH_2SiMe_3)_2 + 6 \rightarrow (6)Co(CH_2SiMe_3)_2 + TMEDA$	+2.8	-13.0
$(TMEDA)CoMe_2 + 1 \rightarrow (1)CoMe_2 + TMEDA$	+7.0	-29.5
$(TMEDA)Co(CH_2SiMe_3)_2 + 1 \rightarrow (1)Co(CH_2SiMe_3)_2 + TMEDA$	+12.7	-14.6

^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

System	Н	Aiso (MHz)	δ _{orb} (ppm) ^a	δ _{pred} (ppm)	δ _{obs} (ppm)
(6)CoR ₂	Py H3	0.223	8.423	37.83	44.4
(HS κ^{2^*})	Py H4	-2.633	7.580	-339.13	-66.5
	OCH2	0.380	4.242	54.34	-5.6
	NCMe ₂	0.083	1.317	12.29	-16.9
	CoCH ₂	4.146	1.177	547.13	n.o.
	SiMe ₃	0.044	-0.109	5.72	21.8
(6)CoR ₂	Ру НЗ	3.047	8.423	409.67	44.4
(LS κ^3)	Py H4	1.438	7.580	196.87	-66.5
	OCH2	-0.250	4.242	-28.66	-5.6
	NCMe ₂	-0.015	1.317	-0.72	-16.9
	CoCH ₂	8.614	1.177	1135.41	n.o.
	SiMe ₃	0.030	-0.109	3.78	21.8

Table C.3. Paramagnetic ¹H NMR shifts for Co complexes ($R = CH_2SiMe_3$) calculated at BP86

^a For Co complexes of **6**, the Gaussian 03 SCF calculations needed for calculating δ^{orb} did not converge, therefore we used the values calculated for the free ligand and (for the CH₂SiMe₃ group) (TMEDA)CoR₂. The errors this introduces should be of the order of 1-2 ppm, which is small relative to the δ^{FC} contribution.

				b3-lyp				ri	-b-p	
Species		Sz	$\Delta E_{\rm rel}({\rm SVP})$	⊿G _{rel} (SVP)	$\Delta E_{\rm rel}({\rm TZVP})$	$\Delta G_{\rm est}({\rm TZVP})^{\rm d}$	$\Delta E_{\rm rel}({\rm SVP})$	$\Delta G_{\rm rel}({ m SVP})$	$\Delta E_{\rm rel}({\rm TZVP})$	$\Delta G_{\rm rel}({\rm TZVP})$
(1)CoMe ₂	κ^2	³ / ₂	4.53	1.59	3.08	0.15	25.17	22.33	23.95	22.40
	κ^2	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	5.08	a	4.26	a	25.13	a	24.06	a
	κ^2	¹ / ₂	4.04	1.64	3.47	1.08	b	b	b	b
	κ^3	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	6.17	a	5.79	a	с	c	с	c
	κ^3	¹ / ₂	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
(1)CoMe	κ^3	0	25.58	10.64	22.03	7.09	34.31	19.25	30.66	17.23
(1)CoR ₂	κ ²	³ / ₂	(0)	(0)	(0)	(0)	16.16	13.35	15.46	12.86
	κ^2	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	1.32	а	2.32	a	16.29	а	15.78	а
	κ^2	¹ / ₂	1.09	3.92	2.18	5.02	b	b	b	b
	κ^3	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	5.91	а	6.95	a	с	с	с	c
	κ^3	¹ / ₂	3.81	9.24	5.07	10.51	(0)	(0)	(0)	(0)
(1)CoR	κ^3	0	17.43	5.43	14.38	2.38	22.17	7.69	17.75	4.27
(6)CoMe ₂	κ^2	³ / ₂	(0)	0.45	0.23	0.89	10.79	7.79	10.10	7.02
	κ^{2*}	³ / ₂	0.20	(0)	(0)	(0)	11.19	8.15	10.29	7.05
	κ^{2*}	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	2.50	a	3.35	а	11.80	a	11.23	a
	κ^{2*}	¹ / ₂	2.31	4.60	3.09	5.58	7.10	5.12	5.57	4.02
	κ^2	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	1.76	a	2.86	а	с	с	c	с

Table C.4. Relative electronic and free energies for all cobalt complexes in Figure 6.12 (kcal/mol; 298K, 1 bar, gas phase) ($R = CH_2SiMe_3$)

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			b3-lyp					ri	i-b-p	
Species		Sz	$\Delta E_{\rm rel}({ m SVP})$	$\Delta G_{\rm rel}({ m SVP})$	$\Delta E_{\rm rel}({\rm TZVP})$	$\Delta G_{\rm est}({\rm TZVP})^{\rm d}$	$\Delta E_{\rm rel}({ m SVP})$	$\Delta G_{\rm rel}({ m SVP})$	$\Delta E_{\rm rel}({\rm TZVP})$	$\Delta G_{\rm rel}({\rm TZVP})$
	κ^2	¹ / ₂	1.37	3.41	2.52	4.76	b	b	b	b
	κ^3	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	4.15	a	5.72	a	11.30	a	10.96	a
	κ^3	¹ / ₂	6.32	10.54	7.43	11.85	(0)	(0)	(0)	(0)
(6)CoMe	κ^3	0	28.83	20.98	26.92	19.27	28.15	15.34	24.59	12.38
(6)CoR ₂	κ^2	³ / ₂	2.28	1.34	2.06	1.12	8.39	5.85	7.26	4.17
	κ^{2*}	³ / ₂	(0)	(0)	(0)	(0)	7.09	4.05	6.21	2.39
	κ^{2*}	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	7.70	а	8.98	a	9.89	a	9.22	a
	κ^{2*}	¹ / ₂	7.09	5.62	8.18	6.71	4.68	1.99	2.99	0.08
	κ^2	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	7.66	a	8.84	a	с	с	c	c
	κ^2	¹ / ₂	7.65	5.96	8.74	7.04	7.57	3.75	b	b
	κ^3	$^{3}/_{2} \leftrightarrow ^{1}/_{2}$	14.97	а	15.96	a	10.24	a	9.54	а
	κ^3	¹ / ₂	11.42	14.77	13.16	16.50	(0)	(0)	(0)	(0)
(6)CoR	κ^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. ^c No crossing point located. ^d $G_{est}(TZVP) =$

E(TZVP) + G(SV(P)) - E(SV(P)).



Figure C.3. Structures along the profile for CH_2SiMe_3 loss from (1)Co(CH_2SiMe_3)₂ in Figure 6.12



Figure C.4. Structures along the profile for R loss from $(6)Co(CH_2SiMe_3)_2$ in Figure 6.12



Figure D.1. Si-H HMBC for the hydrolysis of the mixture from the reaction of (1)CoCH₂SiMe₃ with MeI



Figure D.2. ¹H NMR spectrum of the reaction between (1)Co(N₂) and C₆F₁₃CH=CH₂



Figure D.3. IR spectrum of (1)Co(N₂) prepared by hydrogenolysis of (1)CoCH₂SiMe₃



Figure D.4. ¹H NMR spectrum of (1)CoC(Ph)=C(H)CCPh



Figure D.5. ¹H NMR spectrum for the reaction of $(1)Co(N_2)$ with 0.5eq. allyl chloride



Figure D.6. ¹H NMR spectrum for the reaction of $(1)Co(N_2)$ with 0.5eq. cyclopropylmethyl chloride

Complex	Py H4 (t, 1H) δ, J	Py, H3 (d, 2H) δ, J	Ar o- CH ₃ (s, 12H) δ	N=CCH ₃ (s, 6H) δ	CoAr <i>o</i> -H (≈d, 2H) δ, J	Additional assignments
(1)CoC ₆ H ₅	10.36, 7.6	7.56, 7.6	2.05	-1.07	4.74	
$(1)CoCH_2CMe_2(C_6H_3-3,5-tBu_2)^b$	10.83, 7.5	7.83, 7.5	1.96	-1.93		0.53 (s, 6H, CMe2)
$(1)CoC_6H_4$ -4-COMe	10.26, 7.4	а	2.00	-0.95	4.92, 7.3	
(1)CoC ₆ H ₄ -4-COOMe	10.26, 7.4	a	1.98	-0.96	4.91, 7.5	3.34 (s, 3H, COOC <i>H</i> ₃)
$(1)CoC_6H_4-4-CF_3$	10.26, 7.4	7.36, 7.4	1.95	-0.95	4.83, 7.3	¹⁹ F NMR: -61.3 (s)
$(1)CoC_{6}H_{4}-4-F$	10.32, 7.5	7.46, 7.5	1.97	-1.05	$4.62 (t)$ $J_{\rm HF} \approx J_{\rm HH} \approx 6.8$	¹⁹ F NMR: -124.9 (s)
$(1)CoC_6H_3-3,5-(OMe)_2$	10.32, 7.4	7.52, 7.4	2.05	-1.05	3.90	5.80 (s, 1H, CoAr <i>Hp</i>) 3.25 (s, 6H, OC <i>H</i> ₃)
(1)CoC ₆ H ₄ -4-Cl	10.29, 7.3	7.42, 7.3	1.96	-1.01	4.65, 7.3	
$(1)CoC_6H_4$ -4-Me	10.36, 7.4	7.57, 7.4	2.05	-1.12	4.68, 6.9	
$(1)CoC_6H_4-4-OMe$	10.35, 7.4	7.56, 7.4	2.02	-1.12	4.69, 7.3	3.20 (s, 3H, OC <i>H</i> ₃) 6.28 (d, <i>J</i> 7.3, 2H, CoAr <i>Hm</i>)
(1)CoMe	10.1 (br)	7.88 (br)	1.95	-1.27		0.51 (s, 3H, CoC <i>H</i> ₃)

Table D.1. ¹H NMR assignments for all (1)Co complexes relevant to Table 7.2. (δ in ppm, J in Hz)

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Complex	Py H4 (t, 1H) δ, J	Py, H3 (d, 2H) δ, J	Ar o- CH ₃ (s, 12H) δ	N=CCH ₃ (s, 6H) δ	CoAr <i>o</i> -H (≈d, 2H) δ, <i>J</i>	Additional assignments
(1)Co- <i>n</i> -C ₄ H ₉	10.23 (br)	8.04 (br)	2.01	-1.60		
(1)Co- <i>n</i> -C ₆ H ₁₃	10.23 (br d)	8.05, (br d)	2.01	-1.60		
$(1)CoCH_2C_6H_5$	10.40, 7.4	7.72, 7.4	1.91	-1.53		5.81 (d, <i>J</i> 7.3, 2H, Bz <i>Ho</i>) 6.56 (t, <i>J</i> 7.0, 2H, Bz <i>Hm</i>)
2-(1)Co-6-Cl-C ₅ H ₃ N	10.11, 7.5	7.45, 7.5	2.06	-0.85	5.55, 6.9 (CoPy H3)	5.98 (t, <i>J</i> 7.3, 1H, CoPy <i>H</i> 4) 6.09 (d, <i>J</i> 7.5, 1H, CoPy <i>H</i> 5)
$(1)CoCH_2CH=CF-n-C_5F_{11}$	10.17, 7.5	7.39, 7.5	2.03	-1.12		4.66 (dt, <i>J</i> _{HF} 35.7, <i>J</i> _{HH} 10.0, 1H, <i>CH</i> =CF) 1.55 (d, <i>J</i> 10.0, 2H, CoC <i>H</i> ₂) ¹⁹ F NMR: -148.6 (1F), -115.1 (2F)
(1)Co(η^3 -allyl)	7.41, 7.7	7.84, 7.7	1.76	1.55		5.15 (quintet, <i>J</i> 10.2, 1H, CH ₂ C <i>H</i> CH ₂),
						2.43 (br, 2H, CH_2CHCH_2
(1)Co(η ³ -crotyl)	7.40, 7.5	7.89, 7.5	1.82	1.57		5.18 (tt, <i>J</i> ₁ 11.2, <i>J</i> ₂ 9.2, 1H, CH ₂ C <i>H</i>)), 2.48 (qq, <i>J</i> ₁ 11.2, <i>J</i> ₂ 6.5, 1H, CH3C <i>H</i>), 1.82 (2H, C <i>H</i> ₂ CH), 1.24 (d, <i>J</i> 6.5, 3H, C <i>H</i> ₃ CH)
(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	Py H4 (t, 1H) δ, J	Py, H3 (d, 2H) δ, J	Ar o- CH ₃ (s, 12H) δ	N=CCH ₃ (s, 6H) δ	CoAr <i>o</i> -H (≈d, 2H) δ, <i>J</i>	Additional assignments
(1)CoBr	9.72 (br t)	6.86 (br d)	2.17	-0.27		
(1)CoI	10.06 (br t)	а	2.18	-0.58		

^a Resonance could not be assigned. ^b the correction to the original published results



Figure D.7. ¹H NMR spectrum of liquid part from reaction of (1)Co(Py-6-Cl) and (1)CoCl with 0.5 eq. BzBr



Figure D.8. ¹H NMR spectrum of solid part in CD_2Cl_2 from reaction of (1)Co(Py-6-Cl) and (1)CoCl with 0.5 eq. BzBr

Supporting Information

Name of compound	Name of the CIF file			
CIF files for X-ray structures in Section 9.1				
Ligand 8 in Chapter 3	zd03			
(3)CoCl ₂ in Chapter 3	zd01			
(7)CoCl ₂ in Chapter 3	budz06			
(10)CoCl ₂ in Chapter 3	phc0m			
(7)FeCl ₂ in Chapter 3	budz05			
(10)FeCl ₂ in Chapter 3	zd05			
(8)FeCl ₂ in Chapter 3	ddi60			
(9)FeCl ₂ in Chapter 3	zx0m			
(Pybox)Fe(CH ₂ SiMe ₃) ₂ in Chapter 3	fesi0m			
CIF files for X-ray structures in Section 9.5				
(1)CoNCHC ₆ H ₄ -4-Cl	zd10			

CIF file: (zd03.cif):

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Budzelaar'
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        University of Manitoba
        Fort Garry Campus
        Winnipeg, MB R3T 2N2
        Canada
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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
molecules in adjacent cells. However, we could not
develop a satisfactory refinement model for this
using the supercell in either P1 or P-1.
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# 4. TEXT
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Crystal and Molecular Structure of budz02
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_publ_section_references
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.
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.
University of G\"ottingen, Germany.
Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University,
Utrecht, The Netherlands.
publ section figure captions
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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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408

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C53B C 0.5570(5) 0.6645(6) -0.0818(7) 0.0758(8) Uiso 0.50 1 d PD A -2 H53B H 0.5919 0.6586 -0.1331 0.091 Uiso 0.50 1 calc PR A -2 C55B C 0.3713(9) 0.6402(6) -0.0381(6) 0.0758(8) Uiso 0.50 1 d PD A -2 H55B H 0.2838 0.6171 -0.0651 0.091 Uiso 0.50 1 calc PR A -2 C56B C 0.4536(4) 0.6838(6) 0.0774(8) 0.0758(8) Uiso 0.50 1 d PD A -2 H56B H 0.4188 0.6898 0.1288 0.091 Uiso 0.50 1 calc PR A -2 C77 C 0.2691(9) -0.089(2) -0.105(2) 0.155(3) Uiso 0.50 1 d PD B -3 H77A H 0.2321 -0.0676 -0.1607 0.233 Uiso 0.50 1 calc PR B -3 H77B H 0.2311 -0.0654 -0.0508 0.233 Uiso 0.50 1 calc PR B -3 H77C H 0.2544 -0.1691 -0.1452 0.233 Uiso 0.50 1 calc PR B -3 C71 C 0.4093(9) -0.0369(16) -0.0413(16) 0.155(3) Uiso 0.50 1 d PGD B -3 C72 C 0.4821(16) -0.0135(16) -0.0906(12) 0.155(3) Uiso 0.50 1 d PG B -3 H72 H 0.4445 -0.0323 -0.1677 0.186 Uiso 0.50 1 calc PR B -3 C73 C 0.6111(15) 0.0379(15) -0.0246(17) 0.155(3) Uiso 0.50 1 d PG B -3 H73 H 0.6598 0.0536 -0.0576 0.186 Uiso 0.50 1 calc PR B -3 C74 C 0.6673(9) 0.0660(13) 0.0907(17) 0.155(3) Uiso 0.50 1 d PG B -3 H74 H 0.7537 0.1004 0.1348 0.186 Uiso 0.50 1 calc PR B -3 C75 C 0.5946(16) 0.0426(14) 0.1400(12) 0.155(3) Uiso 0.50 1 d PG в -3 H75 H 0.6322 0.0614 0.2171 0.186 Uiso 0.50 1 calc PR B -3 C76 C 0.4656(15) -0.0088(16) 0.0740(16) 0.155(3) Uiso 0.50 1 d PG в -3 H76 H 0.4169 -0.0245 0.1070 0.186 Uiso 0.50 1 calc PR B -3 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 N1 0.0379(16) 0.0460(18) 0.0435(17) 0.0291(15) 0.0204(14) 0.0142(13)C2 0.040(2) 0.044(2) 0.040(2) 0.0235(17) 0.0204(16) 0.0111(16)C3 0.035(2) 0.075(3) 0.055(3) 0.041(2) 0.0181(19) 0.0102(19)C4 0.042(2) 0.092(4) 0.059(3) 0.054(3) 0.020(2) 0.024(2) C5 0.044(2) 0.067(3) 0.053(2) 0.044(2) 0.0236(19) 0.0182(19) C6 0.0390(19) 0.045(2) 0.040(2) 0.0250(17) 0.0217(16) 0.0155(16) C7 0.039(2) 0.051(2) 0.050(2) 0.0333(19) 0.0222(18) 0.0157(17)

C8 0.039(2) 0.130(5) 0.088(4) 0.087(4) 0.018(2) 0.015(3) $N2 \ 0.0390(17) \ 0.0498(19) \ 0.0522(19) \ 0.0339(17) \ 0.0242(15)$ 0.0154(14)C11 0.038(2) 0.058(2) 0.053(2) 0.041(2) 0.0189(18) 0.0134(17) $C12 \ 0.046(2) \ 0.066(3) \ 0.067(3) \ 0.047(2) \ 0.032(2) \ 0.023(2)$ $C13 \ 0.050(3) \ 0.094(4) \ 0.089(4) \ 0.061(3) \ 0.043(3) \ 0.029(3)$ C14 0.043(3) 0.102(4) 0.097(4) 0.064(4) 0.029(3) 0.008(3)C15 0.060(3) 0.075(3) 0.075(3) 0.043(3) 0.023(3) -0.001(3) C16 0.049(2) 0.065(3) 0.057(3) 0.040(2) 0.021(2) 0.011(2) C17 0.067(3) 0.064(3) 0.086(4) 0.043(3) 0.050(3) 0.028(2) C18 0.099(5) 0.076(4) 0.093(5) 0.028(4) 0.030(4) 0.023(4) C19 0.097(5) 0.091(4) 0.151(7) 0.071(5) 0.085(5) 0.056(4) $C20 \ 0.072(3) \ 0.056(3) \ 0.076(3) \ 0.027(3) \ 0.037(3) \ 0.012(2)$ $C21 \ 0.156(9) \ 0.230(12) \ 0.073(5) \ 0.035(7) \ 0.041(6) \ 0.103(9)$ C22 0.231(12) 0.221(12) 0.128(7) 0.111(8) 0.111(8) 0.179(11) P1 0.0395(6) 0.0469(6) 0.0414(6) 0.0258(5) 0.0201(4) 0.0085(4) N3 0.052(2) 0.097(3) 0.077(3) 0.059(3) 0.037(2) 0.021(2) C31 0.0317(18) 0.058(2) 0.052(2) 0.033(2) 0.0194(17) 0.0109(17) C32 0.045(2) 0.065(3) 0.058(3) 0.036(2) 0.018(2) 0.005(2) C33 0.052(3) 0.102(4) 0.076(4) 0.056(3) 0.022(3) -0.005(3) $C34 \ 0.042(3) \ 0.155(7) \ 0.069(4) \ 0.066(4) \ 0.028(3) \ 0.016(3)$ C35 0.062(3) 0.115(5) 0.054(3) 0.036(3) 0.031(3) 0.047(3) C36 0.051(3) 0.067(3) 0.054(3) 0.030(2) 0.017(2) 0.018(2) C37 0.095(4) 0.061(3) 0.099(5) 0.041(3) 0.042(4) 0.022(3) $C38 \ 0.073(5) \ 0.314(15) \ 0.134(7) \ 0.135(9) \ 0.071(5) \ 0.050(7)$ C39 0.120(6) 0.056(3) 0.097(5) 0.032(3) 0.037(4) 0.021(3) C41 0.043(2) 0.046(2) 0.048(2) 0.0270(19) 0.0232(18) 0.0115(17) C42 0.066(3) 0.077(3) 0.051(3) 0.021(3) 0.021(2) 0.024(3) C43 0.089(4) 0.080(4) 0.060(3) 0.016(3) 0.033(3) 0.015(3) C44 0.105(5) 0.052(3) 0.092(4) 0.036(3) 0.063(4) 0.029(3) C45 0.113(5) 0.101(5) 0.094(5) 0.055(4) 0.042(4) 0.066(4) $C46 \ 0.082(4) \ 0.083(4) \ 0.058(3) \ 0.028(3) \ 0.020(3) \ 0.044(3)$ _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.

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loop
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geom bond publ flag
N1 C6 1.336(5) . ?
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C3 H3 0.9300 . ?
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C4 H4 0.9300 . ?
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C5 H5 0.9300 . ?
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C7 C8 1.502(6) . ?
C8 H81 0.9600 . ?
C8 H82 0.9600 . ?
C8 H83 0.9600 . ?
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C11 C16 1.400(6) . ?
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C14 C15 1.361(8) . ?
C14 H14 0.9300 . ?
C15 C16 1.400(6) . ?
C15 H15 0.9300 . ?
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C17 C19 1.516(7) . ?
C17 H17 0.9800 . ?
C18 H181 0.9600 . ?
C18 H182 0.9600 . ?
C18 H183 0.9600 . ?
C19 H191 0.9600 . ?
C19 H192 0.9600 . ?
C19 H193 0.9600 . ?
C20 C22 1.474(10) . ?
C20 C21 1.481(10) . ?
C20 H20 0.9800 . ?
C21 H211 0.9600 . ?
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C21 H212 0.9600 . ? C21 H213 0.9600 . ? C22 H221 0.9600 . ? C22 H222 0.9600 . ? C22 H223 0.9600 . ? P1 N3 1.543(4) . ? P1 C51 1.810(5) . ? P1 C41 1.831(4) . ? N3 C31 1.397(5) . ? C31 C32 1.398(6) . ? C31 C36 1.399(6) . ? C32 C33 1.381(7) . ? C32 C37 1.501(8) . ? C33 C34 1.361(9) . ? СЗЗ НЗЗ 0.9300 . ? C34 C35 1.371(9) . ? C34 C38 1.523(8) . ? C35 C36 1.391(8) . ? C35 H35 0.9300 . ? C36 C39 1.496(8) . ? СЗ7 НЗ71 0.9600 . ? СЗ7 НЗ72 0.9600 . ? СЗ7 НЗ73 0.9600 . ? C38 H381 0.9600 . ? C38 H382 0.9600 . ? СЗ8 Н383 0.9600 . ? C39 H391 0.9600 . ? C39 H392 0.9600 . ? СЗ9 НЗ93 0.9600 . ? C41 C46 1.347(7) . ? C41 C42 1.363(7) . ? C42 C43 1.379(8) . ? C42 H42 0.9300 . ? C43 C44 1.351(9) . ? C43 H43 0.9300 . ? C44 C45 1.328(9) . ? C44 H44 0.9300 . ? C45 C46 1.393(8) . ? C45 H45 0.9300 . ? C46 H46 0.9300 . ? C51 C52B 1.387(3) . ? C51 C56A 1.387(3) . ? C51 C52A 1.387(3) . ? C51 C56B 1.388(3) . ? C54 C53B 1.387(3) . ? C54 C55A 1.387(3) . ? C54 C53A 1.388(3) . ? C54 C55B 1.388(3) . ?

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C54 H54 0.9300 . ?
C52A C53A 1.387(3) . ?
C52A H52A 0.9300 . ?
C53A H53A 0.9300 . ?
C55A C56A 1.387(3) . ?
C55A H55A 0.9300 . ?
C56A H56A 0.9300 . ?
C52B C53B 1.387(3) . ?
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C53B H53B 0.9300 . ?
C55B C56B 1.388(3) . ?
С55В Н55В 0.9300 . ?
C56B H56B 0.9300 . ?
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C77 H77A 0.9600 . ?
С77 Н77В 0.9600 . ?
C77 H77C 0.9600 . ?
C71 C72 1.3900 . ?
C71 C76 1.3900 . ?
C72 C73 1.3900 . ?
C72 H72 0.9300 . ?
C73 C74 1.3900 . ?
C73 H73 0.9300 . ?
C74 C75 1.3900 . ?
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C75 H75 0.9300 . ?
C76 H76 0.9300 . ?
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geom angle atom site label 3
geom angle
geom angle site symmetry 1
_geom_angle_site_symmetry_3
geom angle publ flag
C6 N1 C2 117.4(3) . . ?
N1 C2 C3 123.4(3) . . ?
N1 C2 P1 117.9(3) . . ?
C3 C2 P1 118.7(3) . . ?
C4 C3 C2 118.5(4) . . ?
C4 C3 H3 120.7 . . ?
C2 C3 H3 120.7 . . ?
C5 C4 C3 119.0(4) . . ?
C5 C4 H4 120.5 . . ?
C3 C4 H4 120.5 . . ?
C4 C5 C6 119.1(4) . . ?
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C4	C5	Н	15	1	20).	5		•		•		?						
C6	C5	H	15	1	20).	5				•		?						
N1	С6	C	25	1	22	2.	5	(3)						?			
N1	С6	C	27	1	16	5.	8	(3)						?			
С5	C6	C	:7	1	20).	7	(3)				•		?			
N2	C7	C	28	1	25	5.	5	(4)				•		?			
N2	C7	C	6	1	16	5.	6	(3)		•		•		?			
С8	C7	C	6	1	17	7.	9	(3)		•		•		?			
C7	С8	H	18	1	10)9	•	5		•		•		?					
C7	С8	H	18	2	10)9	•	5		•		•		?					
H81	С	8	Η	82	1	. 0	9	•	5		•		•		?				
C7	С8	H	81	3	10)9	•	5		•		•		?					
H81	С	8	Η	83	1	. 0	9	•	5		•		•		?				
H82	С	8	Η	83	1	0	9	•	5		•		•		?				
C7	N2	C	21	1	12	21	•	7	(3)		•		•		?		
C12	С	11	. (С1	6	1	2	2	•	1	(4)		•		•	,	?
C12	С	11	. 1	N2	1	.1	8	•	9	(4)		•		•		?	
C16	С	11	. 1	N2	1	.1	8	•	8	(4)		•		•		?	
C13	С	12	2	С1	1	1	1	7	•	5	(5)		•		•	,	?
C13	С	12	2	С1	7	1	2	1	•	9	(4)		•		•	,	?
C11	С	12	2	С1	7	1	2	0	•	5	(4)		•		•	,	?
C14	С	13	3 (С1	2	1	2	1	•	3	(5)		•		•	,	?
C14	С	13	3	Η1	3	1	1	9	•	4		•		•		?			
C12	С	13	3	Η1	3	1	1	9	•	4		•		•		?			
C15	С	14	Ł (С1	3	1	2	0	•	3	(5)		•		•	,	?
C15	С	14	1	Η1	4	1	1	9	•	9		•		•		?			
C13	С	14	1	Н1	4	1	1	9	•	9		•		•		?			
C14	С	15	5 (С1	6	1	2	1	•	6	(5)		•		•	,	?
C14	С	15	5	Н1	5	1	1	9	•	2		•		•		?			
C16	С	15	5	Н1	5	1	1	9	•	2		•		•		?			
C11	С	16	5 (С1	5	1	1	7	•	2	(5)		•		•	,	?
C11	С	16	5 (C2	0	1	2	1	•	6	(4)		•		•	,	?
C15	С	16	5 (C2	0	1	2	1	•	1	(5)		•		•	,	?
C18	С	17	' (С1	2	1	1	1	•	0	(4)		•		•	,	?
C18	С	17	/ (C1	9	1	0	9	•	9	(5)		•		•	,	?
C12	С	17	/ (C1	9	1	1	4	•	7	(5)		•	_	•	,	?
C18	С	17		H1	7	1	0	6	•	9		•		•		?			
C12	С	17		Η1	7	1	0	6	•	9		•		•		?			
C19	C	17		H1	./	1	0	6	•	9	_	•		•		?	~		
CI7	C	15	š.	Ηl	81	-	1	0	9	•	5		•		•		?		
C17	C	18	3	H1	82	2	1	0	9	•	5	_	•		•		?	_	
HT8	1	CI	. 8	Н	15	32		T	0	9	•	5		•		•	_	?	
CL7	C	18	5	H1	83	5 \	T	0	9	•	5	_	•		•		?	~	
H18	Ţ	C1	. 8	H	16	33		1	0	9	•	5		•		•		?	
HT8	۷ _	CI	.8	H 	ΤC	53	-	T	U	9	•	5		•		•	~	?	
CI7	C	10	<u>ا</u> ا	H L	91	-	1	0	9	•	5		•		•		?		
CI7	_ C	T 5	<u>ر</u> ر	н 1 	92	<u>.</u>	T	0	9	•	5	_	•		•		?	~	
HT ð	\bot	C1	. 9	Η	ΤÇ	12		Τ	υ	9	•	5		•		•		?	

C17 C19 H193 109.5 . . ? H191 C19 H193 109.5 . . ? H192 C19 H193 109.5 . . ? C22 C20 C21 109.6(8) . . ? C22 C20 C16 113.4(5) . . ? C21 C20 C16 114.6(6) . . ? C22 C20 H20 106.2 . . ? C21 C20 H20 106.2 . . ? C16 C20 H20 106.2 . . ? C20 C21 H211 109.5 . . ? C20 C21 H212 109.5 . . ? H211 C21 H212 109.5 . . ? C20 C21 H213 109.5 . . ? H211 C21 H213 109.5 . . ? H212 C21 H213 109.5 . . ? C20 C22 H221 109.5 . . ? C20 C22 H222 109.5 . . ? H221 C22 H222 109.5 . . ? C20 C22 H223 109.5 . . ? H221 C22 H223 109.5 . . ? H222 C22 H223 109.5 . . ? N3 P1 C51 116.5(2) . . ? N3 P1 C41 115.2(2) . . ? C51 P1 C41 106.21(19) . . ? N3 P1 C2 107.1(2) . . ? C51 P1 C2 109.01(19) . . ? C41 P1 C2 101.69(17) . . ? C31 N3 P1 138.0(4) . . ? C32 C31 C36 119.2(4) . . ? C32 C31 N3 120.7(4) . . ? C36 C31 N3 120.1(4) . . ? C33 C32 C31 118.9(5) . . ? C33 C32 C37 121.1(5) . . ? C31 C32 C37 120.0(4) . . ? C34 C33 C32 123.4(5) . . ? C34 C33 H33 118.3 . . ? C32 C33 H33 118.3 . . ? C33 C34 C35 117.0(5) . . ? C33 C34 C38 121.6(8) . . ? C35 C34 C38 121.4(8) . . ? C34 C35 C36 123.0(5) . . ? C34 C35 H35 118.5 . . ? C36 C35 H35 118.5 . . ? C35 C36 C31 118.5(5) . . ? C35 C36 C39 120.3(6) . . ? C31 C36 C39 121.2(5) . . ? C32 C37 H371 109.5 . . ? C32 C37 H372 109.5 . . ?

H371 C37 H372 109.5 . . ? СЗ2 СЗ7 НЗ73 109.5 . . ? H371 C37 H373 109.5 . . ? H372 C37 H373 109.5 . . ? C34 C38 H381 109.5 . . ? C34 C38 H382 109.5 . . ? H381 C38 H382 109.5 . . ? C34 C38 H383 109.5 . . ? H381 C38 H383 109.5 . . ? H382 C38 H383 109.5 . . ? C36 C39 H391 109.5 . . ? C36 C39 H392 109.5 . . ? H391 C39 H392 109.5 . . ? C36 C39 H393 109.5 . . ? H391 C39 H393 109.5 . . ? H392 C39 H393 109.5 . . ? C46 C41 C42 118.2(5) . . ? C46 C41 P1 123.5(4) . . ? C42 C41 P1 118.3(4) . . ? C41 C42 C43 121.0(5) . . ? C41 C42 H42 119.5 . . ? C43 C42 H42 119.5 . . ? C44 C43 C42 120.2(6) . . ? C44 C43 H43 119.9 . . ? C42 C43 H43 119.9 . . ? C45 C44 C43 119.2(6) . . ? C45 C44 H44 120.4 . . ? C43 C44 H44 120.4 . . ? C44 C45 C46 121.2(6) . . ? C44 C45 H45 119.4 . . ? C46 C45 H45 119.4 . . ? C41 C46 C45 120.2(5) . . ? C41 C46 H46 119.9 . . ? C45 C46 H46 119.9 . . ? C52B C51 C56A 101.0(6) . . ? C52B C51 C52A 41.1(3) . . ? C56A C51 C52A 122.7(6) . . ? C52B C51 C56B 112.7(7) . . ? C56A C51 C56B 41.1(3) . . ? C52A C51 C56B 104.8(5) . . ? C52B C51 P1 122.7(5) . . ? C56A C51 P1 123.4(5) . . ? C52A C51 P1 113.9(4) . . ? C56B C51 P1 124.5(5) . . ? C53B C54 C55A 108.7(5) . . ? C53B C54 C53A 42.6(3) . . ? C55A C54 C53A 118.6(7) . . ? C53B C54 C55B 128.1(7) . . ? C55A C54 C55B 41.9(3) . . ? C53A C54 C55B 105.5(6) . . ? C53B C54 H54 114.0 . . ? C55A C54 H54 120.7 . . ? C53A C54 H54 120.7 . . ? C55B C54 H54 118.0 . . ? C53A C52A C51 116.2(7) . . ? C53A C52A H52A 121.9 . . ? C51 C52A H52A 121.9 . . ? C52A C53A C54 123.1(8) . . ? C52A C53A H53A 118.5 . . ? C54 C53A H53A 118.5 . . ? C54 C55A C56A 120.3(8) . . ? C54 C55A H55A 119.8 . . ? C56A C55A H55A 119.8 . . ? C51 C56A C55A 119.0(8) . . ? C51 C56A H56A 120.5 . . ? C55A C56A H56A 120.5 . . ? C51 C52B C53B 131.0(9) . . ? C51 C52B H52B 114.5 . . ? C53B C52B H52B 114.5 . . ? C54 C53B C52B 108.9(8) . . ? C54 C53B H53B 125.6 . . ? C52B C53B H53B 125.6 . . ? C56B C55B C54 115.4(8) . . ? C56B C55B H55B 122.3 . . ? C54 C55B H55B 122.3 . . ? C55B C56B C51 123.9(8) . . ? C55B C56B H56B 118.0 . . ? C51 C56B H56B 118.0 . . ? C72 C71 C76 120.0 . . ? C72 C71 C77 123.5(18) . . ? C76 C71 C77 116.5(18) . . ? C73 C72 C71 120.0 . . ? С73 С72 Н72 120.0 . . ? С71 С72 Н72 120.0 . . ? C72 C73 C74 120.0 . . ? С72 С73 Н73 120.0 . . ? C74 C73 H73 120.0 . . ? C75 C74 C73 120.0 . . ? C75 C74 H74 120.0 . . ? C73 C74 H74 120.0 . . ? C76 C75 C74 120.0 . . ? С76 С75 Н75 120.0 . . ? C74 C75 H75 120.0 . . ? C75 C76 C71 120.0 . . ? С75 С76 Н76 120.0 . . ? С71 С76 Н76 120.0 . . ?

diffrn measured fraction	theta max 1.000
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_refine_diff_density_max	1.363
_refine_diff_density_min	-1.182
_refine_diff_density_rms	0.083

CIF file: (zd01.cif):

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data zd01
publ requested journal
                                'Ph.D thesis of Di Zhu'
                               Dr. Peter H.M.
publ contact author name
Budzelaar'
publ contact author address
;
       Department of Chemistry
       University of Manitoba
       Fort Garry Campus
       Winnipeg, MB R3T 2N2
       Canada
;
publ contact author email
                              budzelaa@cc.umanitoba.ca
publ contact author phone
                                '+1 204 474 8796'
publ contact author fax
                               '+1 204 474 7608'
loop
publ author name
publ author address
'Budzelaar, Peter H.M.'
    Department of Chemistry
;
    University of Manitoba
    Fort Garry Campus
    Winnipeg, MB R3T 2N2
    Canada
;
'Zhu, Di'
    Department of Chemistry
;
    University of Manitoba
    Fort Garry Campus
    Winnipeg, MB R3T 2N2
    Canada
;
publ requested coeditor name
                               ?
publ_contact_letter
;
publ section experimental
;
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 deq. 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 \%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. ; _____ # 4. TEXT publ section title Crystal and Molecular Structure of zd01 publ section abstract publ section references 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. Sheldrick, G. M. (1997). SHELXL-97, Program for the refinement of 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\"ottingen, Germany.
Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University,
Utrecht, The Netherlands.
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publ section figure captions
_publ_section_acknowledgements
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
valuable discussions.
#______
_____
audit creation method
                               SHELXL-97
chemical name systematic
;2,6-bis-(1-(2,4,6-trimethylphenyl)iminoethyl)pyridine
cobalt(II) chloride (monohydrate)
;
chemical name common
                               ?
chemical formula moiety
                              ?
_chemical_formula_sum
                              'C27 H31 Cl2 Co N3 O'
exptl crystal recrystallization method CH2Cl2
chemical melting point
                               ?
exptl crystal description
                               'fragment of needle'
exptl crystal colour
                              'light-green'
diffrn ambient temperature
                               293(2)
chemical formula weight
                               543.38
loop
atom type symbol
_atom_type_description
atom type scat dispersion real
atom type scat dispersion imag
atom type scat source
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C C 0.0033 0.0016 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' H H 0.0000 0.0000 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' N N 0.0061 0.0033 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' Co Co 0.3494 0.9721 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' Cl Cl 0.1484 0.1585 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' 0 0 0.0106 0.0060 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4' symmetry_cell_setting monoclinic _symmetry_space_group_name_H-M 'P 21/c' symmetry int tables number 14 chemical absolute configuration ? loop symmetry equiv pos as xyz 'x, y, z' '-x, y+1/2, -z+1/2' '-x, -y, -z' 'x, -y-1/2, z-1/2' _cell_length a 7.986(3)cell length b 13.707(4)cell length c 25.479(8) _cell_angle alpha 90.00 cell angle beta 95.414(5) cell angle gamma 90.00 _cell_volume 2776.8(15)cell formula units Z 4 _cell_measurement_temperature 293(2) cell measurement reflns used 773 cell measurement theta min 2.562 _cell_measurement theta max 14.927 exptl crystal size max 0.30 exptl crystal size mid 0.04 _exptl_crystal size min 0.01 exptl crystal density meas ? exptl crystal density diffrn 1.300 _exptl_crystal_density_method 'not measured' exptl crystal F 000 1132 exptl absorpt coefficient mu 0.834 exptl absorpt correction type multi-scan exptl absorpt correction T min 0.618 exptl absorpt correction T max 0.992

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exptl absorpt process details
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exptl special details
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;
_diffrn_radiation probe
                                 x-ray
diffrn radiation type
                                 MoK∖a
                                 0.71073
diffrn radiation wavelength
_diffrn source
                                 'fine-focus sealed tube'
diffrn radiation monochromator
                                 graphite
diffrn measurement device type
                                 'Bruker 4-circle, APEX detector'
diffrn measurement method
                                 'area detector \f and \w scan'
diffrn detector area resol mean 0.0
_diffrn_standards number
                                 \cap
diffrn standards interval count 0
diffrn standards interval time
                                 0?
_diffrn_standards decay %
                                 0
diffrn reflns number
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_diffrn_reflns_av_R_equivalents
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_diffrn_reflns_av_sigmaI/netI
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diffrn reflns limit h max
                                 6
diffrn reflns limit k min
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diffrn reflns limit k max
                                 11
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_diffrn_reflns_limit l max
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diffrn reflns theta min
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_diffrn_reflns_theta max
                                 17.50
reflns number total
                                 1762
_reflns_number_gt
                                 927
reflns threshold expression
                                 >2sigma(I)
                                 'Bruker Smart program suite V6
computing data collection
(Bruker) '
                                 'Bruker Smart program suite V6
computing cell refinement
(Bruker) '
computing data reduction
                                 'Bruker Saint program suite V6
(Bruker) '
_computing_structure solution
                                 'SHELXS-97 (Sheldrick, 1990)'
                                 'SHELXL-97 (Sheldrick, 1997)'
computing structure refinement
computing molecular graphics
                                 ?
computing publication material
                                 ?
refine special details
;
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. Rfactors based on F^2 are statistically about twice as large as those based on F, and Rfactors based on ALL data will be even larger. ; refine ls structure factor coef Fsqd refine ls matrix type full refine ls weighting scheme calc refine ls weighting details 'calc w=1/[\s^2^(Fo^2^)+(0.1426P)^2^+0.0000P] where $P = (Fo^2^+ 2Fc^2^) / 3'$ atom sites solution primary direct _atom_sites_solution secondary difmap atom sites solution hydrogens geom refine ls hydrogen treatment constr refine ls extinction method SHELXL _refine_ls_extinction coef 0.041(5)refine ls extinction expression $Fc^*^=kFc[1+0.001xFc^2^1/1^3^/sin(2)q)^{-1/4^-}$ refine ls number reflns 1762 _refine_ls_number_parameters 161 refine ls number restraints 0 _refine_ls_R_factor all 0.1768 _refine_ls_R_factor_gt 0.1065 refine ls wR factor ref 0.2652 _refine_ls_wR_factor_gt 0.2279 refine ls goodness of fit ref 1.004 refine ls restrained S all 1.004 _refine_ls_shift/su max 0.000 refine ls shift/su mean 0.000 loop atom site label atom site type symbol _atom_site_fract x atom site fract y _atom_site_fract_z atom site U iso or equiv atom site adp type atom site occupancy

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atom site symmetry multiplicity
atom site calc flag
atom site refinement flags
atom site disorder assembly
atom site disorder group
0 0 0.127(4) 0.438(2) 0.6376(13) 0.258(14) Uiso 1 1 d . . .
Col Co 0.0826(4) 0.1591(2) 0.78617(11) 0.0569(16) Uani 1 1 d . .
Cl1 Cl -0.1631(8) 0.1590(4) 0.8222(2) 0.080(2) Uani 1 1 d . . .
Cl2 Cl 0.1603(8) 0.3051(4) 0.7554(2) 0.072(2) Uani 1 1 d . . .
N1 N 0.243(2) 0.1634(11) 0.8633(6) 0.048(5) Uiso 1 1 d . . .
N2 N 0.223(2) 0.0350(11) 0.7851(6) 0.049(5) Uiso 1 1 d . . .
N3 N 0.002(2) 0.0894(11) 0.7095(6) 0.053(5) Uiso 1 1 d . . .
C1 C 0.477(3) 0.0748(17) 0.9139(9) 0.102(9) Uiso 1 1 d . . .
H11 H 0.4751 0.1273 0.9388 0.153 Uiso 1 1 calc R . .
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 . .
C2 C 0.344(3) 0.0919(15) 0.8686(8) 0.064(7) Uiso 1 1 d . . .
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 . . .
H41 H 0.5111 -0.0858 0.8537 0.085 Uiso 1 1 calc R . .
C5 C 0.394(3) -0.1373(15) 0.7841(8) 0.067(7) Uiso 1 1 d . . .
H51 H 0.4539 -0.1951 0.7827 0.080 Uiso 1 1 calc R . .
C6 C 0.272(2) -0.1147(14) 0.7452(8) 0.051(6) Uiso 1 1 d . . .
H6 H 0.2444 -0.1601 0.7187 0.061 Uiso 1 1 calc R . .
C7 C 0.190(3) -0.0284(14) 0.7436(8) 0.049(6) Uiso 1 1 d . . .
C8 C 0.074(3) 0.0084(14) 0.7032(8) 0.050(6) Uiso 1 1 d . . .
C9 C 0.044(3) -0.0502(14) 0.6528(7) 0.060(6) Uiso 1 1 d . . .
H91 H -0.0461 -0.0211 0.6305 0.090 Uiso 1 1 calc R . .
H92 H 0.0138 -0.1159 0.6612 0.090 Uiso 1 1 calc R . .
H93 H 0.1442 -0.0509 0.6349 0.090 Uiso 1 1 calc R . .
C11 C 0.259(3) 0.2384(14) 0.9015(8) 0.053(6) Uiso 1 1 d . . .
C12 C 0.361(3) 0.3152(14) 0.8966(8) 0.056(6) Uiso 1 1 d . . .
C13 C 0.352(3) 0.3936(15) 0.9306(8) 0.062(7) Uiso 1 1 d .
H131 H 0.4242 0.4460 0.9271 0.075 Uiso 1 1 calc R . .
C14 C 0.245(3) 0.3981(15) 0.9683(8) 0.063(7) Uiso 1 1 d . . .
C15 C 0.142(3) 0.3204(14) 0.9734(8) 0.070(7) Uiso 1 1 d . . .
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 . . . C22 C -0.039(3) 0.1926(13) 0.6295(8) 0.051(6) Uiso 1 1 d . . . C23 C -0.143(3) 0.2375(15) 0.5912(9) 0.074(7) Uiso 1 1 d . . . H231 H -0.0979 0.2782 0.5669 0.089 Uiso 1 1 calc R . . C24 C -0.314(3) 0.2221(16) 0.5888(9) 0.070(7) Uiso 1 1 d . . . C25 C -0.379(3) 0.1657(13) 0.6243(7) 0.056(6) Uiso 1 1 d . . . H251 H -0.4947 0.1563 0.6216 0.067 Uiso 1 1 calc R . . C26 C -0.283(3) 0.1206(13) 0.6649(8) 0.051(6) Uiso 1 1 d . . . C27 C 0.155(3) 0.2028(15) 0.6297(9) 0.082(8) Uiso 1 1 d . . . H271 H 0.2011 0.1431 0.6176 0.123 Uiso 1 1 calc R . . 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 . . C28 C -0.424(3) 0.2703(17) 0.5446(9) 0.095(8) Uiso 1 1 d . . . H281 H -0.4708 0.2213 0.5205 0.142 Uiso 1 1 calc R . . 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 . . H292 H -0.2822 0.0100 0.7177 0.112 Uiso 1 1 calc R . . H293 H -0.4567 0.0230 0.6847 0.112 Uiso 1 1 calc R . . 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 Col 0.067(3) 0.059(2) 0.046(2) -0.0011(17) 0.0123(17) 0.0066(18) Cl1 0.079(5) 0.091(4) 0.074(4) 0.005(4) 0.025(4) 0.014(4) $C12 \ 0.090(5) \ 0.067(4) \ 0.061(4) \ 0.001(3) \ 0.007(4) \ -0.001(4)$ _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 geom bond atom site label 1 _geom_bond_atom_site_label_2 geom bond distance _geom_bond_site_symmetry 2 geom bond publ flag Col N2 2.037(15) . ? Col N3 2.214(16) . ? Col N1 2.244(15) . ? Col Cll 2.244(7) . ? Col Cl2 2.257(6) . ? N1 C2 1.27(2) . ? N1 C11 1.41(2) . ? N2 C3 1.35(2) . ? N2 C7 1.37(2) . ? N3 C8 1.27(2) . ? N3 C21 1.43(2) . ? C1 C2 1.51(3) . ? C1 H11 0.9600 . ? C1 H12 0.9600 . ? C1 H13 0.9600 . ? C2 C3 1.49(2) . ? C3 C4 1.41(2) . ? C4 C5 1.41(2) . ? C4 H41 0.9300 . ? C5 C6 1.36(2) . ? C5 H51 0.9300 . ? C6 C7 1.35(2) . ? C6 H6 0.9300 . ? C7 C8 1.41(2) . ? C8 C9 1.51(2) . ? C9 H91 0.9600 . ? C9 H92 0.9600 . ? С9 Н93 0.9600 . ? C11 C12 1.34(2) . ? C11 C16 1.41(2) . ? C12 C13 1.39(2) . ? C12 C17 1.50(3) . ? C13 C14 1.35(2) . ? C13 H131 0.9300 . ? C14 C15 1.36(2) . ? C14 C18 1.47(3) . ? C15 C16 1.42(2) . ? C15 H151 0.9300 . ?

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C16 C19 1.48(3) . ?
C17 H171 0.9600 . ?
C17 H172 0.9600 . ?
C17 H173 0.9600 . ?
C18 H181 0.9600 . ?
C18 H182 0.9600 . ?
                  ?
C18 H183 0.9600 .
C19 H191 0.9600 . ?
C19 H192 0.9600 . ?
C19 H193 0.9600 . ?
C21 C22 1.40(2) . ?
C21 C26 1.44(2) . ?
C22 C23 1.36(2) . ?
C22 C27 1.55(3) . ?
C23 C24 1.38(3) . ?
C23 H231 0.9300 . ?
C24 C25 1.33(2) . ?
C24 C28 1.51(3) . ?
C25 C26 1.37(2) . ?
C25 H251 0.9300 . ?
C26 C29 1.49(2) . ?
C27 H271 0.9600 . ?
C27 H272 0.9600 . ?
C27 H273 0.9600 . ?
C28 H281 0.9600 . ?
C28 H282 0.9600 . ?
C28 H283 0.9600 . ?
C29 H291 0.9600 . ?
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N2 Col Cl2 124.5(4) . . ?
N3 Co1 Cl2 98.2(4) . . ?
N1 Co1 Cl2 97.3(4) . . ?
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Cl1 Co1 Cl2 114.9(2) . . ? C2 N1 C11 118.3(18) . . ? C2 N1 Co1 112.2(14) . . ? C11 N1 Co1 129.0(12) . . ? C3 N2 C7 122.9(16) . . ? C3 N2 Co1 118.5(13) . . ? C7 N2 Co1 118.2(14) . . ? C8 N3 C21 121.4(17) . . ? C8 N3 Co1 113.1(14) . . ? C21 N3 Co1 125.0(11) . . ? C2 C1 H11 109.5 . . ? C2 C1 H12 109.5 . . ? H11 C1 H12 109.5 . . ? C2 C1 H13 109.5 . . ? H11 C1 H13 109.5 . . ? H12 C1 H13 109.5 . . ? N1 C2 C3 118(2) . . ? N1 C2 C1 127(2) . . ? C3 C2 C1 115.0(19) . . ? N2 C3 C4 118.4(18) . . ? N2 C3 C2 114.1(17) . . ? C4 C3 C2 127(2) . . ? C5 C4 C3 118(2) . . ? C5 C4 H41 120.9 . . ? C3 C4 H41 120.9 . . ? C6 C5 C4 119(2) . . ? C6 C5 H51 120.3 . . ? C4 C5 H51 120.3 . . ? C7 C6 C5 122(2) . . ? С7 С6 Н6 118.9 . . ? C5 C6 H6 118.9 . . ? C6 C7 N2 118.3(19) . . ? C6 C7 C8 128(2) . . ? N2 C7 C8 113.6(17) . . ? N3 C8 C7 119.6(19) . . ? N3 C8 C9 122.3(19) . . ? C7 C8 C9 118.1(18) . . ? C8 C9 H91 109.5 . . ? C8 C9 H92 109.5 . . ? H91 C9 H92 109.5 . . ? C8 C9 H93 109.5 . . ? Н91 С9 Н93 109.5 . . ? H92 C9 H93 109.5 . . ? C12 C11 C16 120.9(19) . . ? C12 C11 N1 121.5(18) . . ? C16 C11 N1 116.8(18) . . ? C11 C12 C13 119(2) . . ? C11 C12 C17 122.8(19) . . ?

C13	C12	C17	118.	2(18)	•••?
C14	C13	C12	124(2).	. ?
C14	C13	H131	118	.1 .	. ?
C12	C13	H131	118	.1 .	. ?
C13	C14	C15	117(2).	• ?
C13	C14	C18	122(2).	. ?
C15	C14	C18	120(2).	• ?
C14	C15	C16	122(2).	. ?
C14	C15	H151	118	.9.	• ?
C16	C15	H151	118	.9.	• ?
C11	C16	C15	116.	8(19)	•••?
C11	C16	C19	123.	8(18)	•••?
C15	C16	C19	119.	1(18)	••?
C12	C17	H171	109	.5 .	• ?
C12	C17	H172	109	.5.	• ?
H171	C17	7 H17	2 10	9.5	. ?
C12	C17	H173	109	.5.	• ?
H171	C17	7 H17	3 10	9.5	••?
H172	C17	7 H17	3 10	9.5	?
C14	C18	H181	109	.5 .	• ?
C14	C18	H182	109	.5.	• ?
HI81	CIE	3 HI8	2 10	9.5	?
CI4	CT8	HI83	109 2 1 0	.5.	• ?
HIOL	CIE	5 H18	3 IU 2 10	9.5 . 0 E	:
HI82	C10		3 IU 100	9.J.	· • :
C16	C19	птэт u1 Q 2	109	.J . 5	• •
С10 H1 Q1	C10	птэс а н1а	2 10	• J •	• •
C16	C19	н193	109	5	· • •
H191	C10	лтээ Эн19	3 10	• • • 9 5	•••
H192	$C1^{\circ}$	9 н19	3 10	9.5	· · ·
C22	C21	N.3 1	22.1	(18)	?
C22	C21	C2.6	117.	8(18)	?
N3 C	21 0	26 1	20.1	(17)	?
C23	C22	C21	121(2)	. ?
C23	C22	C27	120.	0(19)	?
C21	C22	C27	118.	8(19)	?
C22	C23	C24	120(2).	. ?
C22	C23	H231	120	.1 .	. ?
C24	C23	H231	120	.1 .	. ?
C25	C24	C23	120(2).	. ?
C25	C24	C28	122 (2).	. ?
C23	C24	C28	118(2).	. ?
C24	C25	C26	123(2).	• ?
C24	C25	H251	118	.4 .	• ?
C26	C25	H251	118	.4 .	• ?
C25	<u> </u>	001	117	~ ~ ~ .	-
	C26	CZI	$\perp \perp /$.	8(18)	••?

C21 C26 C29 121.7(19) . . ? C22 C27 H271 109.5 . . ? C22 C27 H272 109.5 . . ? H271 C27 H272 109.5 . . ? C22 C27 H273 109.5 . . ? H271 C27 H273 109.5 . . ? H272 C27 H273 109.5 . . ? C24 C28 H281 109.5 . . ? C24 C28 H282 109.5 . . ? H281 C28 H282 109.5 . . ? C24 C28 H283 109.5 . . ? H281 C28 H283 109.5 . . ? H282 C28 H283 109.5 . . ? C26 C29 H291 109.5 . . ? C26 C29 H292 109.5 . . ? H291 C29 H292 109.5 . . ? C26 C29 H293 109.5 . . ? H291 C29 H293 109.5 . . ? H292 C29 H293 109.5 . . ? _diffrn_measured_fraction_theta max 1.000 diffrn reflns theta full 17.50 _diffrn_measured_fraction_theta_full 1.000

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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.
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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 dichloromethane of crystallization was located
and refined. Analysis using PLATON (Spek, 2003) showed
there were no further solvent-accessible voids.
_____
# 4. TEXT
publ section title
Crystal and Molecular Structure of budz02
publ section abstract
publ section references
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.
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\"ottingen, Germany.
Spek, A. L. (2003).
PLATON. A Multipurpose Crystallographic Tool. Utrecht University,
Utrecht, The Netherlands.
publ section figure captions
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Refinement of F^2^ against ALL reflections. The weighted R-
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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
```

```
on F^2 are statistically about twice as large as those based on
F, and R-
 factors based on ALL data will be even larger.
;
refine ls structure factor coef Fsqd
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Cl1 Cl 0.0524(2) 0.23425(8) 0.27213(11) 0.0645(5) Uani 1 1 d . .
Cl2 Cl 0.4559(2) 0.29676(8) 0.28019(9) 0.0564(5) Uani 1 1 d . . .
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F11 F 0.2997(7) 0.1311(2) -0.0318(3) 0.1025(18) Uani 1 1 d . . . F12 F 0.5373(6) 0.1520(2) 0.0092(3) 0.0943(16) Uani 1 1 d . . . F13 F 0.4196(7) 0.08995(19) 0.0715(3) 0.1008(19) Uani 1 1 d . . . C1 C 0.4018(10) 0.1395(3) 0.0333(4) 0.065(2) Uani 1 1 d . . . C2 C 0.3456(7) 0.1894(3) 0.0828(3) 0.0429(15) Uani 1 1 d . . . C3 C 0.3137(7) 0.2459(3) 0.0404(3) 0.0407(14) Uani 1 1 d . . . C4 C 0.3451(9) 0.2582(3) -0.0370(4) 0.0592(19) Uani 1 1 d . . . H4 H 0.3878 0.2300 -0.0674 0.071 Uiso 1 1 calc R . . C5 C 0.3122(10) 0.3124(4) -0.0675(4) 0.069(2) Uani 1 1 d . . . H5 H 0.3351 0.3217 -0.1186 0.083 Uiso 1 1 calc R . . C6 C 0.2451(9) 0.3534(3) -0.0228(4) 0.062(2) Uani 1 1 d . . . H6 H 0.2191 0.3900 -0.0439 0.075 Uiso 1 1 calc R . . C7 C 0.2174(7) 0.3388(3) 0.0539(3) 0.0435(15) Uani 1 1 d . . . C8 C 0.1394(7) 0.3774(3) 0.1083(3) 0.0425(15) Uani 1 1 d . . . C9 C 0.0794(10) 0.4366(3) 0.0742(5) 0.064(2) Uani 1 1 d . . . F91 F 0.0113(7) 0.4684(2) 0.1230(3) 0.106(2) Uani 1 1 d . . . F92 F -0.0212(7) 0.4287(2) 0.0083(3) 0.1004(17) Uani 1 1 d . . . F93 F 0.1967(6) 0.46726(19) 0.0522(3) 0.0909(16) Uani 1 1 d . . . N1 N 0.3216(6) 0.1858(2) 0.1562(3) 0.0407(12) Uani 1 1 d . . . N2 N 0.2530(6) 0.2862(2) 0.0850(2) 0.0372(11) Uani 1 1 d . . . N3 N 0.1256(6) 0.3589(2) 0.1785(3) 0.0428(12) Uani 1 1 d . . . C11 C 0.3510(7) 0.1354(3) 0.2068(3) 0.0412(14) Uani 1 1 d . . . C12 C 0.2253(8) 0.0993(3) 0.2184(4) 0.0459(15) Uani 1 1 d . . . C13 C 0.2518(9) 0.0547(3) 0.2734(4) 0.0522(17) Uani 1 1 d . . . H13 H 0.1691 0.0303 0.2813 0.063 Uiso 1 1 calc R . . C14 C 0.3961(9) 0.0454(3) 0.3168(4) 0.0559(18) Uani 1 1 d . . . C15 C 0.5195(8) 0.0805(3) 0.3033(4) 0.0546(17) Uani 1 1 d . . . H15 H 0.6182 0.0738 0.3319 0.066 Uiso 1 1 calc R . . C16 C 0.4998(8) 0.1265(3) 0.2470(4) 0.0471(16) Uani 1 1 d . . . C17 C 0.0653(8) 0.1053(3) 0.1677(4) 0.0604(19) Uani 1 1 d . . . H171 H 0.0261 0.1439 0.1733 0.091 Uiso 1 1 calc R . . H172 H -0.0063 0.0778 0.1858 0.091 Uiso 1 1 calc R . . H173 H 0.0752 0.0980 0.1122 0.091 Uiso 1 1 calc R . . C18 C 0.4212(11) -0.0039(4) 0.3777(5) 0.086(3) Uani 1 1 d . . . H181 H 0.3287 -0.0086 0.4035 0.128 Uiso 1 1 calc R . . H182 H 0.5089 0.0050 0.4175 0.128 Uiso 1 1 calc R . . H183 H 0.4416 -0.0393 0.3506 0.128 Uiso 1 1 calc R . . C19 C 0.6392(8) 0.1624(3) 0.2309(5) 0.070(2) Uani 1 1 d . . . H191 H 0.6131 0.2029 0.2324 0.106 Uiso 1 1 calc R . . H192 H 0.6664 0.1529 0.1788 0.106 Uiso 1 1 calc R . . H193 H 0.7266 0.1543 0.2712 0.106 Uiso 1 1 calc R . . C21 C 0.0413(8) 0.3880(2) 0.2364(3) 0.0411(14) Uani 1 1 d . . . C22 C 0.1213(8) 0.4237(3) 0.2945(4) 0.0474(16) Uani 1 1 d . . . C23 C 0.0380(10) 0.4457(3) 0.3535(4) 0.0573(19) Uani 1 1 d . . . H23 H 0.0890 0.4699 0.3930 0.069 Uiso 1 1 calc R . . C24 C -0.1188(10) 0.4325(3) 0.3552(4) 0.0567(18) Uani 1 1 d . . . C25 C -0.1931(8) 0.3981(3) 0.2954(4) 0.0565(18) Uani 1 1 d . . . H25 H -0.2989 0.3899 0.2956 0.068 Uiso 1 1 calc R . .

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C27 C 0.2901(9) 0.4407(3) 0.2937(5) 0.068(2) Uani 1 1 d . . .
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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 . .
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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 . . .
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0.0036(9)
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0.0099(9)
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F13 0.183(6) 0.051(3) 0.082(3) -0.007(2) 0.069(4) 0.017(3)
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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)
C7 \ 0.043(4) \ 0.054(4) \ 0.034(3) \ 0.009(3) \ 0.008(3) \ -0.003(3)
C8 0.042(4) 0.047(4) 0.040(3) 0.011(3) 0.013(3) -0.002(3)
C9 \ 0.076(5) \ 0.060(5) \ 0.059(4) \ 0.025(4) \ 0.016(4) \ 0.014(4)
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)
N1 0.043(3) 0.044(3) 0.035(2) -0.004(2) 0.009(2) -0.005(2)
N2 0.043(3) 0.047(3) 0.024(2) 0.003(2) 0.011(2) -0.007(2)
N3 0.047(3) 0.041(3) 0.043(3) 0.002(2) 0.014(2) -0.002(2)
C11 0.048(4) 0.038(3) 0.041(3) -0.007(3) 0.017(3) 0.003(3)
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)
C14 0.070(5) 0.055(4) 0.044(4) 0.006(3) 0.014(4) 0.011(4)
C15 0.046(4) 0.060(4) 0.056(4) -0.004(3) 0.001(3) 0.015(4)
C16 0.044(4) 0.053(4) 0.047(3) -0.008(3) 0.013(3) 0.004(3)
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)
C23 0.086(6) 0.033(3) 0.053(4) -0.005(3) 0.012(4) 0.008(4)
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)
C191 0.118(2) 0.167(3) 0.130(2) 0.047(2) -0.036(2) -0.028(2)
C192 0.218(4) 0.147(3) 0.094(2) -0.0141(19) -0.010(2) 0.031(3)
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.
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loop
geom bond atom site label 1
geom bond atom site label 2
geom bond distance
geom bond site symmetry 2
geom bond publ flag
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Col N2 2.047(4) . ?
Col Cll 2.2159(17) . ?
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F11 C1 1.320(9) . ?
F12 C1 1.314(9) . ?
F13 C1 1.307(9) . ?
C1 C2 1.532(9) . ?
C2 N1 1.278(7) . ?
C2 C3 1.491(9) . ?
C3 N2 1.339(7) . ?
C3 C4 1.388(8) . ?
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C4 H4 0.9300 . ?
C5 C6 1.377(10) . ?
C5 H5 0.9300 . ?
C6 C7 1.379(8) . ?
С6 Н6 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) . ?
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N1 C11 1.438(8) . ?
N3 C21 1.450(7) . ?
C11 C16 1.380(9) . ?
C11 C12 1.398(9) . ?
C12 C13 1.377(9) . ?
C12 C17 1.523(9) . ?
C13 C14 1.369(10) . ?
C13 H13 0.9300 . ?
C14 C15 1.376(10) . ?
C14 C18 1.523(10) . ?
C15 C16 1.412(9) . ?
C15 H15 0.9300 . ?
C16 C19 1.510(9) . ?
C17 H171 0.9600 . ?
C17 H172 0.9600 . ?
C17 H173 0.9600 . ?
C18 H181 0.9600 . ?
C18 H182 0.9600 . ?
C18 H183 0.9600 . ?
C19 H191 0.9600 . ?
C19 H192 0.9600 . ?
C19 H193 0.9600 . ?
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C21 C22 1.385(9) . ?
C21 C26 1.396(9) . ?
C22 C23 1.391(9) . ?
C22 C27 1.505(10) . ?
C23 C24 1.386(10) . ?
C23 H23 0.9300 . ?
C24 C25 1.367(10) . ?
C24 C28 1.518(9) . ?
C25 C26 1.394(9) . ?
C25 H25 0.9300 . ?
C26 C29 1.496(9) . ?
C27 H271 0.9600 . ?
C27 H272 0.9600 . ?
C27 H273 0.9600 . ?
C28 H281 0.9600 . ?
C28 H282 0.9600 . ?
C28 H283 0.9600 . ?
С29 Н291 0.9600 . ?
C29 H292 0.9600 . ?
C29 H293 0.9600 . ?
C91 C192 1.711(10) 4 566 ?
C91 C191 1.739(9) 4 466 ?
С91 Н911 0.9700 . ?
C91 H912 0.9700 . ?
Cl91 C91 1.739(9) 4 665 ?
Cl92 C91 1.711(10) 4 565 ?
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geom angle atom site label 2
_geom_angle_atom_site_label_3
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geom angle site symmetry 1
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Cl1 Co1 Cl2 114.03(7) . . ?
N2 Co1 N3 75.34(18) . . ?
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F13 C1 F12 106.9(7) . . ?
F13 C1 F11 107.4(7) . . ?
F12 C1 F11 107.3(6) . . ?
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F13 C1 C2 114.4(6) . . ? F12 C1 C2 111.0(6) . . ? F11 C1 C2 109.5(7) . . ? N1 C2 C3 118.2(5) . . ? N1 C2 C1 125.2(6) . . ? C3 C2 C1 116.6(5) . . ? N2 C3 C4 121.3(6) . . ? N2 C3 C2 113.5(5) . . ? C4 C3 C2 125.2(6) . . ? C5 C4 C3 118.6(6) . . ? C5 C4 H4 120.7 . . ? C3 C4 H4 120.7 . . ? C4 C5 C6 120.3(6) . . ? C4 C5 H5 119.9 . . ? C6 C5 H5 119.9 . . ? C5 C6 C7 118.5(7) . . ? C5 C6 H6 120.8 . . ? С7 С6 Н6 120.8 . . ? N2 C7 C6 121.5(6) . . ? N2 C7 C8 113.5(5) . . ? C6 C7 C8 124.9(6) . . ? N3 C8 C7 118.1(5) . . ? N3 C8 C9 124.8(6) . . ? C7 C8 C9 117.1(5) . . ? F91 C9 F92 107.8(7) . . ? F91 C9 F93 107.6(7) . . ? F92 C9 F93 106.1(6) . . ? F91 C9 C8 115.1(6) . . ? F92 C9 C8 109.7(7) . . ? F93 C9 C8 110.2(6) . . ? C2 N1 C11 125.6(5) . . ? C2 N1 Co1 112.6(4) . . ? C11 N1 Co1 121.8(3) . . ? C7 N2 C3 119.7(5) . . ? C7 N2 Co1 119.5(4) . . ? C3 N2 Co1 120.6(4) . . ? C8 N3 C21 125.6(5) . . ? C8 N3 Co1 112.8(4) . . ? C21 N3 Co1 121.5(3) . . ? C16 C11 C12 121.8(6) . . ? C16 C11 N1 119.2(6) . . ? C12 C11 N1 118.9(6) . . ? C13 C12 C11 118.3(6) . . ? C13 C12 C17 119.8(6) . . ? C11 C12 C17 121.7(6) . . ? C14 C13 C12 122.0(6) . . ? C14 C13 H13 119.0 . . ? C12 C13 H13 119.0 . . ?

C13	3	С	1	4	С	1	5		1	1	8	•	9	(6)		•		•		?
C13	3	С	1	4	С	1	8		1	2	0		7	(7)		•			,	?
C15	5	С	1	4	С	1	8		1	2	0		3	(7)					,	?
C14	4	С	1	5	С	1	6		1	2	1		6	(6)					,	?
C14	4	Ċ	1	5	Н	1	5		1	1	9		2	`		<i>,</i>			?	-		
C16	6	C	1	5	Н	1	5		1	1	9	Ī	2		Ī		Ī		?			
C11	1	C	1	6	C	1	5		1	1	7	•	3	(• 6)	•		·		,	2
C11	⊥ 1	C	1	6	C	1	g		1	2	2	•	5		6	, ۱		•		•	,	• >
C1 0	5	C	⊥ 1	6	C	⊥ 1	a		1 1	2	∠ ∩	•	2 2	(6) \		•		•	,	• >
C1	2	C	⊥ 1	7	Ц	⊥ 1	כ ר	1	-	2	0	• a	2	י 5	0	'		•		• ?		•
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	/エ つ	C	1	エ / フ	тт	п 1	т 7	7 2	2	1		0	9	•	5		•		•	S	÷	
	2 7 1	C	T C	/	, п	1 11	1	с 7	S	T	1	9	•	5	5	•		•		:		
П⊥ 111 г	/ ⊥ フ つ			1 / 1 -	,	п 	1	7	с 2		⊥ 1	0	9	•	5		•		•		: ^	
HI Q1	12	~		1 / 0		н 1	T	1	3	1	T	0	9	•	С		•		•	~	:	
CI4	4	C	1	8	H	1	8	T		1	0	9	•	Э г		•		•		:		
CI4	4	C	T	8 1 c	, H	1	8	2	~	Τ	1	9	•	5	_	•		•		2	~	
HI 8	3 T	~	C 1	۲۲ م	\$ 	H 1	T	8	Ζ	1	T	0	9	•	5		•		•	~	2	
CL4	4	С	1	8	Н	1	8	3	~	T	0	9	•	5	_	•		•		2	~	
HI 8	3 T 2 O		C	15	3	н	1	8	3		1	0	9	•	5		•		•		?	
HI 8	32	~	C	1 E	3 	Н	T	8	3	_	T	0	9	•	5		•		•	_	?	
CI	ò	C	1	9	Н	1	9	T		1	0	9	•	5		•		•		?		
C16	ó	С	1	9	Н	1	9	2	~	1	0	9	•	5	_	•		•		?	_	
H19	91		С	19)	Η	1	9	2		1	0	9	•	5		•		•		?	
C10	5	С	1	9	Η	1	9	3	~	1	0	9	•	5	_	•		•		?	_	
H19	91		С	19)	H	1	9	3		1	0	9	•	5		•		•		?	
H19	92	_	С	19)	H	1	9	3	~	1	0	9	•	5		•		•		?	_
C22	2	С	2	1	С	2	6		1	2	2	•	9	(6)		•		•	,	?
C22	2	С	2	1	Ν	3		1	1	9	•	9	(6)		•		•		?	
C26	5	С	2	1	Ν	3	_	1	1	7	•	0	(5)		•		•		?	_
C21	1	С	2	2	С	2	3		1	1	7	•	4	(6)		•		•		?
C21	1	С	2	2	С	2	7		1	2	2	•	5	(6)		•		•		?
C23	3	С	2	2	С	2	7		1	2	0	•	0	(6)		•		•		?
C22	2	С	2	3	С	2	4		1	2	2	•	0	(7)		•		•	,	?
C22	2	С	2	3	Η	2	3		1	1	9	•	0		•		•		?			
C24	4	С	2	3	Η	2	3		1	1	9	•	0		•		•		?			
C25	5	С	2	4	С	2	3		1	1	8	•	2	(6)		•		•	,	?
C25	5	С	2	4	С	2	8		1	2	1	•	1	(7)		•		•		?
C23	3	С	2	4	С	2	8		1	2	0	•	7	(7)		•		•	,	?
C24	4	С	2	5	С	2	6		1	2	3	•	1	(7)		•		•	,	?
C24	4	С	2	5	Η	2	5		1	1	8	•	4		•		•		?			
C26	б	С	2	5	Η	2	5		1	1	8	•	4		•		•		?			
C25	ō	С	2	6	С	2	1		1	1	6	•	4	(6)		•		•	,	?
C25	ō	С	2	6	С	2	9		1	2	0	•	9	(6)		•		•	,	?
C21	1	С	2	6	С	2	9		1	2	2	•	8	(6)		•		•	,	?
C22	2	С	2	7	Η	2	7	1		1	0	9	•	5		•		•		?		
C22	2	С	2	7	Η	2	7	2		1	0	9	•	5		•		•		?		
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   Department of Chemistry
;
    University of Manitoba
    Fort Garry Campus
    Winnipeg, MB R3T 2N2
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;budzelaa@cc.umanitoba.ca
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# 4. TEXT
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Crystal and Molecular Structure of phcOm
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International Tables for X-ray Crystallography (1974).
Vol. IV, Birmingham, England: Kynoch Press.
Sheldrick, G.M. (1996).
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Utrecht, The Netherlands.
publ section figure captions
publ section acknowledgements
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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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(Bruker) '
computing data reduction
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(Bruker) '
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_computing_publication material
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_refine_special details
;
Refinement of F^{2^{-1}} against ALL reflections. The weighted R-
factor wR and
goodness of fit S are based on F^{2^{\prime}}, conventional R-factors R
are based
 on F, with F set to zero for negative F^{2^{-}}. The threshold
expression of
F^2^2 > 2 \text{sigma}(F^2^2) is used only for calculating R-factors(gt)
etc. and is
not relevant to the choice of reflections for refinement. R-
factors based
 on F^2 are statistically about twice as large as those based on
F, and R-
 factors based on ALL data will be even larger.
;
_refine_ls_structure_factor coef Fsqd
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refine ls matrix type
_refine_ls_weighting_scheme
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refine ls weighting details
'calc w=1/[s^2^{(Fo^2^)}+(0.0873P)<sup>2^+</sup>+0.7060P] where
P = (Fo^2 + 2Fc^2) / 3'
atom sites solution primary
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atom sites solution secondary
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refine ls goodness of fit ref
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C46 C 0.0750(2) 0.34946(11) 1.04856(14) 0.0592(5) Uani 1 1 d . . C66 C 0.5028(3) 0.09862(13) 1.06391(17) 0.0833(8) Uani 1 1 d . . H661 H 0.5101 0.0686 1.0243 0.125 Uiso 1 1 calc R . . H662 H 0.4476 0.0838 1.0996 0.125 Uiso 1 1 calc R . . H663 H 0.5868 0.1070 1.0924 0.125 Uiso 1 1 calc R . . Cl1 Cl 0.19269(6) 0.22790(3) 0.82018(3) 0.06654(17) Uani 1 1 d . Cl2 Cl 0.54108(5) 0.29324(3) 0.90265(4) 0.06801(17) Uani 1 1 d . C68 C 0.4463(2) 0.15586(10) 1.02529(12) 0.0543(5) Uani 1 1 d . . C21 C 0.4122(2) 0.11335(10) 0.89812(13) 0.0627(6) Uani 1 1 d . . C22 C 0.3041(3) 0.07677(12) 0.88622(18) 0.0825(8) Uani 1 1 d . . C26 C 0.1887(3) 0.08679(16) 0.9271(3) 0.1092(12) Uani 1 1 d . . . H26 H 0.1976 0.1268 0.9520 0.164 Uiso 1 1 calc R . . C23 C 0.5183(3) 0.10441(14) 0.85876(17) 0.0837(9) Uani 1 1 d . . C24 C 0.6331(4) 0.14434(19) 0.8696(3) 0.1160(14) Uani 1 1 d . . . H24 H 0.6037 0.1845 0.8836 0.174 Uiso 1 1 calc R . . C61 C 0.7005(5) 0.1525(3) 0.7971(3) 0.189(3) Uani 1 1 d . . . H611 H 0.7571 0.1868 0.8046 0.283 Uiso 1 1 calc R . . H612 H 0.6371 0.1589 0.7516 0.283 Uiso 1 1 calc R . . H613 H 0.7497 0.1168 0.7896 0.283 Uiso 1 1 calc R . . C25 C 0.5112(5) 0.05471(19) 0.8071(2) 0.1157(15) Uani 1 1 d . . . H25 H 0.5804 0.0470 0.7803 0.139 Uiso 1 1 calc R . . C51 C 0.2190(2) 0.38799(9) 0.87551(11) 0.0517(5) Uani 1 1 d . . . C52 C 0.2797(2) 0.38462(11) 0.80959(13) 0.0622(6) Uani 1 1 d . . H52 H 0.3414 0.3548 0.8064 0.075 Uiso 1 1 calc R . . C53 C 0.1270(3) 0.43306(13) 0.87687(15) 0.0745(7) Uani 1 1 d . . H53 H 0.0844 0.4367 0.9205 0.089 Uiso 1 1 calc R . . C54 C 0.0977(3) 0.47255(14) 0.81489(19) 0.0905(9) Uani 1 1 d . . H54 H 0.0348 0.5020 0.8169 0.109 Uiso 1 1 calc R . . C55 C 0.1598(3) 0.46902(14) 0.75037(18) 0.0859(8) Uani 1 1 d . . H55 H 0.1408 0.4961 0.7088 0.103 Uiso 1 1 calc R . . C56 C 0.2502(3) 0.42495(14) 0.74829(16) 0.0782(7) Uani 1 1 d . . H56 H 0.2929 0.4220 0.7046 0.094 Uiso 1 1 calc R . . C41 C -0.0141(2) 0.32397(13) 0.99155(18) 0.0770(7) Uani 1 1 d . . H41 H 0.0087 0.3140 0.9428 0.092 Uiso 1 1 calc R . .

C42 C -0.1392(3) 0.31307(18) 1.0071(3) 0.1076(12) Uani 1 1 d . . H42 H -0.2002 0.2959 0.9687 0.129 Uiso 1 1 calc R . . C43 C -0.1713(4) 0.3276(2) 1.0785(4) 0.1346(17) Uani 1 1 d . . . H43 H -0.2553 0.3213 1.0882 0.162 Uiso 1 1 calc R . . C44 C -0.0807(4) 0.3517(2) 1.1374(3) 0.1337(16) Uani 1 1 d . . . H44 H -0.1033 0.3601 1.1867 0.160 Uiso 1 1 calc R . . C45 C 0.0430(3) 0.36329(17) 1.12246(19) 0.0946(10) Uani 1 1 d . . H45 H 0.1040 0.3801 1.1612 0.114 Uiso 1 1 calc R . . C33 C 0.4851(4) 0.4950(2) 1.09499(19) 0.1103(13) Uani 1 1 d . . . H33 H 0.5743 0.4996 1.1034 0.132 Uiso 1 1 calc R . . C34 C 0.4071(6) 0.54308(18) 1.1028(2) 0.1267(18) Uani 1 1 d . . . H34 H 0.4435 0.5806 1.1169 0.152 Uiso 1 1 calc R . . C35 C 0.2761(6) 0.53700(15) 1.0902(2) 0.1248(16) Uani 1 1 d . . . H35 H 0.2238 0.5706 1.0938 0.150 Uiso 1 1 calc R . . C20 C 0.4085(7) 0.0181(2) 0.7953(2) 0.138(2) Uani 1 1 d . . . H20 H 0.4073 -0.0143 0.7607 0.166 Uiso 1 1 calc R . . C27 C 0.3062(5) 0.02812(17) 0.8335(2) 0.1223(15) Uani 1 1 d . . . H27 H 0.2355 0.0022 0.8248 0.147 Uiso 1 1 calc R . . C64 C 0.1825(6) 0.0395(3) 0.9922(4) 0.169(2) Uani 1 1 d . . . H641 H 0.1652 0.0004 0.9688 0.253 Uiso 1 1 calc R . . H642 H 0.1148 0.0501 1.0219 0.253 Uiso 1 1 calc R . . H643 H 0.2634 0.0386 1.0265 0.253 Uiso 1 1 calc R . . C65 C 0.0639(4) 0.0866(2) 0.8693(4) 0.175(3) Uani 1 1 d . . . H651 H 0.0691 0.1163 0.8292 0.262 Uiso 1 1 calc R . . H652 H -0.0072 0.0960 0.8968 0.262 Uiso 1 1 calc R . . H653 H 0.0510 0.0473 0.8457 0.262 Uiso 1 1 calc R . . C62 C 0.7347(5) 0.1246(3) 0.9352(3) 0.171(2) Uani 1 1 d . . . H621 H 0.7059 0.1327 0.9848 0.256 Uiso 1 1 calc R . . H622 H 0.8130 0.1466 0.9323 0.256 Uiso 1 1 calc R . . H623 H 0.7503 0.0821 0.9306 0.256 Uiso 1 1 calc R . . 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 Col 0.04204(17) 0.05480(18) 0.03275(16) -0.00244(10) 0.00146(11) 0.00324(10) $P2 \ 0.0497(3) \ 0.0533(3) \ 0.0399(3) \ -0.0080(2) \ 0.0070(2) \ 0.0010(2)$ N2 0.0445(9) 0.0559(9) 0.0356(8) 0.0003(7) 0.0024(7) 0.0004(7) N3 0.0557(10) 0.0573(9) 0.0382(8) -0.0027(7) 0.0031(7) 0.0121(8) N1 0.0445(9) 0.0541(9) 0.0468(9) 0.0026(7) 0.0034(7) 0.0078(7)

C15 0.0466(10) 0.0615(12) 0.0364(9) -0.0018(8) 0.0057(8) -0.0027(9) $C11 \ 0.0470(11) \ 0.0647(12) \ 0.0426(10) \ 0.0096(9) \ 0.0033(8) -$ 0.0006(9) $C14 \ 0.0676(14) \ 0.0799(16) \ 0.0442(11) \ 0.0147(11) \ -0.0002(10)$ 0.0001(12)C13 0.0820(17) 0.0940(18) 0.0330(11) 0.0060(11) -0.0003(11) -0.0069(14)c12 0.0729(14) 0.0779(15) 0.0384(10) -0.0070(10) 0.0088(10) -0.0071(12)C31 0.0830(16) 0.0567(12) 0.0441(11) -0.0066(9) 0.0089(10) -0.0110(11)C32 0.095(2) 0.0876(18) 0.0626(15) -0.0117(13) 0.0206(14) -0.0329(16)C36 0.123(3) 0.0656(16) 0.0767(18) -0.0155(13) -0.0015(17) 0.0107(16)C46 0.0498(12) 0.0665(13) 0.0623(13) -0.0036(10) 0.0112(10) 0.0054(10)C66 0.106(2) 0.0765(17) 0.0671(15) 0.0220(13) 0.0108(14) 0.0322(15)Cl1 0.0663(4) 0.0704(3) 0.0551(3) -0.0039(2) -0.0173(3) -0.0020(3)C12 0.0458(3) 0.0716(4) 0.0861(4) -0.0094(3) 0.0075(3) -0.0097(2) C68 0.0506(11) 0.0623(12) 0.0490(11) 0.0110(9) 0.0041(9) 0.0104(9)C21 0.0774(15) 0.0584(12) 0.0501(12) 0.0030(10) 0.0016(11) 0.0271(11) $C22 \ 0.095(2) \ 0.0602(14) \ 0.0837(18) \ -0.0141(13) \ -0.0155(16)$ 0.0075(14) $C26 \ 0.086(2) \ 0.080(2) \ 0.160(4) \ -0.016(2) \ 0.009(2) \ -0.0251(17)$ C23 0.108(2) 0.0784(17) 0.0693(16) 0.0145(13) 0.0268(15) 0.0472(17)C24 0.117(3) 0.105(3) 0.142(3) 0.011(2) 0.074(3) 0.041(2) C61 0.152(4) 0.239(6) 0.202(5) 0.131(5) 0.114(4) 0.106(4) $C25 \ 0.181(4) \ 0.096(3) \ 0.075(2) \ 0.0029(19) \ 0.037(2) \ 0.069(3)$ $C51 \ 0.0562(12) \ 0.0523(11) \ 0.0442(10) \ -0.0008(8) \ -0.0004(9)$ 0.0034(9)C52 0.0670(14) 0.0645(13) 0.0560(13) 0.0073(10) 0.0118(10) 0.0079(11)C53 0.0829(18) 0.0798(17) 0.0608(14) 0.0047(12) 0.0102(12) 0.0265(14)C54 0.104(2) 0.0770(18) 0.090(2) 0.0157(15) 0.0120(17) 0.0385(16) C55 0.104(2) 0.0786(18) 0.0740(17) 0.0287(14) 0.0076(15)0.0113(16)C56 0.0857(18) 0.0886(18) 0.0621(15) 0.0230(13) 0.0172(13) 0.0076(14) $C41 \ 0.0557(14) \ 0.0844(17) \ 0.0884(18) \ -0.0006(14) \ 0.0023(12) \ -$ 0.0029(12)

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C45 0.0725(18) 0.128(3) 0.091(2) -0.0220(19) 0.0372(16) -
0.0036(17)
C33 0.146(3) 0.114(3) 0.0731(19) -0.0087(18) 0.0234(19) -0.074(3)
C34 0.231(6) 0.072(2) 0.073(2) -0.0013(16) 0.005(3) -0.054(3)
C35 0.212(5) 0.0582(18) 0.096(3) -0.0103(17) -0.006(3) 0.012(2)
C20 \ 0.239(6) \ 0.096(3) \ 0.072(2) \ -0.023(2) \ -0.004(3) \ 0.063(4)
C27 0.165(4) 0.077(2) 0.108(3) -0.0260(19) -0.037(3) 0.017(2)
C64 0.162(5) 0.176(5) 0.174(5) -0.010(4) 0.046(4) -0.042(4)
C65 0.087(3) 0.139(4) 0.281(7) 0.009(4) -0.028(4) -0.039(3)
C62 \ 0.125(4) \ 0.280(8) \ 0.113(3) \ 0.003(4) \ 0.036(3) \ -0.040(5)
_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
geom bond atom site label 1
geom bond atom site label 2
geom bond distance
geom bond site symmetry 2
geom bond publ flag
Col N2 2.0603(16) . ?
Col N3 2.1094(17) . ?
Col Cll 2.2550(6) . ?
Col Cl2 2.2940(6) . ?
Col N1 2.3114(16) . ?
P2 N3 1.5982(16) . ?
P2 C46 1.797(2) . ?
P2 C31 1.795(2) . ?
P2 C15 1.824(2) . ?
N2 C15 1.337(3) . ?
N2 C11 1.339(3) . ?
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N3 C51 1.422(3) . ?

N1 C68 1.276(3) . ? N1 C21 1.451(3) . ? C15 C12 1.384(3) . ? C11 C14 1.383(3) . ? C11 C68 1.485(3) . ? C14 C13 1.374(4) . ? C14 H14 0.9300 . ? C13 C12 1.382(4) . ? C13 H13 0.9300 . ? C12 H12 0.9300 . ? C31 C36 1.373(4) . ? C31 C32 1.386(4) . ? C32 C33 1.384(4) . ? C32 H32 0.9300 . ? C36 C35 1.390(5) . ? C36 H36 0.9300 . ? C46 C41 1.372(4) . ? C46 C45 1.394(4) . ? C66 C68 1.509(3) . ? C66 H661 0.9600 . ? C66 H662 0.9600 . ? C66 H663 0.9600 . ? C21 C22 1.382(4) . ? C21 C23 1.396(4) . ? C22 C27 1.407(5) . ? C22 C26 1.500(5) . ? C26 C65 1.522(6) . ? C26 C64 1.538(6) . ? C26 H26 0.9800 . ? C23 C25 1.407(5) . ? C23 C24 1.481(6) . ? C24 C62 1.497(6) . ? C24 C61 1.529(5) . ? C24 H24 0.9800 . ? C61 H611 0.9600 . ? C61 H612 0.9600 . ? С61 Н613 0.9600 . ? C25 C20 1.337(7) . ? C25 H25 0.9300 . ? C51 C52 1.379(3) . ? C51 C53 1.388(3) . ? C52 C56 1.380(3) . ? C52 H52 0.9300 . ? C53 C54 1.376(4) . ? С53 Н53 0.9300 . ? C54 C55 1.367(4) . ? C54 H54 0.9300 . ? C55 C56 1.362(4) . ?

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C56 H56 0.9300 . ?
C41 C42 1.395(4) . ?
C41 H41 0.9300 . ?
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C42 H42 0.9300 . ?
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C43 H43 0.9300 . ?
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C45 H45 0.9300 . ?
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СЗ4 НЗ4 0.9300 . ?
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C20 C27 1.354(7) . ?
C20 H20 0.9300 . ?
C27 H27 0.9300 . ?
C64 H641 0.9600 . ?
С64 Н642 0.9600 . ?
С64 Н643 0.9600 . ?
С65 Н651 0.9600 . ?
C65 H652 0.9600 . ?
C65 H653 0.9600 . ?
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C62 H623 0.9600 . ?
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geom angle atom site label 3
geom angle
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_geom_angle_site_symmetry_3
geom angle publ flag
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N2 Co1 Cl1 135.03(5) . . ?
N3 Co1 Cl1 98.07(5) . . ?
N2 Co1 Cl2 100.96(5) . . ?
N3 Co1 Cl2 99.14(5) . . ?
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N2 Col N1 73.39(6) . . ?
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N3 P2 C46 115.14(10) . . ?
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N3 P2 C31 114.98(10) ?	
C46 P2 C31 110.01(11) ?	
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C14 C13 H13 120.1 ?	
C12 C13 H13 120.1 ?	
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С15 С12 Н12 121.2 ?	
С13 С12 Н12 121.2 ?	
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СЗ1 СЗ2 НЗ2 119.8 ?	
СЗЗ СЗ2 НЗ2 119.8 ?	
C31 C36 C35 119.8(4) ?	
СЗ1 СЗ6 НЗ6 120.1 ?	
СЗ5 СЗ6 НЗ6 120.1 ?	
C41 C46 C45 120.7(2) ?	
C41 C46 P2 117.58(19) ?	
C45 C46 P2 121.6(2) ?	
C68 C66 H661 109.5 ?	
C68 C66 H662 109.5 ?	
H661 C66 H662 109.5 ?	
С68 С66 Н663 109.5 ?	
H661 C66 H663 109.5 ?	
H662 C66 H663 109.5 ?	
N1 C68 C11 116.17(18) ?	

N1 (C68 (C66 1	26.3(2) ?
C11	C68	C66	117.55(19) ?
C22	C21	C23	122.6(3) ?
C22	C21	N1 1	17.8(2) ?
C23	C21	N1 1	19.6(3) ?
C21	C22	C27	116.9(4) ?
C21	C22	C26	122.9(2) ?
C27	C22	C26	120.2(3) ?
C22	C26	C65	111.6(4) ?
C22	C26	C64	111.3(4) ?
C65	C26	C64	110.4(4) ?
C22	C26	H26	107.8 ?
C65	C26	H26	107.8 ?
C64	C26	H26	107.8 ?
C21	C23	C25	116.3(4) ?
C21	C23	C24	122.9(3) ?
C25	C23	C24	120.8(3) ?
C23	C24	C62	113.4(4) ?
C23	C24	C61	115.5(4) ?
C62	C24	C61	106.5(4) ?
C23	C24	H24	107.0 ?
C62	C24	H24	107.0 ?
C61	C24	H24	107.0 ?
C24	C61	H611	109.5 ?
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H61	1 C61	H61	2 109.5 ?
C24	C61	H613	3 109.5 ?
H61	1 C61	L H61	3 109.5 ?
H612	2 C61	H61	3 109.5 ?
C20	C25	C23	122.4(4) ?
C20	C25	H25	118.8 ?
C23	C25	H25	118.8 ?
C52	C51	C53	117.2(2) ?
C52	C51	N3 1	18.51(19) ?
C53	C51	N3 1	24.3(2) ?
C51	C52	C56	120.8(2) ?
C51	C52	H52	119.6 ?
C56	C52	H52	119.6 ?
C54	C53	C51	121.3(2) ?
C54	C53	H53	119.4 ?
C51	C53	H53	119.4 ?
C55	C54	C53	120.8(3) ?
C55	C54	H54	119.6 ?
C53	C54	H54	119.6 ?
C56	C55	C54	118.5(2) ?
C56	C55	H55	120.8 ?
C54	C55	H55	120.8 ?
C55	C56	C52	121.4(3) ?

| 55 | | С | 5 | 6

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52	

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<td>55C56H5652C56H5654C41C4246C41H4142C41H4143C42C4143C42H4241C42H4242C43H4344C43H4345C44H4443C44H4444C45C4644C45C4644C45C4644C45C4644C45H4534C33C3233C34H3333C34C3533C34H3434C35C3634C35H3535C20C2725C20H2020C27H2726C64H64126C65H65126C65H65126C65H65126C65H65126C65H65126C65H65126C65H65126C65H65226C65H65226C65H65126C65H65226C65H65227C26C6528C62H62129C27C2620C27H2721C65H65222C65H65223C65H652<!--</td--><td>55C56H56152C56H56154C41C42146C41H41142C41H41143C42C41143C42C42143C42H42142C43C44142C43H43144C43H43145C44H44144C45C46144C45C46144C45C46144C45H45145C44H44144C45C46144C45C46145C44H44146C45H45137C33C32138C34H33139C34H34131C35C36132C34H34133C34H34134C35H35135C20C27120C27H20120C27H27120C27H27120C27H27120C27H27121C64H643641C65H653651C65H653651C65H65324</td><td>55C56H561152C56H561146C41C421146C41H411242C41H411243C42C411143C42H421241C42H421242C43C441242C43H431144C43H431145C44H441244C45C461145C44H441244C45C461145C44H441246C45H451234C33C321134C33C321135C34H341134C35C361233C34C35H351234C35H351225C20C271226C64H641126C64H642127C20H201126C64H643127C20H271126C64H643127C64H643126C65H653127C65H653126C65H653126C65H653127C65H653126C65H6531<</td><td>55C56H5611952C56H5611954C41C4211946C41H4112042C41H4112043C42C4111943C42C4111943C42H4212041C42H4212042C43C4412142C43H4311944C43H4311945C44C4311944C45C4611944C45C4611944C45H4512044C45H4512034C33C3211934C33C3211934C35C3612033C34H3411934C35C3612035C34H3411934C35C3612035C20C2712026C64H6411026C64H6421026C64H6431026C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651<td>55$C56$$H56$$119$.$52$$C56$$H56$$119$.$52$$C56$$H56$$119$.$52$$C56$$H56$$119$.$54$$C41$$H41$$120$.$42$$C41$$H41$$120$.$43$$C42$$H42$$120$.$43$$C42$$H42$$120$.$42$$C43$$C44$$121$.$42$$C43$$H43$$119$.$44$$C43$$H43$$119$.$45$$C44$$H44$$120$.$44$$C45$$C46$$119$.$44$$C45$$C46$$119$.$44$$C45$$H45$$120$.$34$$C33$$C32$$119$.$34$$C33$$C32$$119$.$34$$C35$$C36$$120$.$33$$C34$$H34$$119$.$34$$C35$$G36$$120$.$35$$C34$$H34$$119$.$34$$C35$$H35$$120$.$25$$C20$$C27$$120$.$25$$C20$$H20$$119$.$26$$C64$$H642$$109$$26$$C64$$H643$$109$$641$$C64$$H643$$109$$26$$C65$$H653$$109$$651$$C65$$H653$$109$$651$$C65$$H653$$109$$651$$C65$$H653$$109$$651$</td><td>55C56H56119.352C56H56119.354C41C42119.654C41H41120.242C41H41120.243C42C41119.743C42H42120.241C42H42120.242C43C44121.142C43H43119.444C43H43119.444C43H43119.444C43H43119.745C44C43119.745C44H44120.144C45C46119.044C45C46119.044C45C46119.044C45H45120.534C33C32119.633C34H34119.634C35C36120.034C35C36120.034C35H35120.035C34H34119.634C35H35120.035C20C27120.225C20H20119.920C27C22121.620C27H27119.221C64H64210922C27H27119.223C64H64310924C65H65310925C65H65310926<!--</td--><td>55$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$54$$C41$$C42$$119.6$ 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H3</td></td></td></td></t<></td></td></td></td> | 55C56H5652C56H5654C41C4246C41H4142C41H4143C42C4143C42H4241C42H4242C43H4344C43H4345C44H4443C44H4444C45C4644C45C4644C45C4644C45C4644C45H4534C33C3233C34H3333C34C3533C34H3434C35C3634C35H3535C20C2725C20H2020C27H2726C64H64126C65H65126C65H65126C65H65126C65H65126C65H65126C65H65126C65H65126C65H65226C65H65226C65H65126C65H65226C65H65227C26C6528C62H62129C27C2620C27H2721C65H65222C65H65223C65H652 </td
<td>55C56H56152C56H56154C41C42146C41H41142C41H41143C42C41143C42C42143C42H42142C43C44142C43H43144C43H43145C44H44144C45C46144C45C46144C45C46144C45H45145C44H44144C45C46144C45C46145C44H44146C45H45137C33C32138C34H33139C34H34131C35C36132C34H34133C34H34134C35H35135C20C27120C27H20120C27H27120C27H27120C27H27120C27H27121C64H643641C65H653651C65H653651C65H65324</td> <td>55C56H561152C56H561146C41C421146C41H411242C41H411243C42C411143C42H421241C42H421242C43C441242C43H431144C43H431145C44H441244C45C461145C44H441244C45C461145C44H441246C45H451234C33C321134C33C321135C34H341134C35C361233C34C35H351234C35H351225C20C271226C64H641126C64H642127C20H201126C64H643127C20H271126C64H643127C64H643126C65H653127C65H653126C65H653126C65H653127C65H653126C65H6531<</td> <td>55C56H5611952C56H5611954C41C4211946C41H4112042C41H4112043C42C4111943C42C4111943C42H4212041C42H4212042C43C4412142C43H4311944C43H4311945C44C4311944C45C4611944C45C4611944C45H4512044C45H4512034C33C3211934C33C3211934C35C3612033C34H3411934C35C3612035C34H3411934C35C3612035C20C2712026C64H6411026C64H6421026C64H6431026C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651C65H65310651<td>55$C56$$H56$$119$.$52$$C56$$H56$$119$.$52$$C56$$H56$$119$.$52$$C56$$H56$$119$.$54$$C41$$H41$$120$.$42$$C41$$H41$$120$.$43$$C42$$H42$$120$.$43$$C42$$H42$$120$.$42$$C43$$C44$$121$.$42$$C43$$H43$$119$.$44$$C43$$H43$$119$.$45$$C44$$H44$$120$.$44$$C45$$C46$$119$.$44$$C45$$C46$$119$.$44$$C45$$H45$$120$.$34$$C33$$C32$$119$.$34$$C33$$C32$$119$.$34$$C35$$C36$$120$.$33$$C34$$H34$$119$.$34$$C35$$G36$$120$.$35$$C34$$H34$$119$.$34$$C35$$H35$$120$.$25$$C20$$C27$$120$.$25$$C20$$H20$$119$.$26$$C64$$H642$$109$$26$$C64$$H643$$109$$641$$C64$$H643$$109$$26$$C65$$H653$$109$$651$$C65$$H653$$109$$651$$C65$$H653$$109$$651$$C65$$H653$$109$$651$</td><td>55C56H56119.352C56H56119.354C41C42119.654C41H41120.242C41H41120.243C42C41119.743C42H42120.241C42H42120.242C43C44121.142C43H43119.444C43H43119.444C43H43119.444C43H43119.745C44C43119.745C44H44120.144C45C46119.044C45C46119.044C45C46119.044C45H45120.534C33C32119.633C34H34119.634C35C36120.034C35C36120.034C35H35120.035C34H34119.634C35H35120.035C20C27120.225C20H20119.920C27C22121.620C27H27119.221C64H64210922C27H27119.223C64H64310924C65H65310925C65H65310926<!--</td--><td>55$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$54$$C41$$C42$$119.6$ ($46$$C41$$H41$$120.2$$43$$C42$$C41$$119.7$ ($43$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$42$$C43$$C44$$120.1$$42$$C43$$H43$$119.4$$44$$C43$$H43$$119.4$$45$$C44$$C43$$119.7$ ($44$$C45$$C46$$119.0$ ($44$$C45$$C46$$119.0$ ($44$$C45$$H45$$120.5$$34$$C33$$C32$$119.6$ ($34$$C33$$C32$$119.6$ ($34$$C35$$C36$$120.0$ ($34$$C35$$C36$$120.0$ ($34$$C35$$C36$$120.0$ ($25$$C20$$C27$$120.2$ ($25$$C20$$C27$$120.2$ ($25$$C20$$H27$$119.2$$26$$C64$$H642$$109.5$$541$$C64$$H643$$109.5$$541$$C64$$H643$$109.5$$541$$C65$$H653$$109.5$$561$$C65$$H653$$109.5$$561$$C$</td><td>$\begin{array}{r} 55 \ C56 \ H56 \ 119.3 \ . \\ 52 \ C56 \ H56 \ 119.3 \ . \\ 46 \ C41 \ C42 \ 119.6 (3) \\ 46 \ C41 \ H41 \ 120.2 \ . \\ 42 \ C41 \ H41 \ 120.2 \ . \\ 42 \ C41 \ H41 \ 120.2 \ . \\ 43 \ C42 \ C41 \ 119.7 (4) \\ 43 \ C42 \ C41 \ 120.2 \ . \\ 41 \ C42 \ H42 \ 120.2 \ . \\ 41 \ C42 \ H42 \ 120.2 \ . \\ 42 \ C43 \ C44 \ 120.1 \ . \\ 42 \ C43 \ H43 \ 119.4 \ . \\ 42 \ C43 \ H43 \ 119.4 \ . \\ 44 \ C43 \ H43 \ 119.4 \ . \\ 45 \ C44 \ C43 \ H44 \ 120.1 \ . \\ 45 \ C44 \ C43 \ H44 \ 120.1 \ . \\ 45 \ C44 \ H44 \ 120.1 \ . \\ 45 \ C44 \ H44 \ 120.1 \ . \\ 45 \ C44 \ H44 \ 120.1 \ . \\ 45 \ C44 \ H44 \ 120.1 \ . \\ 45 \ C44 \ H44 \ 120.1 \ . \\ 46 \ C45 \ H45 \ 120.5 \ . \\ 46 \ C45 \ H45 \ 120.5 \ . \\ 46 \ C45 \ H45 \ 120.5 \ . \\ 46 \ C45 \ H45 \ 120.5 \ . \\ 46 \ C45 \ H45 \ 120.6 \ . \\ 33 \ C34 \ H34 \ 119.6 \ . \\ 34 \ C33 \ C34 \ H34 \ 119.6 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 33 \ C34 \ H34 \ 119.6 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C41 \ C64 \ H642 \ 109.5 \ . \\ 3641 \ C64 \ H642 \ 109.5 \ . \\ 3641 \ C64 \ H643 \ 109.5 \ . \\ 3641 \ C64 \ H643 \ 109.5 \ . \\ 3641 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \ . \ . \ . \ . \ . \ . \ . \ . \$</td><td>55C56H56119.352C56H56119.354C41C42119.6(3)46C41H41120.242C41H41120.243C42C42120.243C42H42120.241C42H42120.242C43C44121.1(3)42C43C44121.1(3)42C43H43119.444C43H43119.445C44C43119.7(4)45C44C43119.7(4)45C44C43119.7(4)45C44H44120.143C44H44120.144C45C46119.0(3)44C45C46119.0(3)44C45C46119.0(3)44C45C46119.0(3)44C45C46119.0(2)34C33C32119.6(4)34C33H33120.233C34H34119.634C35H35120.035C34H34119.634C35H35120.035C34H34119.634C35H35120.035C20C27120.220C27H27119.220C27H27119.221C64H643109.524C65<t< td=""><td>55 C56 H56 119.3 . 52 C56 H56 119.3 . 54 C41 C42 119.6(3) 46 C41 H41 120.2 . 42 C41 H41 120.2 . 43 C42 C41 119.7(4) 43 C42 H42 120.2 . 41 C42 H42 120.2 . 41 C42 H42 120.2 . 42 C43 C44 120.1 . 42 C43 H43 119.4 . 44 C43 H43 119.4 . 45 C44 H44 120.1 . 45 C44 H44 120.1 . 45 C44 H44 120.1 . 46 C45 H45 120.5 . 34 C33 C32 119.0(3) . 34 C33 C32 120.5 . 35<td>55 C56 H56 119.3 52 C56 H56 119.3 46 C41 C42 119.6(3) 46 C41 H41 120.2 42 C41 H41 120.2 43 C42 C41 119.7(4) 43 C42 H42 120.2 41 C42 H42 120.2 42 C43 C44 120.1 42 C43 H43 119.4 44 C43 H43 119.4 45 C44 C43 119.7(4) 45 C44 C43 119.7(4) 45 C44 C43 119.7(4) 45 C44 C43 119.7(4) 45 C44 C43 120.1 46 C45 H45 120.5 34 C33 C32<!--</td--><td>$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$</td><td>55 C56 H56 119.3 ? 52 C56 H56 119.3 ? 46 C41 C42 119.6(3) . 46 C41 H41 120.2 ? 43 C42 C41 119.7(4) . 43 C42 H42 120.2 ? 41 C42 H42 120.2 ? 42 C43 C44 121.1(3) . 42 C43 C44 120.1 ? 44 C43 H43 119.4 ? 45 C44 C43 119.7(4) . 45 C44 H44 120.1 . 45 C44 H44 120.1 . 44 C45 H45 120.5 . 44 C45 H45 120.5 . 44 C45 H45 120.5 . 34 C33 H33 120.2 . 35 C34 H34 119.6 .<td>55 C56 H56 119.3 ? 52 C56 H56 119.3 ? 46 C41 C42 119.6 (3) . 46 C41 H41 120.2 ? 43 C42 C41 119.7 (4) . 43 C42 C41 120.2 ? 43 C42 H42 120.2 ? 41 C42 H42 120.2 ? 42 C43 C42 120.2 ? 41 C42 H42 120.2 ? 42 C43 C44 120.1 ? 44 C43 H19.4 ? ? 45 C44 H44 120.1 ? 45 C44 H44 120.5 ? 44 C45 H45 120.5 ? 44 C45 H45 120.5 ? 34 C33 C32 119.6 (4) . 34 C33 H3</td></td></td></td></t<></td></td></td> | 55C56H56152C56H56154C41C42146C41H41142C41H41143C42C41143C42C42143C42H42142C43C44142C43H43144C43H43145C44H44144C45C46144C45C46144C45C46144C45H45145C44H44144C45C46144C45C46145C44H44146C45H45137C33C32138C34H33139C34H34131C35C36132C34H34133C34H34134C35H35135C20C27120C27H20120C27H27120C27H27120C27H27120C27H27121C64H643641C65H653651C65H653651C65H65324 | 55C56H561152C56H561146C41C421146C41H411242C41H411243C42C411143C42H421241C42H421242C43C441242C43H431144C43H431145C44H441244C45C461145C44H441244C45C461145C44H441246C45H451234C33C321134C33C321135C34H341134C35C361233C34C35H351234C35H351225C20C271226C64H641126C64H642127C20H201126C64H643127C20H271126C64H643127C64H643126C65H653127C65H653126C65H653126C65H653127C65H653126C65H6531< |
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<td>55$C56$$H56$$119$.$52$$C56$$H56$$119$.$52$$C56$$H56$$119$.$52$$C56$$H56$$119$.$54$$C41$$H41$$120$.$42$$C41$$H41$$120$.$43$$C42$$H42$$120$.$43$$C42$$H42$$120$.$42$$C43$$C44$$121$.$42$$C43$$H43$$119$.$44$$C43$$H43$$119$.$45$$C44$$H44$$120$.$44$$C45$$C46$$119$.$44$$C45$$C46$$119$.$44$$C45$$H45$$120$.$34$$C33$$C32$$119$.$34$$C33$$C32$$119$.$34$$C35$$C36$$120$.$33$$C34$$H34$$119$.$34$$C35$$G36$$120$.$35$$C34$$H34$$119$.$34$$C35$$H35$$120$.$25$$C20$$C27$$120$.$25$$C20$$H20$$119$.$26$$C64$$H642$$109$$26$$C64$$H643$$109$$641$$C64$$H643$$109$$26$$C65$$H653$$109$$651$$C65$$H653$$109$$651$$C65$$H653$$109$$651$$C65$$H653$$109$$651$</td> <td>55C56H56119.352C56H56119.354C41C42119.654C41H41120.242C41H41120.243C42C41119.743C42H42120.241C42H42120.242C43C44121.142C43H43119.444C43H43119.444C43H43119.444C43H43119.745C44C43119.745C44H44120.144C45C46119.044C45C46119.044C45C46119.044C45H45120.534C33C32119.633C34H34119.634C35C36120.034C35C36120.034C35H35120.035C34H34119.634C35H35120.035C20C27120.225C20H20119.920C27C22121.620C27H27119.221C64H64210922C27H27119.223C64H64310924C65H65310925C65H65310926<!--</td--><td>55$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$54$$C41$$C42$$119.6$ ($46$$C41$$H41$$120.2$$43$$C42$$C41$$119.7$ ($43$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$42$$C43$$C44$$120.1$$42$$C43$$H43$$119.4$$44$$C43$$H43$$119.4$$45$$C44$$C43$$119.7$ ($44$$C45$$C46$$119.0$ ($44$$C45$$C46$$119.0$ ($44$$C45$$H45$$120.5$$34$$C33$$C32$$119.6$ ($34$$C33$$C32$$119.6$ ($34$$C35$$C36$$120.0$ ($34$$C35$$C36$$120.0$ ($34$$C35$$C36$$120.0$ ($25$$C20$$C27$$120.2$ ($25$$C20$$C27$$120.2$ 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C33 \ C34 \ H34 \ 119.6 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 33 \ C34 \ H34 \ 119.6 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 34 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C35 \ H35 \ 120.0 \ . \\ 36 \ C41 \ C64 \ H642 \ 109.5 \ . \\ 3641 \ C64 \ H642 \ 109.5 \ . \\ 3641 \ C64 \ H643 \ 109.5 \ . \\ 3641 \ C64 \ H643 \ 109.5 \ . \\ 3641 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \\ 3651 \ C65 \ H653 \ 109.5 \ . \ . \ . \ . \ . \ . \ . \ . \ . \$</td><td>55C56H56119.352C56H56119.354C41C42119.6(3)46C41H41120.242C41H41120.243C42C42120.243C42H42120.241C42H42120.242C43C44121.1(3)42C43C44121.1(3)42C43H43119.444C43H43119.445C44C43119.7(4)45C44C43119.7(4)45C44C43119.7(4)45C44H44120.143C44H44120.144C45C46119.0(3)44C45C46119.0(3)44C45C46119.0(3)44C45C46119.0(3)44C45C46119.0(2)34C33C32119.6(4)34C33H33120.233C34H34119.634C35H35120.035C34H34119.634C35H35120.035C34H34119.634C35H35120.035C20C27120.220C27H27119.220C27H27119.221C64H643109.524C65<t< td=""><td>55 C56 H56 119.3 . 52 C56 H56 119.3 . 54 C41 C42 119.6(3) 46 C41 H41 120.2 . 42 C41 H41 120.2 . 43 C42 C41 119.7(4) 43 C42 H42 120.2 . 41 C42 H42 120.2 . 41 C42 H42 120.2 . 42 C43 C44 120.1 . 42 C43 H43 119.4 . 44 C43 H43 119.4 . 45 C44 H44 120.1 . 45 C44 H44 120.1 . 45 C44 H44 120.1 . 46 C45 H45 120.5 . 34 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55C56H56119.352C56H56119.354C41C42119.654C41H41120.242C41H41120.243C42C41119.743C42H42120.241C42H42120.242C43C44121.142C43H43119.444C43H43119.444C43H43119.444C43H43119.745C44C43119.745C44H44120.144C45C46119.044C45C46119.044C45C46119.044C45H45120.534C33C32119.633C34H34119.634C35C36120.034C35C36120.034C35H35120.035C34H34119.634C35H35120.035C20C27120.225C20H20119.920C27C22121.620C27H27119.221C64H64210922C27H27119.223C64H64310924C65H65310925C65H65310926 </td <td>55$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$52$$C56$$H56$$119.3$$54$$C41$$C42$$119.6$ ($46$$C41$$H41$$120.2$$43$$C42$$C41$$119.7$ ($43$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$41$$C42$$H42$$120.2$$42$$C43$$C44$$120.1$$42$$C43$$H43$$119.4$$44$$C43$$H43$$119.4$$45$$C44$$C43$$119.7$ ($44$$C45$$C46$$119.0$ ($44$$C45$$C46$$119.0$
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H621 C62 H623 109.5 . . ? H622 C62 H623 109.5 . . ?

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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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# 3. AUTHOR LIST
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Crystal and Molecular Structure of budz05
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_____
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reflns threshold expression
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(Bruker) '
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computing molecular graphics
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computing publication material
                                   ?
refine special details
;
Refinement of F^2^ against ALL reflections. The weighted R-
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factor wR and
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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. Rfactors based on F^2 are statistically about twice as large as those based on F, and Rfactors based on ALL data will be even larger. ; refine ls structure factor coef Fsqd refine ls matrix type full refine ls weighting scheme calc refine ls weighting details $'calc w=1/[\s^2^{(Fo^2^)}+(0.1477P)^2^+0.0000P]$ where $P = (Fo^2^+ 2Fc^2^) / 3'$ atom sites solution primary direct _atom_sites_solution secondary difmap atom sites solution hydrogens geom refine ls hydrogen treatment constr refine ls extinction method none refine ls extinction coef ? _refine_ls_number_reflns 4940 refine ls number parameters 380 refine ls number restraints 3 _refine_ls_R_factor all 0.0958 refine ls R factor gt 0.0721 _refine_ls_wR_factor ref 0.2264 _refine_ls_wR_factor_gt 0.2091 refine ls goodness of fit ref 1.070 _refine_ls_restrained S all 1.070 refine ls shift/su max 0.294 _refine_ls_shift/su mean 0.006 loop atom site label _atom_site_type symbol atom site fract x

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atom site symmetry multiplicity

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All esds (except the esd in the dihedral angle between two l.s. planes)

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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)
treatment of cell esds is used for estimating esds involving
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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
publ section title
Crystal and Molecular Structure of budz02
publ section abstract
publ section references
International Tables for X-ray Crystallography (1974).
Vol. IV, Birmingham, England: Kynoch Press.
Sheldrick, G.M. (1996).
SADABS. Program for Emperical Absorption Correction.
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PLATON. A Multipurpose Crystallographic Tool. Utrecht University,
Utrecht, The Netherlands.
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publ section acknowledgements
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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and 6.1.1.4'
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6.1.1.4'
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symmetry int tables number
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'x, -y-1/2, z-1/2'
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cell angle gamma
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482

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                                 x-ray
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diffrn radiation wavelength
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diffrn source
diffrn radiation monochromator
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(Bruker) '
computing cell refinement
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(Bruker) '
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computing data reduction
(Bruker) '
computing structure solution
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                                  'SHELXL-97 (Sheldrick, 1997)'
computing molecular graphics
                                  ?
computing publication material
                                 ?
_refine_special details
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
```

?

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483
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```
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
on F^2 are statistically about twice as large as those based on
F, and R-
 factors based on ALL data will be even larger.
;
refine ls structure factor coef Fsqd
refine ls matrix type
                                 full
refine ls weighting scheme
                                 calc
refine ls weighting details
'calc w=1/[\s^2^{(Fo^2^)}+(0.1057P)^{2^+10.0987P}] where
P = (Fo^2 + 2Fc^2) / 3'
atom sites solution primary
                                 direct
atom sites solution secondary
                                 difmap
_atom_sites_solution hydrogens
                                 geom
refine ls hydrogen treatment
                                 constr
_refine_ls_extinction method
                                 none
_refine_ls_extinction coef
                                 ?
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refine ls number reflns
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                                 431
refine ls number restraints
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refine ls R factor all
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_refine_ls_R_factor_gt
                                 0.0962
refine_ls_wR_factor ref
                                 0.2406
refine ls wR factor gt
                                 0.2268
_refine_ls_goodness of fit ref
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refine ls restrained S all
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refine_ls_shift/su_mean
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loop
atom site label
atom site type symbol
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atom site fract y
atom site fract z
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atom site adp type
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atom site refinement flags
atom site disorder assembly
atom site disorder group
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Fel Fe 0.16288(7) 0.25736(3) 0.08488(4) 0.0386(2) Uani 1 1 d . . Cl1 Cl -0.04231(14) 0.29237(7) 0.09938(11) 0.0650(5) Uani 1 1 d . Cl2 Cl 0.30989(17) 0.22725(8) 0.18603(10) 0.0683(5) Uani 1 1 d . N1 N 0.0902(4) 0.16192(19) 0.0514(3) 0.0430(10) Uani 1 1 d . . . C8 C 0.0928(7) 0.1110(3) 0.1042(4) 0.0585(16) Uani 1 1 d . . . C9 C -0.0123(8) 0.1021(3) 0.1458(4) 0.076(2) Uani 1 1 d . . . C10 C -0.0020(14) 0.0518(5) 0.1973(6) 0.118(4) Uani 1 1 d . . . H110 H -0.0682 0.0439 0.2263 0.141 Uiso 1 1 calc R . . C11 C 0.1035(18) 0.0146(5) 0.2052(7) 0.136(5) Uani 1 1 d . . . H111 H 0.1069 -0.0188 0.2381 0.163 Uiso 1 1 calc R . . C12 C 0.1985(13) 0.0255(4) 0.1671(7) 0.116(4) Uani 1 1 d . . . H112 H 0.2696 -0.0001 0.1751 0.140 Uiso 1 1 calc R . . C13 C 0.2011(8) 0.0740(3) 0.1142(5) 0.080(2) Uani 1 1 d . . . C14 C -0.1248(11) 0.1408(5) 0.1376(7) 0.112(4) Uani 1 1 d . . . H114 H -0.0946 0.1815 0.1267 0.169 Uiso 1 1 calc R . . C15 C -0.1873(12) 0.1464(6) 0.2123(8) 0.162(6) Uani 1 1 d . . . H115 H -0.1221 0.1553 0.2556 0.243 Uiso 1 1 calc R . . H116 H -0.2289 0.1089 0.2217 0.243 Uiso 1 1 calc R . . H117 H -0.2499 0.1784 0.2061 0.243 Uiso 1 1 calc R . . C16 C -0.2241(13) 0.1248(9) 0.0713(8) 0.176(7) Uani 1 1 d . . . H118 H -0.3056 0.1415 0.0796 0.264 Uiso 1 1 calc R . . H119 H -0.2311 0.0815 0.0671 0.264 Uiso 1 1 calc R . . H120 H -0.2001 0.1410 0.0240 0.264 Uiso 1 1 calc R . . C17 C 0.3138(10) 0.0848(4) 0.0729(7) 0.111(3) Uani 1 1 d . . . H121 H 0.3031 0.1245 0.0474 0.166 Uiso 1 1 calc R . . C18 C 0.4380(11) 0.0855(7) 0.1292(11) 0.187(7) Uani 1 1 d . . . H122 H 0.5083 0.0960 0.1019 0.281 Uiso 1 1 calc R . . H123 H 0.4529 0.0461 0.1524 0.281 Uiso 1 1 calc R . . H124 H 0.4318 0.1149 0.1693 0.281 Uiso 1 1 calc R . . C19 C 0.3203(14) 0.0360(7) 0.0093(10) 0.173(6) Uani 1 1 d . . . H125 H 0.2375 0.0325 -0.0224 0.259 Uiso 1 1 calc R . . H126 H 0.3436 -0.0023 0.0336 0.259 Uiso 1 1 calc R . . H127 H 0.3837 0.0475 -0.0228 0.259 Uiso 1 1 calc R . . C1 C -0.0010(8) 0.0966(3) -0.0588(4) 0.079(2) Uani 1 1 d . . . H101 H 0.0105 0.0641 -0.0215 0.118 Uiso 1 1 calc R . . H102 H 0.0424 0.0868 -0.1023 0.118 Uiso 1 1 calc R . . H103 H -0.0913 0.1021 -0.0765 0.118 Uiso 1 1 calc R . . C2 C 0.0544(5) 0.1539(3) -0.0212(3) 0.0490(13) Uani 1 1 d . . . C3 C 0.0741(5) 0.2052(2) -0.0726(3) 0.0441(12) Uani 1 1 d . . . C4 C 0.0340(6) 0.2054(3) -0.1527(3) 0.0595(15) Uani 1 1 d . . . H104 H -0.0135 0.1731 -0.1764 0.071 Uiso 1 1 calc R . . C5 C 0.0649(7) 0.2534(3) -0.1961(4) 0.0692(18) Uani 1 1 d . . . H105 H 0.0396 0.2536 -0.2497 0.083 Uiso 1 1 calc R . . C6 C 0.1341(6) 0.3017(3) -0.1602(3) 0.0591(15) Uani 1 1 d . . . H106 H 0.1571 0.3345 -0.1891 0.071 Uiso 1 1 calc R . .

C7 C 0.1679(5) 0.2996(2) -0.0803(3) 0.0444(12) Uani 1 1 d . . . N2 N 0.1383(4) 0.25292(19) -0.0383(2) 0.0420(10) Uani 1 1 d . . . P1 P 0.26281(13) 0.35837(6) -0.02487(8) 0.0427(4) Uani 1 1 d . . C20 C 0.2000(6) 0.4300(3) -0.0612(3) 0.0537(14) Uani 1 1 d . . . C21 C 0.0671(8) 0.4374(4) -0.0738(4) 0.074(2) Uani 1 1 d . . . H128 H 0.0148 0.4041 -0.0682 0.089 Uiso 1 1 calc R . . C22 C 0.0102(10) 0.4924(5) -0.0945(5) 0.098(3) Uani 1 1 d . . . 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 1 1 d . . . H130 H 0.0551 0.5798 -0.1126 0.143 Uiso 1 1 calc R . . C24 C 0.2213(14) 0.5357(4) -0.0868(6) 0.110(4) Uani 1 1 d . . . H131 H 0.2738 0.5693 -0.0902 0.132 Uiso 1 1 calc R . . C25 C 0.2753(9) 0.4800(3) -0.0686(4) 0.081(2) Uani 1 1 d . . . H132 H 0.3646 0.4760 -0.0612 0.097 Uiso 1 1 calc R . . C26 C 0.4230(6) 0.3490(3) -0.0477(4) 0.0548(14) Uani 1 1 d . . . C27 C 0.5136(7) 0.3240(3) 0.0072(5) 0.0749(19) Uani 1 1 d . . . H133 H 0.4911 0.3140 0.0556 0.090 Uiso 1 1 calc R . . C28 C -0.3626(8) 0.3131(5) -0.0067(7) 0.106(3) Uani 1 1 d . . . H134 H -0.3025 0.2956 0.0316 0.127 Uiso 1 1 calc R . . C29 C -0.3289(9) 0.3284(6) -0.0773(10) 0.127(4) Uani 1 1 d . . . H135 H -0.2446 0.3226 -0.0866 0.152 Uiso 1 1 calc R . . C30 C 0.5827(12) 0.3518(6) -0.1338(8) 0.130(4) Uani 1 1 d . . . H136 H 0.6060 0.3599 -0.1825 0.157 Uiso 1 1 calc R . . C31 C 0.4559(8) 0.3642(4) -0.1203(5) 0.088(2) Uani 1 1 d . . . H137 H 0.3961 0.3819 -0.1586 0.105 Uiso 1 1 calc R . . N3 N 0.2458(5) 0.3444(2) 0.0632(3) 0.0483(11) Uani 1 1 d . . . C32 C 0.2808(5) 0.3871(2) 0.1243(3) 0.0479(13) Uani 1 1 d . . . C33 C 0.2188(6) 0.3852(3) 0.1886(4) 0.0583(15) Uani 1 1 d . . . H138 H 0.1563 0.3558 0.1920 0.070 Uiso 1 1 calc R . . C34 C 0.2479(8) 0.4264(3) 0.2484(4) 0.076(2) Uani 1 1 d . . . 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) 0.083(2) Uani 1 1 d . . . H140 H -0.3580 -0.0036 0.2126 0.099 Uiso 1 1 calc R . . C36 C 0.4007(8) 0.4725(4) 0.1833(5) 0.085(2) Uani 1 1 d . . . H141 H 0.4630 0.5022 0.1810 0.102 Uiso 1 1 calc R . . C37 C 0.3728(7) 0.4317(3) 0.1218(4) 0.0682(18) Uani 1 1 d . . . H142 H 0.4162 0.4346 0.0788 0.082 Uiso 1 1 calc R . . C91 C 0.5426(18) 0.3251(10) 0.2902(15) 0.261(13) Uani 1 1 d . . . H911 H 0.4725 0.3491 0.2631 0.313 Uiso 1 1 calc R . . H912 H 0.5133 0.2837 0.2954 0.313 Uiso 1 1 calc R . . Cl91 Cl -0.3110(8) 0.1721(5) -0.2610(7) 0.353(5) Uani 1 1 d . . . Cl92 Cl -0.4057(16) 0.1476(5) -0.1311(6) 0.498(11) Uani 1 1 d . . •

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atom site aniso U 33
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Cl1 0.0427(8) 0.0690(10) 0.0825(12) 0.0081(8) 0.0067(7) 0.0100(7)
C12 \ 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 \quad 0.244(17) \quad 0.082(7) \quad 0.073(7) \quad 0.018(6) \quad -0.009(9) \quad -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)
C7 0.043(3) 0.054(3) 0.036(3) 0.005(2) 0.006(2) 0.003(2)
N2 \ 0.045(2) \ 0.049(2) \ 0.031(2) \ 0.0003(18) \ 0.0051(19) \ -0.0001(19)
P1 0.0463(7) 0.0447(7) 0.0376(8) 0.0081(6) 0.0075(6) -0.0016(6)
C20 \ 0.077(4) \ 0.047(3) \ 0.038(3) \ 0.006(2) \ 0.013(3) \ 0.010(3)
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)
C23 0.226(14) 0.061(5) 0.066(6) 0.002(4) 0.006(7) 0.056(8)
C24 \ 0.191(12) \ 0.056(5) \ 0.078(6) \ 0.008(4) \ 0.003(7) \ -0.001(6)
C25 0.117(6) 0.054(4) 0.068(5) 0.014(3) 0.002(4) -0.010(4)
C26 0.048(3) 0.057(3) 0.060(4) 0.006(3) 0.008(3) -0.003(3)
C27 \ 0.059(4) \ 0.077(4) \ 0.086(5) \ -0.003(4) \ 0.002(4) \ 0.003(3)
C28 \ 0.044(4) \ 0.127(8) \ 0.142(9) \ -0.002(7) \ -0.005(5) \ 0.012(4)
C29 \ 0.048(5) \ 0.135(9) \ 0.201(14) \ -0.012(9) \ 0.032(7) \ 0.001(5)
C30 0.107(8) 0.158(10) 0.149(10) -0.012(8) 0.094(8) -0.015(7)
C31 \ 0.069(5) \ 0.112(6) \ 0.087(6) \ 0.018(5) \ 0.029(4) \ -0.006(4)
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)
C33 0.062(4) 0.059(3) 0.054(4) -0.007(3) 0.010(3) -0.009(3)
C34 \ 0.087(5) \ 0.078(5) \ 0.065(5) \ -0.024(4) \ 0.017(4) \ -0.001(4)
C35 0.096(6) 0.074(5) 0.075(5) 0.030(4) 0.001(4) 0.009(4)
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C36 0.093(6) 0.072(5) 0.089(6) -0.016(4) 0.006(5) -0.034(4)
C37 \ 0.077(4) \ 0.067(4) \ 0.060(4) \ -0.007(3) \ 0.007(3) \ -0.023(3)
C91 0.151(15) 0.23(2) 0.35(3) -0.11(2) -0.122(18) 0.020(14)
Cl91 0.217(7) 0.399(12) 0.418(13) -0.061(11) -0.046(7) -0.026(8)
C192 \ 0.82(3) \ 0.283(9) \ 0.284(10) \ 0.070(8) \ -0.292(14) \ -0.090(13)
_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
geom bond atom site label 1
geom bond atom site label 2
_geom_bond distance
geom bond site symmetry 2
geom bond publ flag
Fel N2 2.115(4) . ?
Fel N3 2.161(4) . ?
Fe1 Cl2 2.2606(17) . ?
Fel N1 2.284(4) . ?
Fe1 Cl1 2.3320(16) . ?
N1 C2 1.273(7) . ?
N1 C8 1.447(7) . ?
C8 C13 1.388(10) . ?
C8 C9 1.413(10) . ?
C9 C10 1.419(13) . ?
C9 C14 1.445(14) . ?
C10 C11 1.367(17) . ?
C10 H110 0.9300 . ?
C11 C12 1.294(17) . ?
C11 H111 0.9300 . ?
C12 C13 1.410(13) . ?
C12 H112 0.9300 . ?
C13 C17 1.486(13) . ?
C14 C16 1.478(17) . ?
C14 C15 1.537(14) . ?
```

C14 H114 0.9800 . ? C15 H115 0.9600 . ? C15 H116 0.9600 . ? C15 H117 0.9600 . ? C16 H118 0.9600 . ? C16 H119 0.9600 . ? C16 H120 0.9600 . ? C17 C18 1.511(16) . ? C17 C19 1.549(17) . ? C17 H121 0.9800 . ? C18 H122 0.9600 . ? C18 H123 0.9600 . ? C18 H124 0.9600 . ? C19 H125 0.9600 . ? C19 H126 0.9600 . ? C19 H127 0.9600 . ? C1 C2 1.500(8) . ? C1 H101 0.9600 . ? C1 H102 0.9600 . ? C1 H103 0.9600 . ? C2 C3 1.473(8) . ? C3 N2 1.341(7) . ? C3 C4 1.391(8) . ? C4 C5 1.364(9) . ? C4 H104 0.9300 . ? C5 C6 1.384(9) . ? C5 H105 0.9300 . ? C6 C7 1.381(8) . ? C6 H106 0.9300 . ? C7 N2 1.324(7) . ? C7 P1 1.821(6) . ? P1 N3 1.593(5) . ? P1 C26 1.791(6) . ? P1 C20 1.790(6) . ? C20 C21 1.388(10) . ? C20 C25 1.372(9) . ? C21 C22 1.374(11) . ? C21 H128 0.9300 . ? C22 C23 1.393(16) . ? C22 H129 0.9300 . ? C23 C24 1.357(16) . ? C23 H130 0.9300 . ? C24 C25 1.371(12) . ? C24 H131 0.9300 . ? C25 H132 0.9300 . ? C26 C27 1.360(10) . ? C26 C31 1.393(10) . ? C27 C28 1.375(11) 1 655 ?

```
C27 H133 0.9300 . ?
C28 C29 1.364(16) . ?
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C30 C31 1.409(12) . ?
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C31 H137 0.9300 . ?
N3 C32 1.425(7) . ?
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C32 C37 1.382(8) . ?
C33 C34 1.379(9) . ?
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H6 H -0.1169 0.6851 1.2216 0.112 Uiso 1 1 calc R . . C8 C -0.0844(10) 0.6008(6) 1.4098(6) 0.073(3) Uani 1 1 d . . . C9 C 0.0752(13) 0.5629(6) 1.3487(7) 0.089(4) Uani 1 1 d . . . C10 C -0.0547(8) 0.7819(5) 0.7975(5) 0.058(3) Uani 1 1 d . . . C11 C -0.2693(7) 0.7210(5) 0.8150(5) 0.056(3) Uani 1 1 d . . . C12 C -0.0585(10) 0.8082(5) 0.7243(5) 0.071(3) Uani 1 1 d . . . H43 H -0.1181 0.8263 0.7092 0.086 Uiso 1 1 calc R . . C13 C 0.0238(9) 0.8069(6) 0.6766(6) 0.070(3) Uani 1 1 d . . . H44 H 0.0213 0.8237 0.6281 0.083 Uiso 1 1 calc R . . C14 C 0.0451(8) 0.7963(6) 1.1988(5) 0.064(3) Uani 1 1 d . . . H3 H -0.0042 0.7763 1.1622 0.077 Uiso 1 1 calc R . . C15 C 0.4195(8) 0.8874(5) 1.3415(6) 0.065(3) Uani 1 1 d . . . C16 C 0.0457(16) 0.4979(8) 1.3664(9) 0.119(6) Uani 1 1 d . . . H19 H 0.0884 0.4639 1.3532 0.143 Uiso 1 1 calc R . . C17 C -0.1483(11) 0.6553(8) 1.4347(7) 0.096(4) Uani 1 1 d . . . H88 H -0.1161 0.6964 1.4151 0.144 Uiso 1 1 calc R . . C18 C 0.2688(7) 0.6723(5) 0.9133(5) 0.054(2) Uani 1 1 d . . . C19 C 0.3486(9) 0.7818(6) 0.9856(6) 0.076(3) Uani 1 1 d . . . H87 H 0.2909 0.7986 0.9589 0.115 Uiso 1 1 calc R . . C20 C 0.3414(8) 0.7080(6) 0.9663(5) 0.061(3) Uani 1 1 d . . . C21 C 0.4503(12) 0.8198(7) 0.9598(11) 0.147(7) Uani 1 1 d . . . H49 H 0.5088 0.7990 0.9773 0.220 Uiso 1 1 calc R . . H50 H 0.4542 0.8656 0.9823 0.220 Uiso 1 1 calc R . . H51 H 0.4512 0.8185 0.9038 0.220 Uiso 1 1 calc R . . C22 C 0.3377(12) 0.8019(8) 1.0742(7) 0.124(6) Uani 1 1 d . . . H52 H 0.2746 0.7797 1.0927 0.187 Uiso 1 1 calc R . . H53 H 0.3356 0.8496 1.0833 0.187 Uiso 1 1 calc R . . H54 H 0.3961 0.7889 1.1016 0.187 Uiso 1 1 calc R . . C23 C 0.1136(8) 0.7800(5) 0.7001(5) 0.066(3) Uani 1 1 d . . . H45 H 0.1711 0.7782 0.6676 0.079 Uiso 1 1 calc R . . C24 C 0.1146(7) 0.7558(5) 0.7743(5) 0.052(2) Uani 1 1 d . . . C25 C 0.2033(7) 0.7249(4) 0.8067(5) 0.048(2) Uani 1 1 d . . . C26 C 0.2927(9) 0.7101(7) 0.7544(6) 0.095(4) Uani 1 1 d . . . H46 H 0.3234 0.7510 0.7362 0.143 Uiso 1 1 calc R . . H47 H 0.2683 0.6794 0.7105 0.143 Uiso 1 1 calc R . . H48 H 0.3437 0.6905 0.7831 0.143 Uiso 1 1 calc R . . C27 C -0.2029(7) 0.8592(5) 0.8760(5) 0.052(2) Uani 1 1 d . . . C28 C -0.1237(9) 0.9115(6) 0.9005(6) 0.074(3) Uani 1 1 d . . . H64 H -0.0549 0.9018 0.9044 0.089 Uiso 1 1 calc R . . C29 C -0.4360(10) 0.6589(6) 0.8215(7) 0.090(4) Uani 1 1 d . . . H69 H -0.4983 0.6503 0.8476 0.108 Uiso 1 1 calc R . . C30 C -0.3582(8) 0.7059(5) 0.8557(6) 0.062(3) Uani 1 1 d . . . H70 H -0.3670 0.7267 0.9058 0.075 Uiso 1 1 calc R . . C31 C 0.5039(10) 0.9037(6) 1.3914(7) 0.084(3) Uani 1 1 d . . . H23 H 0.4931 0.9127 1.4448 0.101 Uiso 1 1 calc R . . C32 C 0.4375(10) 0.8717(8) 1.2652(6) 0.123(6) Uani 1 1 d . . . H22 H 0.3819 0.8591 1.2308 0.148 Uiso 1 1 calc R . . C33 C 0.2570(8) 0.9676(5) 1.4068(5) 0.051(2) Uani 1 1 d . . .

C34 C 0.1561(9) 0.9776(6) 1.4239(6) 0.074(3) Uani 1 1 d . . . H27 H 0.1055 0.9413 1.4219 0.089 Uiso 1 1 calc R . . C35 C 0.1293(10) 1.0426(6) 1.4442(7) 0.091(4) Uani 1 1 d . . . H28 H 0.0605 1.0492 1.4562 0.109 Uiso 1 1 calc R . . C36 C 0.3020(11) 1.0865(6) 1.4296(8) 0.094(4) Uani 1 1 d . . . H29 H 0.3524 1.1229 1.4318 0.113 Uiso 1 1 calc R . . C37 C 0.2034(11) 1.0980(6) 1.4471(7) 0.083(4) Uani 1 1 d . . . H30 H 0.1853 1.1412 1.4606 0.100 Uiso 1 1 calc R . . C38 C 0.3387(9) 0.8280(6) 1.5084(7) 0.071(3) Uani 1 1 d . . . C39 C -0.0498(19) 0.4839(8) 1.4047(9) 0.125(8) Uani 1 1 d . . . H20 H -0.0704 0.4403 1.4160 0.150 Uiso 1 1 calc R . . C40 C 0.1795(11) 0.5774(7) 1.3135(9) 0.103(4) Uani 1 1 d . . . H89 H 0.1939 0.6262 1.3154 0.154 Uiso 1 1 calc R . . C41 C -0.1520(15) 0.6671(9) 1.5267(7) 0.162(8) Uani 1 1 d . . . H7 H -0.1856 0.6279 1.5470 0.243 Uiso 1 1 calc R . . H8 H -0.1902 0.7049 1.5418 0.243 Uiso 1 1 calc R . . H9 H -0.0824 0.6757 1.5473 0.243 Uiso 1 1 calc R . . C42 C -0.3330(11) 0.6406(8) 0.7092(8) 0.117(5) Uani 1 1 d . . . H71 H -0.3257 0.6192 0.6592 0.140 Uiso 1 1 calc R . . C43 C -0.2533(9) 0.6879(6) 0.7415(6) 0.086(4) Uani 1 1 d . . . H72 H -0.1919 0.6968 0.7145 0.104 Uiso 1 1 calc R . . C44 C -0.4206(13) 0.6260(8) 0.7508(8) 0.131(6) Uani 1 1 d . . . H73 H -0.4708 0.5927 0.7300 0.157 Uiso 1 1 calc R . . C45 C -0.1489(13) 0.9764(6) 0.9185(8) 0.098(4) Uani 1 1 d . . . H65 H -0.0972 1.0100 0.9353 0.118 Uiso 1 1 calc R . . C46 C -0.3017(9) 0.8759(6) 0.8697(7) 0.073(3) Uani 1 1 d . . . H66 H -0.3542 0.8428 0.8526 0.088 Uiso 1 1 calc R . . C47 C 0.4081(10) 0.6002(8) 0.9852(8) 0.093(4) Uani 1 1 d . . . H61 H 0.4550 0.5756 1.0083 0.111 Uiso 1 1 calc R . . C48 C 0.4123(9) 0.6704(7) 1.0012(6) 0.081(4) Uani 1 1 d . . . H62 H 0.4629 0.6925 1.0354 0.098 Uiso 1 1 calc R . . C49 C 0.3317(10) 0.5691(6) 0.9340(8) 0.089(4) Uani 1 1 d . . . H63 H 0.3280 0.5227 0.9233 0.106 Uiso 1 1 calc R . . C50 C 0.2603(9) 0.6036(6) 0.8976(6) 0.073(3) Uani 1 1 d . . . C51 C 0.1806(13) 0.5633(7) 0.8414(10) 0.121(6) Uani 1 1 d . . . H86 H 0.1416 0.5955 0.8172 0.182 Uiso 1 1 calc R . . C52 C 0.1016(13) 0.5215(8) 0.8932(11) 0.150(7) Uani 1 1 d . . . H55 H 0.0547 0.4917 0.8597 0.225 Uiso 1 1 calc R . . H56 H 0.0627 0.5516 0.9257 0.225 Uiso 1 1 calc R . . H57 H 0.1396 0.4958 0.9256 0.225 Uiso 1 1 calc R . . C53 C 0.2249(14) 0.5200(8) 0.7772(8) 0.142(7) Uani 1 1 d . . . H58 H 0.2468 0.5464 0.7355 0.213 Uiso 1 1 calc R . . H59 H 0.1730 0.4849 0.7580 0.213 Uiso 1 1 calc R . . H60 H 0.2836 0.5005 0.7967 0.213 Uiso 1 1 calc R . . C54 C -0.2468(14) 0.9911(7) 0.9121(8) 0.105(5) Uani 1 1 d . . . H67 H -0.2626 1.0351 0.9236 0.127 Uiso 1 1 calc R . . C55 C -0.3262(12) 0.9408(8) 0.8879(8) 0.106(4) Uani 1 1 d . . . H68 H -0.3946 0.9511 0.8843 0.127 Uiso 1 1 calc R . .

C56 C -0.2198(8) 0.6560(5) 0.9957(6) 0.058(3) Uani 1 1 d . . . C57 C -0.1844(7) 0.7241(5) 0.9999(5) 0.054(2) Uani 1 1 d . . . C58 C -0.2099(9) 0.7679(6) 1.0617(6) 0.071(3) Uani 1 1 d . . . 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 . . H11 H -0.2978 0.6789 1.4141 0.276 Uiso 1 1 calc R . . H12 H -0.2935 0.6020 1.4206 0.276 Uiso 1 1 calc R . . 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 0.2430 0.5437 1.2059 0.301 Uiso 1 1 calc R . . H18 H 0.1414 0.5789 1.1950 0.301 Uiso 1 1 calc R . . C76 C 0.5365(12) 0.8740(11) 1.2376(10) 0.178(10) Uani 1 1 d . . . H26 H 0.5474 0.8633 1.1844 0.213 Uiso 1 1 calc R . . C77 C 0.474(2) 0.8217(14) 1.6372(14) 0.174(14) Uani 1 1 d . . . C78 C 0.4781(11) 0.7805(10) 1.5748(14) 0.154(9) Uani 1 1 d . . . H32 H 0.5244 0.7477 1.5742 0.185 Uiso 1 1 calc R . . C79 C 0.3999(17) 0.8648(10) 1.6415(9) 0.142(9) Uani 1 1 d . . . H33 H 0.3952 0.8929 1.6874 0.171 Uiso 1 1 calc R . . C80 C 0.5453(15) 0.8190(14) 1.7062(12) 0.278(18) Uani 1 1 d . . . H40 H 0.5453 0.7734 1.7182 0.417 Uiso 1 1 calc R . . H41 H 0.5210 0.8458 1.7507 0.417 Uiso 1 1 calc R . . H42 H 0.6146 0.8361 1.6937 0.417 Uiso 1 1 calc R . . Cl8 Cl 0.8694(15) 0.0124(9) 0.2049(11) 0.510(10) Uiso 1 1 d . . . Cl9 Cl 0.6953(19) 0.0311(11) 0.1425(14) 0.637(15) Uiso 1 1 d . . 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 Fel 0.0572(9) 0.0622(9) 0.0322(6) 0.0046(6) -0.0056(6) 0.0006(7) Fe2 0.0632(9) 0.0559(9) 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)C12 0.101(2) 0.0716(18) 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) 0.048(5) 0.039(4) 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)

C4 0.045(5) 0.061(6) 0.032(4) 0.010(4) 0.006(4) -0.008(5) C5 0.088(8) 0.061(7) 0.053(6) 0.020(5) -0.011(6) -0.005(6)C6 0.080(8) 0.080(8) 0.042(5) 0.013(5) -0.010(5) -0.009(6)C7 0.100(9) 0.078(8) 0.040(5) 0.014(5) -0.027(5) -0.035(7) C8 0.087(9) 0.075(9) 0.051(6) 0.001(6) -0.018(6) -0.021(7) $C9 \ 0.136(13) \ 0.046(8) \ 0.080(8) \ 0.001(6) \ -0.026(8) \ -0.015(8)$ $C10 \ 0.055(6) \ 0.071(7) \ 0.044(5) \ -0.002(5) \ 0.000(5) \ -0.012(5)$ C11 0.037(5) 0.079(7) 0.053(5) 0.008(5) -0.008(4) 0.005(5) $C12 \ 0.092(9) \ 0.082(8) \ 0.042(5) \ 0.023(5) \ -0.022(6) \ 0.004(7)$ C13 0.078(8) 0.092(8) 0.043(5) 0.026(5) -0.015(6) 0.015(7) $C14 \ 0.064(7) \ 0.093(8) \ 0.030(4) \ 0.003(5) \ -0.007(4) \ -0.013(6)$ C15 0.057(7) 0.058(7) 0.075(7) -0.007(5) -0.010(5) -0.008(5) C16 0.179(18) 0.076(12) 0.097(11) -0.007(8) -0.041(11) 0.007(11) C17 0.083(9) 0.125(12) 0.075(8) 0.018(8) 0.006(7) -0.025(9)C18 0.053(6) 0.067(7) 0.048(5) 0.021(5) -0.003(5) 0.018(5) $C19 \ 0.065(7) \ 0.087(9) \ 0.071(7) \ -0.028(6) \ -0.003(6) \ 0.013(7)$ $C20 \ 0.054(6) \ 0.082(8) \ 0.045(5) \ 0.000(5) \ -0.001(5) \ -0.001(6)$ $C21 \ 0.109(13) \ 0.096(12) \ 0.23(2) \ 0.009(12) \ 0.007(13) \ -0.008(10)$ $C22 \ 0.141(14) \ 0.146(14) \ 0.079(9) \ -0.036(9) \ -0.013(9) \ 0.022(11)$ C23 0.071(7) 0.090(8) 0.037(5) 0.017(5) 0.014(5) 0.004(6) $C24 \ 0.055(6) \ 0.058(6) \ 0.039(5) \ -0.002(4) \ 0.015(4) \ -0.001(5)$ C25 0.053(6) 0.049(6) 0.042(5) 0.008(4) 0.006(4) 0.001(5)C26 0.078(8) 0.143(12) 0.072(7) 0.040(7) 0.027(6) 0.023(8) C27 0.052(6) 0.066(7) 0.041(5) 0.009(4) 0.000(4) 0.015(5)C28 0.070(8) 0.080(9) 0.074(7) 0.014(6) -0.024(6) 0.005(7)C29 0.079(9) 0.103(10) 0.086(8) 0.002(7) -0.008(7) 0.000(8) $C30 \ 0.052(6) \ 0.068(7) \ 0.063(6) \ -0.001(5) \ 0.001(5) \ -0.003(5)$ $C31 \ 0.072(9) \ 0.089(9) \ 0.088(8) \ -0.005(7) \ -0.005(7) \ 0.003(7)$ $C32 \ 0.074(9) \ 0.221(17) \ 0.055(7) \ -0.049(9) \ 0.017(6) \ -0.019(10)$ C33 0.060(6) 0.048(6) 0.045(5) 0.007(4) -0.003(4) -0.006(5) $C34 \ 0.057(7) \ 0.071(8) \ 0.094(8) \ 0.008(6) \ 0.018(6) \ -0.004(6)$ $C35 \ 0.091(10) \ 0.065(9) \ 0.117(10) \ 0.017(7) \ 0.001(8) \ 0.004(8)$ C36 0.100(11) 0.050(8) 0.125(10) -0.009(7) 0.017(9) -0.010(7) C37 0.092(10) 0.052(8) 0.103(9) -0.005(6) 0.019(8) 0.005(7) $C38 \ 0.059(7) \ 0.066(8) \ 0.088(8) \ 0.040(6) \ -0.016(6) \ -0.020(6)$ $C39 \ 0.22(2) \ 0.063(10) \ 0.093(11) \ 0.035(9) \ -0.058(13) \ -0.033(13)$ $C40 \ 0.084(10) \ 0.093(10) \ 0.132(12) \ 0.003(9) \ -0.009(9) \ 0.022(8)$ C41 0.22(2) 0.178(17) 0.070(9) -0.018(9) 0.057(11) -0.034(15) C42 0.100(11) 0.159(14) 0.076(8) -0.041(9) 0.018(8) -0.020(10)C43 0.080(8) 0.100(9) 0.068(7) -0.018(6) 0.016(6) -0.020(7) C44 0.145(14) 0.136(13) 0.087(9) -0.044(9) 0.006(10) -0.061(11) C45 0.123(13) 0.053(9) 0.119(11) 0.003(7) -0.024(9) 0.019(8) $C46 \ 0.057(7) \ 0.064(8) \ 0.101(8) \ 0.011(6) \ -0.008(6) \ 0.018(6)$ C47 0.067(8) 0.112(12) 0.107(10) 0.042(9) -0.017(7) 0.016(8) C48 0.058(7) 0.117(11) 0.065(7) 0.001(7) -0.010(6) -0.005(7) C49 0.083(9) 0.065(8) 0.120(10) 0.026(7) -0.029(8) 0.003(7) $C50 \ 0.069(8) \ 0.074(8) \ 0.077(7) \ 0.014(6) \ -0.023(6) \ 0.005(6)$ C51 0.137(14) 0.064(9) 0.160(14) 0.016(9) -0.074(12) -0.012(9)

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) $C80 \ 0.168(19) \ 0.45(4) \ 0.21(2) \ 0.23(3) \ -0.155(17) \ -0.17(2)$ _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_
_geom_bond_atom_site_label_1

505

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geom bond distance
_geom_bond_site_symmetry_2
geom bond publ flag
Fel N3 2.131(8) . ?
Fel N5 2.152(7) . ?
Fel N4 2.259(7) . ?
Fe1 Cl4 2.267(3) . ?
Fe1 Cl5 2.378(3) . ?
Fe2 N6 2.139(7) . ?
Fe2 N1 2.166(7) . ?
Fe2 N2 2.235(7) . ?
Fe2 Cl2 2.284(3) . ?
Fe2 Cl3 2.359(3) . ?
P1 N3 1.606(7) . ?
P1 C27 1.788(10) . ?
P1 C10 1.803(10) . ?
P1 C11 1.831(9) . ?
P2 N6 1.589(7) . ?
P2 C33 1.813(10) . ?
P2 C4 1.820(9) . ?
P2 C15 1.820(11) . ?
N1 C2 1.340(11) . ?
N1 C4 1.362(11) . ?
N2 C1 1.292(10) . ?
N2 C3 1.459(12) . ?
N3 C57 1.455(11) . ?
N4 C25 1.322(10) . ?
N4 C18 1.455(11) . ?
N5 C10 1.346(12) . ?
N5 C24 1.346(11) . ?
N6 C38 1.427(12) . ?
C1 C7 1.462(12) . ?
C1 C2 1.474(13) . ?
C2 C14 1.423(13) . ?
C3 C9 1.380(17) . ?
C3 C8 1.414(15) . ?
C4 C6 1.363(12) . ?
C5 C14 1.339(13) . ?
C5 C6 1.405(13) . ?
C5 H1 0.9300 . ?
C6 H2 0.9300 . ?
C7 H4 0.9600 . ?
C7 H5 0.9600 . ?
С7 Н6 0.9600 . ?
C8 C64 1.428(17) . ?
C8 C17 1.464(17) . ?
C9 C16 1.391(19) . ?
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C9 C40 1.491(18) . ? C10 C12 1.413(13) . ? C11 C30 1.368(12) . ? C11 C43 1.392(13) . ? C12 C13 1.341(14) . ? C12 H43 0.9300 . ? C13 C23 1.402(14) . ? C13 H44 0.9300 . ? C14 H3 0.9300 . ? C15 C32 1.343(14) . ? C15 C31 1.382(14) . ? C16 C39 1.41(2) . ? C16 H19 0.9300 . ? C17 C63 1.54(2) . ? C17 C41 1.575(16) . ? C17 H88 0.9800 . ? C18 C50 1.376(14) . ? C18 C20 1.403(13) . ? C19 C20 1.484(15) . ? C19 C22 1.544(15) . ? C19 C21 1.543(17) . ? С19 Н87 0.9800 . ? C20 C48 1.411(15) . ? C21 H49 0.9600 . ? С21 Н50 0.9600 . ? С21 Н51 0.9600 . ? C22 H52 0.9600 . ? C22 H53 0.9600 . ? C22 H54 0.9600 . ? C23 C24 1.409(12) . ? C23 H45 0.9300 . ? C24 C25 1.489(13) . ? C25 C26 1.494(13) . ? C26 H46 0.9600 . ? C26 H47 0.9600 . ? C26 H48 0.9600 . ? C27 C46 1.357(13) . ? C27 C28 1.429(14) . ? C28 C45 1.381(15) . ? С28 Н64 0.9300 . ? C29 C44 1.348(16) . ? C29 C30 1.400(14) . ? C29 H69 0.9300 . ? C30 H70 0.9300 . ? C31 C67 1.364(16) . ? C31 H23 0.9300 . ? C32 C76 1.361(17) . ? C32 H22 0.9300 . ?

C33 C34 1.364(13) . ? C33 C68 1.408(13) . ? C34 C35 1.397(15) . ? C34 H27 0.9300 . ? C35 C37 1.395(15) . ? C35 H28 0.9300 . ? C36 C37 1.344(16) . ? C36 C68 1.383(15) . ? C36 H29 0.9300 . ? C37 H30 0.9300 . ? C38 C71 1.375(18) . ? C38 C69 1.430(18) . ? C39 C64 1.33(2) . ? C39 H20 0.9300 . ? C40 C65 1.520(19) . ? C40 C75 1.57(2) . ? C40 H89 0.9800 . ? C41 H7 0.9600 . ? С41 Н8 0.9600 . ? С41 Н9 0.9600 . ? C42 C44 1.360(18) . ? C42 C43 1.409(16) . ? C42 H71 0.9300 . ? C43 H72 0.9300 . ? C44 H73 0.9300 . ? C45 C54 1.333(18) . ? C45 H65 0.9300 . ? C46 C55 1.379(16) . ? С46 Н66 0.9300 . ? C47 C49 1.384(16) . ? C47 C48 1.408(17) . ? С47 Н61 0.9300 . ? C48 H62 0.9300 . ? C49 C50 1.390(15) . ? С49 Н63 0.9300 . ? C50 C51 1.529(16) . ? C51 C53 1.48(2) . ? C51 C52 1.59(2) . ? C51 H86 0.9800 . ? С52 Н55 0.9600 . ? C52 H56 0.9600 . ? C52 H57 0.9600 . ? C53 H58 0.9600 . ? C53 H59 0.9600 . ? С53 Н60 0.9600 . ? C54 C55 1.403(18) . ? C54 H67 0.9300 . ? C55 H68 0.9300 . ?

C56	C57	1.398(13) .	?
C56	C74	1.410(13) .	?
C56	C73	1.513(14) .	?
C57	C58	1.370(13) .	?
C58	C59	1.426(15) .	?
C58	C60	1.510(15) .	?
C59	C61	1.345(16) .	?
C59	H74	0.9300 . ?	
C60	H77	0.9600 . ?	
C60	H78	0.9600 . ?	
C60	H79	0.9600 . ?	
C61	C74	1.370(16) .	?
C61	C62	1.556(14) .	?
C62	H80	0.9600 . ?	
C62	H81	0.9600 . ?	
C62	H82	0.9600 . ?	
C63	H10	0.9600 . ?	
C63	H11	0.9600 . ?	
C63	H12	0.9600 . ?	
C64	H21	0.9300 . ?	
C65	H13	0.9600 . ?	
C65	H14	0.9600 . ?	
C65	H15	0.9600 . ?	
C66	C76	1.308(19) .	?
C66	C67	1.376(18) .	?
C66	H24	0.9300 . ?	
C67	H25	0.9300 . ?	
C68	H31	0.9300 . ?	
C69	C79	1.43(2) . ?	
C69	C70	1.504(19) .	?
C70	H34	0.9600 . ?	
C70	H35	0.9600 . ?	
C70	H36	0.9600 . ?	
C71	C72	1.49(2) . ?	
C71	C78	1.51(2) . ?	
C72	H37	0.9600 . ?	
C72	H38	0.9600 . ?	
C72	H39	0.9600 . ?	
C73	H83	0.9600 . ?	
C73	H84	0.9600 . ?	
C73	H85	0.9600 . ?	
C74	H/5	0.9300 . ?	
C75	H16	0.9600 . ?	
C75	HI'/	0.9600 . ?	
C75	HT8	0.9600 . ?	
C/6	H26	0.9300 . ?	
C'/'/	C78	1.29(3) . ?	
C77	C79	1.35(3) . ?	

C77 C80 1.51(2) . ? C78 H32 0.9300 . ? С79 Н33 0.9300 . ? С80 Н40 0.9600 . ? C80 H41 0.9600 . ? C80 H42 0.9600 . ? loop _geom_angle_atom_site label 1 _geom_angle_atom_site_label_2 geom angle atom site label 3 geom angle geom angle site symmetry 1 geom_angle_site_symmetry_3 geom angle publ flag N3 Fe1 N5 80.7(3) . . ? N3 Fel N4 148.0(2) . . ? N5 Fel N4 72.2(3) . . ? N3 Fe1 Cl4 103.9(2) . . ? N5 Fe1 Cl4 151.8(2) . . ? N4 Fel Cl4 92.9(2) . . ? N3 Fe1 Cl5 100.3(2) . . ? N5 Fe1 Cl5 91.7(2) . . ? N4 Fe1 Cl5 97.1(2) . . ? Cl4 Fe1 Cl5 114.20(11) . . ? N6 Fe2 N1 79.8(3) . . ? N6 Fe2 N2 146.6(3) . . ? N1 Fe2 N2 71.8(3) . . ? N6 Fe2 Cl2 103.1(2) . . ? N1 Fe2 Cl2 157.2(2) . . ? N2 Fe2 Cl2 96.9(2) . . ? N6 Fe2 Cl3 101.7(2) . . ? N1 Fe2 Cl3 88.3(2) . . ? N2 Fe2 Cl3 94.7(2) . . ? Cl2 Fe2 Cl3 112.82(11) . . ? N3 P1 C27 117.8(4) . . ? N3 P1 C10 103.9(4) . . ? C27 P1 C10 104.3(5) . . ? N3 P1 C11 114.0(4) . . ? C27 P1 C11 107.6(5) . . ? C10 P1 C11 108.5(4) . . ? N6 P2 C33 118.8(4) . . ? N6 P2 C4 103.4(4) . . ? C33 P2 C4 103.1(4) . . ? N6 P2 C15 113.6(5) . . ? C33 P2 C15 107.1(5) . . ? C4 P2 C15 110.0(4) . . ? C2 N1 C4 120.9(8) . . ?

C2 N1 Fe2 116.6(6) . . ? C4 N1 Fe2 120.3(5) . . ? C1 N2 C3 119.0(7) . . ? C1 N2 Fe2 118.0(6) . . ? C3 N2 Fe2 122.9(5) . . ? C57 N3 P1 120.4(6) . . ? C57 N3 Fe1 121.7(5) . . ? P1 N3 Fe1 117.8(4) . . ? C25 N4 C18 119.2(8) . . ? . . ? C25 N4 Fel 116.8(6) C18 N4 Fe1 123.9(5) . . ? C10 N5 C24 119.1(8) . . ? C10 N5 Fel 119.4(6) . . ? C24 N5 Fel 119.6(6) . . ? C38 N6 P2 122.6(6) . . ? C38 N6 Fe2 117.8(6) . . ? P2 N6 Fe2 119.7(4) . . ? N2 C1 C7 126.2(9) . . ? N2 C1 C2 113.8(8) . . ? C7 C1 C2 120.0(8) . . ? N1 C2 C14 118.6(9) . . ? N1 C2 C1 115.7(8) . . ? C14 C2 C1 125.5(8) . . ? C9 C3 C8 123.6(11) . . ? C9 C3 N2 117.4(11) . . ? C8 C3 N2 119.0(11) . . ? N1 C4 C6 121.3(8) . . ? N1 C4 P2 114.0(6) . . ? C6 C4 P2 124.6(7) . . ? C14 C5 C6 119.6(9) . . ? C14 C5 H1 120.2 . . ? C6 C5 H1 120.2 . . ? C4 C6 C5 118.9(10) . . ? C4 C6 H2 120.6 . . ? C5 C6 H2 120.6 . . ? C1 C7 H4 109.5 . . ? C1 C7 H5 109.5 . . ? H4 C7 H5 109.5 . . ? C1 C7 H6 109.5 . . ? H4 C7 H6 109.5 . . ? H5 C7 H6 109.5 . . ? C3 C8 C64 114.4(13) . . ? C3 C8 C17 121.8(11) . . ? C64 C8 C17 123.7(13) . . ? C3 C9 C16 118.8(15) . . ? C3 C9 C40 122.6(11) . . ? C16 C9 C40 118.4(16) . . ? N5 C10 C12 121.3(9) . . ?

N5 C10 P1 114.6(7) . . ? C12 C10 P1 124.1(9) . . ? C30 C11 C43 120.7(9) . . ? C30 C11 P1 119.1(7) . . ? C43 C11 P1 119.5(8) . . ? C13 C12 C10 120.0(10) . . ? C13 C12 H43 120.0 . . ? C10 C12 H43 120.0 . . ? C12 C13 C23 119.6(9) . . ? C12 C13 H44 120.2 . . ? C23 C13 H44 120.2 . . ? C5 C14 C2 120.7(9) . . ? С5 С14 НЗ 119.7 . . ? C2 C14 H3 119.7 . . ? C32 C15 C31 118.3(11) . . ? C32 C15 P2 121.9(9) . . ? C31 C15 P2 119.6(8) . . ? C9 C16 C39 119.5(16) . . ? C9 C16 H19 120.3 . . ? C39 C16 H19 120.3 . . ? C8 C17 C63 111.2(13) . . ? C8 C17 C41 110.7(13) . . ? C63 C17 C41 110.5(13) . . ? C8 C17 H88 108.1 . . ? C63 C17 H88 108.1 . . ? С41 С17 Н88 108.1 . . ? C50 C18 C20 123.6(9) . . ? C50 C18 N4 118.8(9) . . ? C20 C18 N4 117.4(9) . . ? C20 C19 C22 112.4(11) . . ? C20 C19 C21 114.8(10) . . ? C22 C19 C21 106.7(11) . . ? С20 С19 Н87 107.5 . . ? С22 С19 Н87 107.5 . . ? С21 С19 Н87 107.5 . . ? C18 C20 C48 116.8(10) . . ? C18 C20 C19 123.9(10) . . ? C48 C20 C19 119.2(10) . . ? C19 C21 H49 109.5 . . ? C19 C21 H50 109.5 . . ? H49 C21 H50 109.5 . . ? C19 C21 H51 109.5 . . ? H49 C21 H51 109.5 . . ? H50 C21 H51 109.5 . . ? C19 C22 H52 109.5 . . ? C19 C22 H53 109.5 . . ? H52 C22 H53 109.5 . . ? C19 C22 H54 109.5 . . ?

C22 C22		Н54 Н54	109 109	.5 .5	• •	· ?		
	C23	C24	118	.3	(9)	•	•	?
2 1	C23	п45 ц/5	120	۰۰ ۵	•	• · · ?		
	~24	C23 1	120	•• 7 (9)	• •	?	
(C24	C25 1	L13.	8(8)		?	
3	C24	C25	124	.5	(8)	•	•	?
(225	C24 1	L15.	2 (8)		?	
(225	C26 1	L26.	0 (9)		?	
4	C25	C26	118	.7	(8)		•	?
5	C26	H46	109	.5	•	. ?		
5	C26	H47	109	.5	•	. ?		
6	C26	H47	109	.5	•	. ?		
5	C26	H48	109	.5	•	• ?		
6	C26	H48	109	.5	•	• ?		
7	C26	H48	109	.5	•	• ?		
6	C27	C28	117	.9	(10) .	•	?
6	C27	PI I	L26.	⊥ (8)	•••	?	
8 E	C27	PI I	LIJ. 120	9(8)	•••	2	2
С Б	C_{28}		110	• 1	(⊥ ⊥) .	•	2
5	C_{20}	п 64 Ц 6 Л	110	.9	•	• · ·		
γ Δ	C20	C30	120	• 9 1		• •		2
4	C29	н69	119	9	(1 2	/ • ?	·	•
n	C29	н69	119	.9	•	· · ·		
1	C30	C29	119	.5	(10)		?
1	C30	H70	120	.2	•	. ?		
9	C30	Н7О	120	.2		. ?		
7	C31	C15	120	.6	(12) .		?
7	C31	H23	119	.7		. ?		
5	C31	H23	119	.7	•	. ?		
5	C32	C76	120	.6	(13) .	•	?
5	C32	H22	119	.7	•	• ?		
6	C32	H22	119	.7	•	• ?		~
4	C33	C68	119	.6	(10) .	•	?
4	033	PZ 1	LI8.	0(8)	•••	?	
ठ ว	C33	PZ I	LZZ. 110	4 (8)	•••	2	2
с 2	C34	U00 U07	120	. 0 2	() · ?	•	:
5	C34	п <i>21</i> H27	120	.) २	•	• • • ?		
7	C35	C34	120	- 5		· ·		?
, 7	C35	H28	119	.2	(′ · ?	•	•
, 4	C35	H28	119	.2	•	. ?		
7	C36	C68	123	.2	(12) .		?
7	C36	H29	118	.4	•	. ?		
8	C36	H29	118	.4	•	. ?		
36	C37	C35	117	.5	(11) .		?
C36 C37 H30 121.3 . . ? СЗ5 СЗ7 НЗО 121.3 . . ? C71 C38 N6 118.7(11) . . ? C71 C38 C69 120.3(13) . . ? N6 C38 C69 120.9(12) . . ? C64 C39 C16 120.4(15) . . ? C64 C39 H20 119.8 . . ? C16 C39 H20 119.8 . . ? C9 C40 C65 115.3(14) . . ? C9 C40 C75 108.3(12) . . ? C65 C40 C75 110.0(15) . . ? С9 С40 Н89 107.7 . . ? С65 С40 Н89 107.7 . . ? С75 С40 Н89 107.7 . . ? C17 C41 H7 109.5 . . ? C17 C41 H8 109.5 . . ? H7 C41 H8 109.5 . . ? С17 С41 Н9 109.5 . . ? H7 C41 H9 109.5 . . ? H8 C41 H9 109.5 . . ? C44 C42 C43 120.3(11) . . ? C44 C42 H71 119.8 . . ? C43 C42 H71 119.8 . . ? C11 C43 C42 118.1(10) . . ? C11 C43 H72 121.0 . . ? C42 C43 H72 121.0 . . ? C29 C44 C42 121.1(12) . . ? C29 C44 H73 119.4 . . ? C42 C44 H73 119.4 . . ? C54 C45 C28 120.6(14) . . ? C54 C45 H65 119.7 . . ? C28 C45 H65 119.7 . . ? C27 C46 C55 121.5(12) . . ? С27 С46 Н66 119.2 . . ? С55 С46 Н66 119.2 . . ? C49 C47 C48 117.7(11) . . ? С49 С47 Н61 121.2 . . ? С48 С47 Н61 121.2 . . ? C47 C48 C20 121.4(10) . . ? C47 C48 H62 119.3 . . ? C20 C48 H62 119.3 . . ? C47 C49 C50 123.4(12) . . ? С47 С49 Н63 118.3 . . ? С50 С49 Н63 118.3 . . ? C18 C50 C49 117.1(10) . . ? C18 C50 C51 124.7(10) . . ? C49 C50 C51 118.2(11) . . ? C53 C51 C50 115.3(14) . . ?

C53	C51	C52	111.9(12) ?	
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н56	C52	H57	109.5 ?	
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C51	C53	н59	109 5 ?	
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U58	C53	н60	109 5 2	
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C45	C54	C 5 5	109.5	
C45	C54	UUUUUUUUU	110 7 2	
C55	C54	н67	1197 2	
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C46	C55	н68	120.3 2	
C54	C55	н68	120.3	
C57	C56	C74	120.5	
C57	C56	C73	123 3(9) 2	
C74	C56	C73	123.3(3) · · · · · · · · · · · · · · · · · · ·	
C58	C57	C56	120.2(10) · · · · · · · · · · · · · · · · · · ·	
C58	C57	N3 1	120 3(9) ?	
C56	C57	N3 1	118 6(8) ?	
C57	C58	C59	1176(11) ?	
C57	C58	C 6 0	127.0(11) · · · · · · · · · · · · · · · · · · ·	
C59	C58	C 60	123.1(10) · · · · · · · · · · · · · · · · · · ·	
C61	C59	C58	122 3(11) 2	
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н78	C 60	н79	109.5	
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C59	C 61	C 6 2	121.4(12) ?	
C74	C 61	C62	121.1(12) · · · · · · · · · · · · · · · · · · ·	
C61	C.62	H80	109.5	
C 6 1	C 62	H81	109 5 ?	
HSU	C 62	H81	109 5 ?	
C61	C 62	H82	109.5 . ?	
~ ~ -	~ ~ ~			

H80	C62	H82	109.5 ?	
H81	C62	H82	109.5 ?	
C17	C63	H10	109.5 ?	
C17	C63	H11	109.5 ?	
H10	C63	H11	109.5 ?	
C17	C63	H12	109.5 ?	
H10	C63	H12	109.5 ?	
H11	C63	H12	109.5 ?	
C39	C64	C8 1	L23.4(16) ?	
C39	C64	H21	118.3 ?	
C8 (C64 B	H21 1	L18.3 ?	
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H13	C65	H14	109.5 ?	
C40	C65	H15	109.5 ?	
H13	C65	H15	109.5 ?	
H14	C65	H15	109.5 ?	
C76	C66	C67	120.5(15) ?	
C76	C66	H24	119.8 ?	
C67	C66	H24	119.8 ?	
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C31	C67	H25	120.7 ?	
C66	C67	H25	120.7 ?	
C36	C68	C33	118.7(11) ?	
C36	C68	H31	120.6 ?	
C33	C68	H31	120.6 ?	
C38	C69	C79	117.3(18) ?	
C38	C69	C70	120.7(11) ?	
C79	C69	C70	122.0(15) ?	
C69	C70	H34	109.5 ?	
C69	C70	H35	109.5 ?	
Н34	C70	H35	109.5 ?	
C69	C70	H36	109.5 ?	
H34	C70	H36	109.5 ?	
Н35	C70	H36	109.5 ?	
C38	C71	C72	122.6(12) ?	
C38	C71	C78	115.9(16) ?	
C72	C71	C78	121.3(17) ?	
C71	C72	H37	109.5 ?	
C71	C72	H38	109.5 ?	
Н37	C72	H38	109.5 ?	
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H41 C80 H42 109.5 ?
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refine special details
Refinement of F^2^ against ALL reflections. The weighted R-
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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
on F^2 are statistically about twice as large as those based on
F, and R-
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;
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Cl8 Cl 0.15820(17) 0.51482(8) 0.93299(10) 0.0818(6) Uani 1 1 d .
. .
Cl9 Cl -0.06059(14) 0.59174(8) 0.82961(13) 0.0781(6) Uani 1 1 d .
. .
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N3 N 0.0879(3) 0.55699(19) 0.6995(2) 0.0429(10) Uani 1 1 d . . . N2 N 0.0304(4) 0.4654(2) 0.7727(3) 0.0487(11) Uani 1 1 d . . . N4 N 0.2008(4) 0.6200(2) 0.8099(3) 0.0458(11) Uani 1 1 d . . . C51 C 0.0353(4) 0.5168(3) 0.6564(3) 0.0474(13) Uani 1 1 d . . . C52 C 0.0127(5) 0.5250(3) 0.5785(4) 0.0579(15) Uani 1 1 d . . . H1 H -0.0223 0.4965 0.5492 0.069 Uiso 1 1 calc R . . C53 C 0.0418(5) 0.5749(3) 0.5446(3) 0.0620(16) Uani 1 1 d . . . H2 H 0.0271 0.5804 0.4922 0.074 Uiso 1 1 calc R . . C54 C 0.0929(5) 0.6169(3) 0.5881(3) 0.0580(16) Uani 1 1 d . . . H3 H 0.1109 0.6518 0.5662 0.070 Uiso 1 1 calc R . . C55 C 0.1173(4) 0.6061(2) 0.6660(3) 0.0468(13) Uani 1 1 d . . . 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 1 1 d . . . H24 H -0.0073 0.4060 0.6124 0.110 Uiso 1 1 calc R . . H25 H -0.1116 0.4282 0.6364 0.110 Uiso 1 1 calc R . . H26 H -0.0486 0.3827 0.6876 0.110 Uiso 1 1 calc R . . C11 C 0.1150(5) 0.7214(2) 0.7233(3) 0.0529(14) Uani 1 1 d . . . C12 C 0.0235(6) 0.7228(4) 0.7543(5) 0.082(2) Uani 1 1 d . . . H4 H 0.0014 0.6907 0.7803 0.099 Uiso 1 1 calc R . . C13 C 0.1440(6) 0.7708(3) 0.6824(4) 0.0648(17) Uani 1 1 d . . . H8 H 0.2056 0.7713 0.6608 0.078 Uiso 1 1 calc R . . C14 C 0.0799(7) 0.8182(3) 0.6748(5) 0.079(2) Uani 1 1 d . . . H7 H 0.0978 0.8507 0.6475 0.095 Uiso 1 1 calc R . . C15 C -0.0086(8) 0.8174(4) 0.7070(6) 0.100(3) Uani 1 1 d . . . H6 H -0.0517 0.8493 0.7013 0.120 Uiso 1 1 calc R . . C16 C -0.0347(7) 0.7719(4) 0.7466(6) 0.100(3) Uani 1 1 d . . . H5 H -0.0948 0.7732 0.7701 0.120 Uiso 1 1 calc R . . C21 C 0.3064(5) 0.6744(3) 0.6921(4) 0.0555(15) Uani 1 1 d . . . C22 C 0.3380(6) 0.6476(4) 0.6271(4) 0.075(2) Uani 1 1 d . . . H9 H 0.2992 0.6186 0.6019 0.090 Uiso 1 1 calc R . . C23 C 0.4295(9) 0.6654(6) 0.6009(6) 0.120(4) Uani 1 1 d . . . H10 H 0.4535 0.6474 0.5586 0.144 Uiso 1 1 calc R . . C24 C 0.4847(7) 0.7104(5) 0.6386(7) 0.103(3) Uani 1 1 d . . . H11 H 0.5439 0.7237 0.6199 0.124 Uiso 1 1 calc R . . C25 C 0.4523(7) 0.7342(4) 0.7014(6) 0.095(3) Uani 1 1 d . . . H12 H 0.4909 0.7633 0.7266 0.114 Uiso 1 1 calc R . . C26 C 0.3662(5) 0.7176(3) 0.7292(4) 0.0659(17) Uani 1 1 d . . . H13 H 0.3462 0.7348 0.7734 0.079 Uiso 1 1 calc R . . C31 C 0.2793(5) 0.6361(2) 0.8689(3) 0.0479(13) Uani 1 1 d . . . C32 C 0.2549(6) 0.6732(3) 0.9285(3) 0.0577(16) Uani 1 1 d . . . C33 C 0.3303(7) 0.6890(3) 0.9843(4) 0.070(2) Uani 1 1 d . . . H14 H 0.3148 0.7135 1.0238 0.084 Uiso 1 1 calc R . . C34 C 0.4301(8) 0.6686(4) 0.9824(5) 0.087(3) Uani 1 1 d . . . H15 H 0.4816 0.6804 1.0187 0.104 Uiso 1 1 calc R . . C35 C 0.4487(6) 0.6303(3) 0.9241(4) 0.0691(18) Uani 1 1 d . . . H16 H 0.5140 0.6158 0.9230 0.083 Uiso 1 1 calc R . . C36 C 0.3766(5) 0.6128(3) 0.8685(3) 0.0542(15) Uani 1 1 d . . . C70 C 0.1510(6) 0.6938(3) 0.9386(4) 0.0667(18) Uani 1 1 d . . .

H22 H 0.1066 0.6780 0.8958 0.080 Uiso 1 1 calc R . . C71 C 0.4047(5) 0.5665(3) 0.8111(4) 0.0633(16) Uani 1 1 d . . . H23 H 0.3512 0.5656 0.7686 0.076 Uiso 1 1 calc R . . C61 C 0.4106(8) 0.5069(4) 0.8477(6) 0.100(3) Uani 1 1 d . . . H39 H 0.4341 0.4792 0.8124 0.150 Uiso 1 1 calc R . . H40 H 0.3447 0.4957 0.8610 0.150 Uiso 1 1 calc R . . H41 H 0.4569 0.5080 0.8932 0.150 Uiso 1 1 calc R . . C62 C 0.5049(6) 0.5803(4) 0.7780(5) 0.091(2) Uani 1 1 d . . . H42 H 0.5600 0.5746 0.8168 0.136 Uiso 1 1 calc R . . H43 H 0.5044 0.6200 0.7611 0.136 Uiso 1 1 calc R . . H44 H 0.5133 0.5551 0.7355 0.136 Uiso 1 1 calc R . . 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 1 1 d . . . C43 C 0.0587(8) 0.3270(3) 0.8805(5) 0.082(2) Uani 1 1 d . . . H17 H 0.1081 0.2993 0.8943 0.098 Uiso 1 1 calc R . . C44 C -0.0399(8) 0.3189(3) 0.9014(5) 0.091(3) Uani 1 1 d . . . H18 H -0.0550 0.2862 0.9293 0.109 Uiso 1 1 calc R . . C45 C -0.1143(7) 0.3590(3) 0.8809(4) 0.076(2) Uani 1 1 d . . . H19 H -0.1794 0.3533 0.8954 0.092 Uiso 1 1 calc R . . C46 C -0.0932(5) 0.4082(3) 0.8389(4) 0.0601(16) Uani 1 1 d . . . C72 C 0.1876(6) 0.3827(3) 0.8151(5) 0.076(2) Uani 1 1 d . . . H20 H 0.1943 0.4236 0.8007 0.091 Uiso 1 1 calc R . . C57 C 0.2723(8) 0.3704(5) 0.8799(7) 0.112(3) Uani 1 1 d . . . H27 H 0.2547 0.3878 0.9267 0.168 Uiso 1 1 calc R . . H28 H 0.3350 0.3867 0.8663 0.168 Uiso 1 1 calc R . . H29 H 0.2798 0.3292 0.8869 0.168 Uiso 1 1 calc R . . C58 C 0.2012(8) 0.3465(5) 0.7432(6) 0.109(3) Uani 1 1 d . . . H30 H 0.2046 0.3060 0.7565 0.163 Uiso 1 1 calc R . . H31 H 0.2627 0.3578 0.7223 0.163 Uiso 1 1 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 1 1 d . . . H21 H -0.1505 0.4827 0.7913 0.087 Uiso 1 1 calc R . . C59 C -0.2132(9) 0.4791(5) 0.8920(6) 0.111(3) Uani 1 1 d . . . H33 H -0.2523 0.4515 0.9180 0.167 Uiso 1 1 calc R . . H34 H -0.2544 0.5123 0.8776 0.167 Uiso 1 1 calc R . . H35 H -0.1556 0.4911 0.9255 0.167 Uiso 1 1 calc R . . C60 C -0.2678(8) 0.4246(6) 0.7711(7) 0.121(4) Uani 1 1 d . . . H36 H -0.2482 0.4176 0.7205 0.181 Uiso 1 1 calc R . . H37 H -0.3241 0.4510 0.7683 0.181 Uiso 1 1 calc R . . H38 H -0.2869 0.3885 0.7932 0.181 Uiso 1 1 calc R . . C63 C 0.1124(8) 0.6701(5) 1.0122(6) 0.105(3) Uani 1 1 d . . . H45 H 0.1265 0.6292 1.0163 0.157 Uiso 1 1 calc R . . H46 H 0.0406 0.6763 1.0109 0.157 Uiso 1 1 calc R . . H47 H 0.1457 0.6899 1.0556 0.157 Uiso 1 1 calc R . . C64 C 0.1420(9) 0.7607(4) 0.9339(6) 0.106(3) Uani 1 1 d . . . H48 H 0.1799 0.7778 0.9775 0.160 Uiso 1 1 calc R . . H49 H 0.0721 0.7717 0.9335 0.160 Uiso 1 1 calc R . . H50 H 0.1683 0.7742 0.8879 0.160 Uiso 1 1 calc R . .

Cl81 Cl 0.2907(3) 0.47650(18) 0.63978(17) 0.1375(11) Uani 1 1 d D . . C182 C1 0.4857(3) 0.4799(2) 0.5845(3) 0.1730(18) Uani 1 1 d D . . C91 C 0.3592(7) 0.4655(6) 0.5637(6) 0.130(5) Uani 1 1 d D . . H51 H 0.3328 0.4902 0.5217 0.156 Uiso 1 1 calc R . . H52 H 0.3511 0.4254 0.5470 0.156 Uiso 1 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 0.7486 0.6089 0.9388 0.247 Uiso 0.301(5) 1 calc PR A 1 H54A H 0.8429 0.6495 0.9418 0.247 Uiso 0.301(5) 1 calc PR A 1 C184 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 0.8304 0.6313 0.9276 0.247 Uiso 0.699(5) 1 calc PR A 2 H54B H 0.7208 0.6561 0.9023 0.247 Uiso 0.699(5) 1 calc PR A 2 Cl85 Cl 0.2346(6) 0.9474(4) 0.1147(5) 0.291(4) Uani 1 1 d D . . C186 C1 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 1 1 d D . . H55 H 0.1945 0.8848 0.2005 0.255 Uiso 1 1 calc R . . H56 H 0.3091 0.9021 0.2138 0.255 Uiso 1 1 calc R . . 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 Fel 0.0461(4) 0.0471(4) 0.0295(3) -0.0002(3) 0.0052(3) -0.0091(4) P5 0.0487(9) 0.0510(8) 0.0383(7) 0.0020(6) 0.0071(6) -0.0067(6) C18 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)

C54	0.07	4(4)	0.	061	(4)	0	.039	(3)	0.0	011	(3)	0	.00	8(3) (0.0	01(3)		
C55	0.05	2(3)	0.	049	(3)	0	.040	(3)	0.0	203	(2)	0	.00	3(3) -	-0.	003(3)		
C6 (0.046	(3)	0.0)49 (3)	0.	047(3) ·	-0.0	009	(2)	0	.00	1(3) -	-0.	001(2)		
C56	0.09	2(5)	0.	066	(4)	0	.060	(4)	-0	.01	5(3) -	-0.	004	(4)) —	0.01	4 (4)	
C11	0.06	2(4)	0.	050	(3)	0	.046	(3)	0.0	007	(2)	0	.00	6(3) -	-0.	008(3)		
C12	0.07	7(5)	0.	076	(5)	0	.097	(6)	0.0	025	(4)	0	.02	0(5) (0.0	13(4)		
C13	0.07	6(5)	0.	059	(4)	0	.058	(4)	0.0	007	(3)	- (0.0	02(3)	-0	.005	(3)		
C14	0.09	6(6)	0.	062	(4)	0	.075	(5)	0.0	018	(3)	- (0.C	11 (4)	-0	.010	(4)		
C15	0.09	8(7)	0.	081	(6)	0	.122	(8)	0.0	013	(5)	0	.01	6(6) (0.0	37(5)		
C16	0.07	7(6)	0.	079	(5)	0	.147	(9)	0.0	031	(5)	0	.03	6(6) (0.0	23(4)		
C21	0.05	0(3)	0.	062	(4)	0	.056	(3)	0.0	015	(3)	0	.01	0(3) -	-0.	003(3)		
C22	0.06	8(5)	0.	093	(5)	0	.067	(4)	0.0	005	(4)	0	.02	4 (4) -	-0.	009(4)		
C23	0.10	8(8)	0.	164	(10) (0.09	6(7) 0	.03	6(7) (0.0	55(7)	0.	007(8)		
C24	0.06	5(5)	0.	132	(8)	0	.115	(8)	0.0	048	(7)	0	.01	6(5) -	-0.	025(6)		
C25	0.07	8(6)	0.	093	(6)	0	.112	(7)	0.0	026	(5)	0	.00	2(5) -	-0.	017(5)		
C26	0.05	4(4)	0.	066	(4)	0	.076	(4)	0.0	012	(3)	- (0.0	01(3)	-0	.016	(3)		
C31	0.05	4(4)	0.	052	(3)	0	.037	(3)	0.0	010	(2)	0	.00	3 (2) -	-0.	017(3)		
C32	0.08	2(5)	0.	047	(3)	0	.043	(3)	0.0	000	(2)	0	.00	6(3) -	-0.	019(3)		
C33	0.09	2(6)	0.	064	(4)	0	.055	(4)	-0	.00	4(3) (0.0	08(4)	-0	.029	(4)		
C34	0.10	6(7)	0.	088	(5)	0	.060	(4)	0.0	014	(4)	- (0.0	21(4)	-0	.043	(5)		
C35	0.06	2(4)	0.	083	(5)	0	.060	(4)	0.0	005	(3)	- (0.0	08(3)	-0	.019	(4)		
C36	0.06	0(4)	0.	057	(3)	0	.046	(3)	0.0	012	(2)	0	.00	3 (3) -	-0.	010(3)		
C70	0.08	6(5)	0.	065	(4)	0	.051	(3)	-0	.01	4(3) (0.0	17(3)	-0	.011	(4)		
C71	0.06	2(4)	0.	067	(4)	0	.061	(4)	0.0	004	(3)	0	.00	6(3) (0.0	00(3)		
C61	0.10	9(7)	0.	085	(6)	0	.107	(7)	0.0	004	(5)	0	.02	5(6) (0.0	02(5)		
C62	0.06	7(5)	0.	111	(6)	0	.098	(6)	0.0	009	(5)	0	.02	8 (5) (0.0	14(5)		
C41	0.06	0(4)	0.	043	(3)	0	.048	(3)	-0	.00	5 (2) (0.0	05(3)	-0	.013	(3)		
C42	0.07	6(5)	0.	055	(3)	0	.057	(4)	-0	.00	6(3) (0.0	09(3)	-0	.002	(3)		
C43	0.12	2(7)	0.	042	(3)	0	.080	(5)	0.0	003	(3)	0	.00	2 (5) (0.0	02(4)		
C44	0.13	4(8)	0.	058	(4)	0	.085	(5)	0.0	207	(4)	0	.03	1 (5) -	-0.	034(5)		
C45	0.09	2(6)	0.	066	(4)	0	.074	(5)	-0	.00	8 (4) (0.0	26(4)	-0	.028	(4)		
C46	0.07	1(4)	0.	056	(3)	0	.053	(3)	-0	.01	3 (3) (0.0	07(3)	-0	.017	(3)		
C72	0.09	2(6)	0.	048	(4)	0	.087	(5)	0.0	007	(3)	0	.00	6(4) (0.0	11(4)		
C57	0.09	0(7)	0.	096	(7)	0	.143	(9)	0.0	023	(6)	- (0.0	23(6)	0.	007(5)		
C58	0.09	7(7)	0.	122	(8)	0	.110	(8)	-0	.02	2(6) (0.0	27 (6)	0.	030(6)		
C73	0.05	4(4)	0.	084	(5)	0	.079	(5)	-0	.00	3(4) (0.0	09(4)	-0	.021	(4)		
C59	0.11	8(8)	0.	109	(7)	0	.114	(8)	-0	.00	6(6) (0.0	53(7)	0.	000 (6)		
C60	0.07	5(6)	0.	173	(11	.)	0.11	0 (8) -(0.0	09(8)	-0	.01	3 (6	6) ·	-0.0	23(7)	
C63	0.11	0(7)	0.	112	(7)	0	.100	(7)	-0	.01	4 (5) (0.0	48(6)	-0	.004	(6)		
C64	0.13	3(9)	0.	078	(5)	0	.110	(7)	-0	.02	4 (5) (0.0	21(6)	-0	.006	(6)		
C181	L 0.1	45 (3) (.17	7 (3)	0.09	18(18)	-0	.02	75	(19) 0	.02	200	(18)	0.	002	(2)
C182	2 0.1	19(3) (.23	2 (4)	J.16	5 (3) -(0.0	86(3)	0.	000	(2)) –	U.01	5(3)	
C91	0.12	2(9)	0.	173	(10)	9.08	9(7) -(0.0	70 (7)	-0	.03	2 (6	6)	0.04	1(8)	
C185	0.2	03(6) ().39	0(1	1)	0.2	83(9) (0.0	84 (8)	0.	033	(6)) ()	.069	(7)	0.0.0	
C186	b 0.3	15(1	0)	0.3	49(11) 0.	494	(17)) –	0.2	10	(12) –	0.1	164	(11)	0.	082	(9)

_geom_special_details;

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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
geom bond atom site label 1
geom bond atom site label 2
_geom_bond_distance
geom bond site symmetry 2
geom bond publ flag
Fel N3 2.086(4) . ?
Fel N4 2.127(5) . ?
Fe1 Cl8 2.2507(18) . ?
Fel N2 2.261(5) . ?
Fe1 Cl9 2.3129(19) . ?
P5 N4 1.600(5) . ?
P5 C21 1.804(6) . ?
P5 C11 1.812(6) . ?
P5 C55 1.815(6) . ?
N3 C55 1.346(7) . ?
N3 C51 1.348(7) . ?
N2 C6 1.291(7) . ?
N2 C41 1.446(7) . ?
N4 C31 1.446(7) . ?
C51 C52 1.384(9) . ?
C51 C6 1.480(8) . ?
C52 C53 1.364(10) . ?
C52 H1 0.9300 . ?
C53 C54 1.371(9) . ?
C53 H2 0.9300 . ?
C54 C55 1.397(8) . ?
C54 H3 0.9300 . ?
C6 C56 1.498(8) . ?
C56 H24 0.9600 . ?
C56 H25 0.9600 . ?
C56 H26 0.9600 . ?
C11 C12 1.373(10) . ?
C11 C13 1.415(9) . ?
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C45 C46 1.391(10) . ?
C45 H19 0.9300 . ?
C46 C73 1.509(11) . ?
C72 C58 1.535(12) . ?
C72 C57 1.549(13) . ?
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C57 H28 0.9600 . ?
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C59 H34 0.9600 . ?
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C33	C32	C70	116.8(6) ?
C31	C32	C70	124.1(6) ?
C32	C33	C34	121.1(7) ?
C32	C33	H14	119.5 ?
C34	C33	H14	119.5 ?
C35	C34	C33	117.3(7) ?
C35	C34	H15	121.3 . ?
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C36	C35	C34	123.7(8) ?
C36	C35	H16	118.2 ?
C34	C35	н16	118.2 ?
C35	C36	C.31	118.1(6) ?
C35	C36	C71	118.6(6) ?
C31	C36	C71	123.2(6)
C32	C70	C63	123.2(0) · · · · · · · · · · · · · · · · · · ·
C32	C70	C 64	112 3(7)
C63	C70	C 6 4	112.3(7) · · · · · · · · · · · · · · · · · · ·
C32	C70	H22	106.8 ?
C63	C70	н22	106.8 ?
C64	C70	н22	106.8 ?
C61	C71	C62	100.0
C61	C71	C36	109.0(7) · · · · · · · · · · · · · · · · · · ·
C62	C71	C36	110.9(0) · · · · · · · · · · · · · · · · · · ·
C61	C71	н23	108 1 2
C62	C71	н23	108 1 2
C36	C71	н23	108 1 2
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ц30	C 61	н40	109.5
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н40	C 61	н41	109.5
C71	C62	ц12	109.5
C71	C62	нд З	109.5
ц 442	C62	нд З	109.5
C71	C62	н44	109.5
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нд З	C62	ндд	109.5
C46	C41	C42	100.0.0.1
C_{46}	C41	N2 1	121.7(0)
C42	C41	N2 1	120.0(0) · · · · · · · · · · · · · · · · · · ·
C43	C42	C41	117 8(7) ?
C43	C42	C72	127.6(7) · · · · · · · · · · · · · · · · · · ·
C_{41}	C42	C72	120.0(7) · · · · · · · · · · · · · · · · · · ·
C42	C12	$C \Delta \Delta$	121.0(8) ?
C12	C13	стт ц17	1195 2
CAA	C43	нт, н17	119 5 2
C15	C10	C73	1205(7)
CI J	~	0-10	<u></u> , , , , , , , , , , , , , , , , , , ,

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C43	C44	H18	119.8 ?	
C44	C45	C46	120.6(8) .	. ?
C44	C45	H19	119.7 ?	
C46	C45	H19	119.7 ?	
C45	C46	C41	118.4(7) .	. ?
C45	C46	C73	117.5(7).	. ?
C41	C46	C73	124.0(6).	. ?
C42	C72	C58	110.9(7) .	?
C42	C72	C57	113.4(7) .	. ?
C58	C72	C57	111.8(8) .	. ?
C42	C72	H20	106.8 ?	
C58	C72	H20	106.8 ?	
C57	C72	H20	106.8 ?	
C72	C57	H27	109.5 ?	
C72	C57	H28	109.5 ?	
H27	C57	H28	109.5 ?	
C72	C57	H29	109.5 ?	
H27	C57	H29	109.5 ?	
Н28	C57	H29	109.5 ?	
C72	C58	Н30	109.5 ?	
C72	C58	H31	109.5 ?	
Н30	C58	Н31	109.5 ?	
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Н30	C58	Н32	109.5 ?	
Н31	C58	Н32	109.5 ?	
C59	C73	C46	113.1(8) .	. ?
C59	C73	C60	110.8(8) .	. ?
C46	C73	C60	112.0(7) .	. ?
C59	C73	H21	106.9 ?	
C46	C73	H21	106.9 ?	
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Н33	C59	Н35	109.5 ?	
Н34	C59	H35	109.5 ?	
C73	C60	Н36	109.5 ?	
C73	C60	H37	109.5 ?	
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computing cell refinement 'Bruker Smart program suite V6 (Bruker) ' computing_data_reduction 'Bruker Saint program suite V6 (Bruker) ' 'SHELXS-97 (Sheldrick, 1990)' computing structure solution 'SHELXL-97 (Sheldrick, 1997)' computing structure refinement _computing_molecular graphics ? computing publication material ? _refine_special details ; Refinement of F^2^ against ALL reflections. The weighted Rfactor wR and goodness of fit S are based on $F^{2^{\prime}}$, conventional R-factors R are based on F, with F set to zero for negative $F^{2^{-1}}$. The threshold expression of $F^2^2 > 2 \text{sigma}(F^2^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. Rfactors based on F^2 are statistically about twice as large as those based on F, and Rfactors based on ALL data will be even larger. ; refine ls structure factor coef Fsqd refine ls matrix type full _refine_ls_weighting_scheme calc refine ls weighting details 'calc $w=1/[\s^2^(Fo^2^)+(0.0644P)^2^+1.1904P]$ where $P = (Fo^2^+ 2Fc^2^)/3'$ atom sites solution primary direct atom sites solution secondary difmap atom sites solution hydrogens geom refine ls hydrogen treatment constr _refine_ls_extinction method none refine ls extinction coef ? refine ls number reflns 10575 _refine_ls_number_parameters 593 refine ls number restraints 0 refine ls R factor all 0.0491 _refine_ls_R_factor_gt 0.0395 refine ls wR factor ref 0.1075 refine ls wR factor gt 0.1009 refine ls goodness of fit ref 1.006 refine ls restrained S all 1.006 refine ls shift/su max 0.001

refine ls shift/su mean 0.000 loop atom site label atom site type symbol atom site fract x _atom_site_fract y atom site fract z _atom_site_U_iso_or equiv _atom_site_adp type atom site occupancy atom site symmetry multiplicity atom site calc flag atom site refinement flags _atom_site_disorder assembly atom site disorder group Fe1 Fe 0.84465(2) 0.485996(13) 0.212833(9) 0.04097(9) Uani 1 1 d . . . Fe2 Fe 0.90364(2) 0.245781(14) -0.014246(10) 0.04463(9) Uani 1 1 d... Si3 Si 1.04993(5) 0.60009(3) 0.26741(2) 0.05383(15) Uani 1 1 d . Si4 Si 0.64567(6) 0.37267(3) 0.15242(2) 0.05313(15) Uani 1 1 d . . . Si5 Si 1.12211(6) 0.13990(4) 0.04610(2) 0.05989(17) Uani 1 1 d . Si6 Si 0.69380(6) 0.36539(3) -0.06124(2) 0.05784(16) Uani 1 1 d . 01 0 0.61088(18) 0.53312(11) 0.32645(6) 0.0852(5) Uani 1 1 d . . 02 0 1.07413(19) 0.30790(9) 0.24267(8) 0.0903(6) Uani 1 1 d . . . 05 0 1.16398(14) 0.30609(9) -0.11665(5) 0.0650(4) Uani 1 1 d . . 06 0 0.66432(17) 0.08057(9) -0.07000(7) 0.0840(5) Uani 1 1 d . . N7 N 0.84513(15) 0.43108(8) 0.27493(6) 0.0466(4) Uani 1 1 d . . . 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 . . N10 N 0.69434(15) 0.53470(9) 0.25412(6) 0.0513(4) Uani 1 1 d . . N11 N 1.06089(14) 0.30336(8) -0.04866(6) 0.0473(4) Uani 1 1 d . . N12 N 0.75642(15) 0.16013(9) -0.01845(7) 0.0542(4) Uani 1 1 d . . 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 . .

C10 C 0.8480(3) 0.35528(15) 0.36164(10) 0.0853(8) Uani 1 1 d . . H5 H 0.8492 0.3301 0.3905 0.102 Uiso 1 1 calc R . . C11 C 0.7699(3) 0.41181(14) 0.35380(8) 0.0730(7) Uani 1 1 d . . . H6 H 0.7181 0.4253 0.3774 0.088 Uiso 1 1 calc R . . C12 C 0.7691(2) 0.44837(12) 0.31051(7) 0.0543(5) Uani 1 1 d . . . C13 C 0.9973(2) 0.36355(10) 0.24379(9) 0.0581(5) Uani 1 1 d . . . C14 C 1.0929(2) 0.38368(12) 0.17646(10) 0.0670(6) Uani 1 1 d . . C15 C 1.2063(2) 0.42925(17) 0.18766(12) 0.0926(9) Uani 1 1 d . . H23 H 1.1838 0.4775 0.1831 0.139 Uiso 1 1 calc R . . H24 H 1.2687 0.4172 0.1662 0.139 Uiso 1 1 calc R . . H25 H 1.2385 0.4219 0.2208 0.139 Uiso 1 1 calc R . . C16 C 1.0490(3) 0.38918(16) 0.12272(10) 0.0894(9) Uani 1 1 d . . H26 H 0.9764 0.3608 0.1160 0.134 Uiso 1 1 calc R . . H27 H 1.1136 0.3732 0.1035 0.134 Uiso 1 1 calc R . . H28 H 1.0295 0.4370 0.1148 0.134 Uiso 1 1 calc R . . C17 C 1.1149(3) 0.30879(15) 0.19348(13) 0.1022(11) Uani 1 1 d . . H7 H 1.0666 0.2763 0.1726 0.123 Uiso 1 1 calc R . . H8 H 1.2021 0.2966 0.1938 0.123 Uiso 1 1 calc R . . C18 C 0.69057(19) 0.50699(12) 0.29591(8) 0.0549(5) Uani 1 1 d . . C19 C 0.5185(3) 0.36692(16) 0.10208(10) 0.0856(8) Uani 1 1 d . . H35 H 0.4580 0.4027 0.1063 0.128 Uiso 1 1 calc R . . H36 H 0.4795 0.3219 0.1028 0.128 Uiso 1 1 calc R . . H37 H 0.5528 0.3732 0.0714 0.128 Uiso 1 1 calc R . . C20 C 0.99626(18) 0.22385(11) -0.11167(7) 0.0480(4) Uani 1 1 d . . . C21 C 0.5638(3) 0.59626(19) 0.30268(11) 0.1024(11) Uani 1 1 d . . H9 H 0.6034 0.6372 0.3178 0.123 Uiso 1 1 calc R . . H10 H 0.4748 0.6001 0.3045 0.123 Uiso 1 1 calc R . . C22 C 0.5951(2) 0.58960(14) 0.24972(9) 0.0678(6) Uani 1 1 d . . . C23 C 0.6439(3) 0.65783(16) 0.23063(12) 0.0969(10) Uani 1 1 d . . H29 H 0.7159 0.6722 0.2508 0.145 Uiso 1 1 calc R . . H30 H 0.5808 0.6931 0.2311 0.145 Uiso 1 1 calc R . . H31 H 0.6657 0.6513 0.1979 0.145 Uiso 1 1 calc R . . C24 C 0.4867(3) 0.5621(2) 0.21688(13) 0.1071(11) Uani 1 1 d . . . H32 H 0.5147 0.5498 0.1859 0.161 Uiso 1 1 calc R . . H33 H 0.4239 0.5976 0.2125 0.161 Uiso 1 1 calc R . . H34 H 0.4528 0.5215 0.2314 0.161 Uiso 1 1 calc R . . C25 C 0.73311(19) 0.45539(10) 0.15147(7) 0.0481(4) Uani 1 1 d . .

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H21 H 0.6735 0.4925 0.1439 0.058 Uiso 1 1 calc R . . H22 H 0.7856 0.4528 0.1246 0.058 Uiso 1 1 calc R . . C26 C 1.0019(2) 0.19572(14) -0.15732(8) 0.0674(6) Uani 1 1 d . . H1 H 1.0598 0.2121 -0.1777 0.081 Uiso 1 1 calc R . . C27 C 0.7493(3) 0.29497(13) 0.14613(11) 0.0800(7) Uani 1 1 d . . H38 H 0.7899 0.2990 0.1166 0.120 Uiso 1 1 calc R . . H39 H 0.7004 0.2530 0.1452 0.120 Uiso 1 1 calc R . . H40 H 0.8105 0.2932 0.1734 0.120 Uiso 1 1 calc R . . C28 C 0.5706(3) 0.36046(16) 0.21065(10) 0.0862(9) Uani 1 1 d . . H41 H 0.6336 0.3544 0.2370 0.129 Uiso 1 1 calc R . . H42 H 0.5182 0.3199 0.2081 0.129 Uiso 1 1 calc R . . H43 H 0.5216 0.4009 0.2167 0.129 Uiso 1 1 calc R . . C29 C 0.83345(19) 0.14961(11) -0.09616(8) 0.0531(5) Uani 1 1 d . C30 C 0.8359(3) 0.11952(14) -0.14156(9) 0.0739(7) Uani 1 1 d . . H3 H 0.7807 0.0838 -0.1511 0.089 Uiso 1 1 calc R . . C31 C 0.9203(3) 0.14269(16) -0.17259(9) 0.0840(8) Uani 1 1 d . . H2 H 0.9227 0.1231 -0.2033 0.101 Uiso 1 1 calc R . . C32 C 1.07420(17) 0.27920(11) -0.09106(7) 0.0477(4) Uani 1 1 d . C33 C 1.1576(2) 0.35876(12) -0.03908(9) 0.0600(6) Uani 1 1 d . . C34 C 1.2106(3) 0.36540(16) -0.08855(10) 0.0860(9) Uani 1 1 d . . H11 H 1.1835 0.4087 -0.1044 0.103 Uiso 1 1 calc R . . H12 H 1.3007 0.3648 -0.0848 0.103 Uiso 1 1 calc R . . C35 C 1.2543(2) 0.33342(17) -0.00018(10) 0.0871(9) Uani 1 1 d . . H68 H 1.2148 0.3223 0.0288 0.131 Uiso 1 1 calc R . . H69 H 1.3149 0.3695 0.0069 0.131 Uiso 1 1 calc R . . H70 H 1.2943 0.2924 -0.0115 0.131 Uiso 1 1 calc R . . C36 C 1.0996(3) 0.42628(15) -0.02325(14) 0.1038(11) Uani 1 1 d . H71 H 1.0384 0.4418 -0.0482 0.156 Uiso 1 1 calc R . . H72 H 1.1628 0.4614 -0.0179 0.156 Uiso 1 1 calc R . . H73 H 1.0608 0.4185 0.0064 0.156 Uiso 1 1 calc R . . C37 C 0.75060(19) 0.13032(11) -0.06012(9) 0.0557(5) Uani 1 1 d . C38 C 0.6575(2) 0.12814(14) 0.00938(10) 0.0721(7) Uani 1 1 d . . C39 C 0.5993(3) 0.07554(19) -0.02706(13) 0.1118(12) Uani 1 1 d . H13 H 0.6064 0.0286 -0.0138 0.134 Uiso 1 1 calc R . .

H14 H 0.5120 0.0860 -0.0345 0.134 Uiso 1 1 calc R . . C40 C 0.7162(3) 0.0917(2) 0.05419(14) 0.1344(16) Uani 1 1 d . . . H74 H 0.7738 0.0570 0.0447 0.202 Uiso 1 1 calc R . . H75 H 0.6527 0.0695 0.0711 0.202 Uiso 1 1 calc R . . H76 H 0.7592 0.1253 0.0752 0.202 Uiso 1 1 calc R . . C41 C 0.5876(3) 0.43808(18) -0.04576(14) 0.1197(13) Uani 1 1 d . . . H62 H 0.5314 0.4214 -0.0232 0.179 Uiso 1 1 calc R . . H63 H 0.5412 0.4541 -0.0748 0.179 Uiso 1 1 calc R . . H64 H 0.6358 0.4760 -0.0313 0.179 Uiso 1 1 calc R . . C42 C 0.5913(3) 0.29825(16) -0.09216(13) 0.1120(12) Uani 1 1 d . H65 H 0.6412 0.2623 -0.1051 0.168 Uiso 1 1 calc R . . H66 H 0.5402 0.3197 -0.1182 0.168 Uiso 1 1 calc R . . H67 H 0.5395 0.2780 -0.0692 0.168 Uiso 1 1 calc R . . C43 C 0.78688(19) 0.33042(11) -0.00793(8) 0.0529(5) Uani 1 1 d . . . H15 H 0.7295 0.3180 0.0159 0.063 Uiso 1 1 calc R . . H16 H 0.8374 0.3686 0.0059 0.063 Uiso 1 1 calc R . . C44 C 0.9495(3) 0.6323(2) 0.31414(12) 0.1148(13) Uani 1 1 d . . . H44 H 0.8929 0.6667 0.2999 0.172 Uiso 1 1 calc R . . H45 H 1.0002 0.6530 0.3406 0.172 Uiso 1 1 calc R . . H46 H 0.9035 0.5939 0.3261 0.172 Uiso 1 1 calc R . . C45 C 1.1621(3) 0.67191(17) 0.25603(14) 0.1123(12) Uani 1 1 d . . H47 H 1.2038 0.6611 0.2275 0.168 Uiso 1 1 calc R . . H48 H 1.2221 0.6762 0.2835 0.168 Uiso 1 1 calc R . . H49 H 1.1178 0.7152 0.2512 0.168 Uiso 1 1 calc R . . C46 C 1.1455(3) 0.52853(14) 0.29662(11) 0.0875(9) Uani 1 1 d . . H50 H 1.0924 0.4910 0.3051 0.131 Uiso 1 1 calc R . . H51 H 1.1910 0.5459 0.3255 0.131 Uiso 1 1 calc R . . H52 H 1.2026 0.5117 0.2744 0.131 Uiso 1 1 calc R . . C51 C 0.95728(18) 0.57308(10) 0.21149(7) 0.0473(4) Uani 1 1 d . . H19 H 1.0144 0.5653 0.1867 0.057 Uiso 1 1 calc R . . H20 H 0.9050 0.6123 0.2008 0.057 Uiso 1 1 calc R . . C50 C 1.00755(19) 0.21087(11) 0.04750(7) 0.0518(5) Uani 1 1 d . . H17 H 1.0516 0.2512 0.0615 0.062 Uiso 1 1 calc R . . H18 H 0.9489 0.1968 0.0704 0.062 Uiso 1 1 calc R . . C47 C 1.1854(3) 0.12877(15) -0.01455(9) 0.0812(8) Uani 1 1 d . . H53 H 1.1201 0.1140 -0.0380 0.122 Uiso 1 1 calc R . . H54 H 1.2500 0.0942 -0.0121 0.122 Uiso 1 1 calc R . . H55 H 1.2186 0.1725 -0.0246 0.122 Uiso 1 1 calc R . . C48 C 1.2594(3) 0.1572(2) 0.09076(12) 0.1160(13) Uani 1 1 d . . . H56 H 1.2997 0.1996 0.0820 0.174 Uiso 1 1 calc R . .

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 . . 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 Fel 0.04482(15) 0.04010(15) 0.03766(15) 0.00104(11) 0.00139(11) -0.00092(11)Fe2 0.04610(16) 0.04834(17) 0.03943(16) -0.00079(12) 0.00344(12) 0.00422(12)Si3 0.0533(3) 0.0442(3) 0.0617(4) -0.0066(3) -0.0094(3) -0.0001(2)Si4 0.0562(3) 0.0554(3) 0.0476(3) -0.0028(3) 0.0029(3) -0.0133(3) Si5 0.0607(4) 0.0701(4) 0.0496(3) 0.0130(3) 0.0084(3) 0.0176(3) Si6 0.0521(3) 0.0548(3) 0.0656(4) 0.0077(3) -0.0012(3) 0.0051(3) 01 0.0914(12) 0.1052(14) 0.0635(11) -0.0004(10) 0.0343(10) 0.0240(11)02 0.1006(13) 0.0583(10) 0.1142(16) 0.0214(10) 0.0229(12) 0.0346(10) $05 \ 0.0634(9) \ 0.0783(11) \ 0.0554(9) \ 0.0095(8) \ 0.0175(7) \ -0.0163(8)$ 06 0.0809(11) 0.0749(11) 0.0973(14) -0.0135(10) 0.0133(10) -0.0373(10)N7 0.0515(9) 0.0463(9) 0.0418(9) 0.0046(7) 0.0023(7) -0.0011(7) N8 0.0516(9) 0.0416(9) 0.0557(10) -0.0034(8) 0.0066(8) 0.0057(7)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)

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) $C15 \ 0.0611(15) \ 0.099(2) \ 0.120(3) \ -0.0093(19) \ 0.0262(16)$ 0.0021(15)C16 0.097(2) 0.096(2) 0.0790(19) -0.0205(16) 0.0311(16) 0.0048(17)c17 0.112(2) 0.0705(18) 0.130(3) 0.0047(18) 0.045(2) 0.0378(17) C18 0.0522(11) 0.0666(13) 0.0473(12) -0.0064(10) 0.0122(9) 0.0002(10) $C19 \ 0.0767(17) \ 0.095(2) \ 0.0821(19) \ -0.0106(16) \ -0.0132(14) \ -$ 0.0171(15)C20 0.0511(11) 0.0525(11) 0.0410(10) 0.0026(9) 0.0072(8) 0.0032(9) $C21 \ 0.102(2) \ 0.122(3) \ 0.087(2) \ -0.0044(19) \ 0.0299(18) \ 0.046(2)$ $C22 \ 0.0573(13) \ 0.0791(16) \ 0.0675(15) \ -0.0068(13) \ 0.0078(11)$ 0.0246(12)C23 0.099(2) 0.0783(19) 0.113(2) 0.0115(17) 0.0110(19) 0.0362(17) $C24 \ 0.0626(16) \ 0.132(3) \ 0.122(3) \ -0.022(2) \ -0.0186(17) \ 0.0319(18)$ 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) $C30 \ 0.0839(17) \ 0.0726(16) \ 0.0652(15) \ -0.0227(13) \ 0.0058(13) \ -$ 0.0174(13)C31 0.106(2) 0.095(2) 0.0523(14) -0.0277(14) 0.0161(14) -0.0141(17)C32 0.0432(10) 0.0538(11) 0.0464(11) 0.0109(9) 0.0060(8) 0.0006(9)

C33 0.0522(12) 0.0607(13) 0.0661(14) 0.0047(11) -0.0010(10) -0.0150(10)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) $C48 \ 0.0805(19) \ 0.182(4) \ 0.081(2) \ 0.015(2) \ -0.0179(16) \ 0.034(2)$ 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) $C53 \ 0.086(2) \ 0.244(5) \ 0.112(3) \ 0.109(3) \ 0.002(2) \ -0.005(3)$ _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. ;

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loop
geom bond atom site label 1
_geom_bond_atom_site label 2
geom bond distance
geom bond site symmetry 2
geom bond publ flag
Fel N7 2.0089(16) . ?
Fe1 C51 2.0647(19) . ?
Fe1 C25 2.0794(19) . ?
Fel N8 2.2348(16) . ?
Fel N10 2.2599(16) . ?
Fe2 N9 2.0123(15) . ?
Fe2 C43 2.068(2) . ?
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) . ?
Si4 C19 1.875(3) . ?
Si4 C27 1.877(3) . ?
Si5 C50 1.839(2) . ?
Si5 C49 1.866(3) . ?
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) . ?
Si6 C41 1.874(3) . ?
O1 C18 1.349(2) . ?
O1 C21 1.446(4) . ?
O2 C13 1.352(3) . ?
O2 C17 1.461(4) . ?
O5 C32 1.348(2) . ?
O5 C34 1.441(3) . ?
O6 C37 1.344(2) . ?
O6 C39 1.429(4) . ?
N7 C12 1.371(3) . ?
N7 C8 1.370(3) . ?
N8 C13 1.279(3) . ?
N8 C14 1.494(3) . ?
N9 C29 1.363(2) . ?
N9 C20 1.373(2) . ?
N10 C18 1.272(3) . ?
N10 C22 1.498(3) . ?
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N11 C32 1.277(3) . ? N11 C33 1.496(3) . ? N12 C37 1.280(3) . ? N12 C38 1.497(3) . ? C8 C9 1.384(3) . ? C8 C13 1.432(3) . ? C9 C10 1.384(4) . ? C9 H4 0.9300 . ? C10 C11 1.378(4) . ? С10 Н5 0.9300 . ? C11 C12 1.383(3) . ? С11 Н6 0.9300 . ? C12 C18 1.443(3) . ? C14 C15 1.515(4) . ? C14 C17 1.520(4) . ? C14 C16 1.522(4) . ? C15 H23 0.9600 . ? C15 H24 0.9600 . ? C15 H25 0.9600 . ? С16 H26 0.9600 . ? C16 H27 0.9600 . ? C16 H28 0.9600 . ? C17 H7 0.9700 . ? С17 Н8 0.9700 . ? C19 H35 0.9600 . ? С19 НЗ6 0.9600 . ? С19 Н37 0.9600 . ? C20 C26 1.375(3) . ? C20 C32 1.440(3) . ? C21 C22 1.532(4) . ? С21 Н9 0.9700 . ? C21 H10 0.9700 . ? C22 C24 1.515(4) . ? C22 C23 1.517(4) . ? C23 H29 0.9600 . ? C23 H30 0.9600 . ? C23 H31 0.9600 . ? C24 H32 0.9600 . ? C24 H33 0.9600 . ? C24 H34 0.9600 . ? C25 H21 0.9700 . ? C25 H22 0.9700 . ? C26 C31 1.386(4) . ? C26 H1 0.9300 . ? С27 Н38 0.9600 . ? C27 H39 0.9600 . ? C27 H40 0.9600 . ? C28 H41 0.9600 . ?

C28 H42 0.9600 . ? C28 H43 0.9600 . ? C29 C30 1.380(3) . ? C29 C37 1.440(3) . ? C30 C31 1.375(4) . ? СЗО НЗ 0.9300 . ? C31 H2 0.9300 . ? C33 C36 1.515(4) . ? C33 C35 1.514(3) . ? C33 C34 1.528(3) . ? C34 H11 0.9700 . ? C34 H12 0.9700 . ? C35 H68 0.9600 . ? C35 H69 0.9600 . ? C35 H70 0.9600 . ? C36 H71 0.9600 . ? C36 H72 0.9600 . ? СЗ6 Н73 0.9600 . ? C38 C52 1.489(4) . ? C38 C40 1.512(4) . ? C38 C39 1.521(4) . ? C39 H13 0.9700 . ? C39 H14 0.9700 . ? C40 H74 0.9600 . ? C40 H75 0.9600 . ? C40 H76 0.9600 . ? С41 Н62 0.9600 . ? С41 Н63 0.9600 . ? С41 Н64 0.9600 . ? C42 H65 0.9600 . ? C42 H66 0.9600 . ? С42 Н67 0.9600 . ? C43 H15 0.9700 . ? C43 H16 0.9700 . ? C44 H44 0.9600 . ? C44 H45 0.9600 . ? C44 H46 0.9600 . ? C45 H47 0.9600 . ? C45 H48 0.9600 . ? C45 H49 0.9600 . ? C46 H50 0.9600 . ? C46 H51 0.9600 . ? C46 H52 0.9600 . ? C51 H19 0.9700 . ? C51 H20 0.9700 . ? C50 H17 0.9700 . ? C50 H18 0.9700 . ? C47 H53 0.9600 . ?

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C47 H54 0.9600 . ?
C47 H55 0.9600 . ?
C48 H56 0.9600 . ?
C48 H57 0.9600 . ?
C48 H57 0.9600 . ?
C49 H59 0.9600 . ?
C49 H60 0.9600 . ?
C49 H61 0.9600 . ?
C52 H77 0.9600 . ?
C52 H78 0.9600 . ?
C53 H80 0.9600 . ?
C53 H81 0.9600 . ?
C53 H82 0.9600 . ?
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loop

geom angle atom site label 1 _geom_angle_atom_site label 2 geom angle atom site label 3 _geom_angle _geom_angle_site_symmetry 1 geom angle site symmetry 3 geom angle publ flag N7 Fe1 C51 118.48(7) . . ? N7 Fe1 C25 120.50(7) . . ? C51 Fe1 C25 121.02(8) . . ? N7 Fel N8 75.12(6) . . ? C51 Fe1 N8 97.00(7) . . ? C25 Fel N8 97.47(7) . . ? N7 Fel N10 74.76(6) . . ? C51 Fe1 N10 97.23(7) . . ? C25 Fel N10 97.68(7) . . ? N8 Fel N10 149.88(6) . . ? N9 Fe2 C43 118.47(7) . . ? N9 Fe2 C50 123.11(7) . . ? C43 Fe2 C50 118.42(8) . . ? N9 Fe2 N12 74.85(6) . . ? C43 Fe2 N12 97.96(8) . . ? C50 Fe2 N12 97.99(8) . . ? N9 Fe2 N11 74.64(6) . . ? C43 Fe2 N11 97.88(7) . . ? C50 Fe2 N11 97.18(7) . . ? N12 Fe2 N11 149.44(6) . . ? C51 Si3 C44 111.45(12) . . ? C51 Si3 C46 113.65(11) . . ? C44 Si3 C46 106.22(17) . . ? C51 Si3 C45 112.29(13) . . ? C44 Si3 C45 107.20(18) . . ?

C46	Si	3 C	45	10	5.	55	(1	5)		•	?
C25	Si	4 C	28	11	2.	19	(1	1)			?
C25	Si	4 C	19	11	2.	65	(1	1)			?
C28	Si	4 C	19	10	6.	56	(1	3)			?
C25	Si	4 C	27	11	1.	56	(1	1)			?
C28	Si	4 C	27	10	6.	52	(1	4)			?
C19	Si	4 C	27	10	6.	96	(1	3)			?
C50	Si	5 C	49	11	2.	52	(1	3)			?
C50	Si	5 C	47	11	3.	50	(1	(0)			?
C49	Si	5 C	47	10	6.	5.3	(1	5)			?
C50	Si	5 C	48	11	0.	66	(1	4)			?
C49	Si	5 C	48	10	6.	97	(1	8)			?
C47	Si	5 C	48	10	6	23	(1	5)			?
C43	Si	6 C	53	11	1	82	(1	3)		••	。 ?
C43	Si	6 C	42	11	2	49 49	(1	2)		••	。 ?
C53	Si	6 C	42	10	6	8 ($\frac{1}{2}$	2)		· ·	•
C43	Si	6 C	41	11	3	12	(1	4)	•	•••	2
C53	Si	6 C	<u>11</u>	10	6	т <u>с</u> 8 ($\frac{1}{2}$	1)	•	· ·	, -
C42	Si	6 C	41	10	5	30 72	(1	6) 6)	•	•••	2
C18	01	C2	1	1 ∩ 4	1	52 7 (19	٥, ١	•	••	۲
C13	02	C1	7	101	• - 1	, (8 (19))	•	•	• ?
C32	02	C 3	, . Д [.]	104	• ±	8 (17) \	•	•	•
C37	05	C3	g .	105	1	(2)	<u>ب</u>	'	•	• ?	•
C12	N7	C8	1	17	• ± 27	(1	י 7 א	•	•	• ?)
C12	N7	Fe	1	121	6	4 (,, 1	、.		• •	ç
C8	N7	гс Гр1	1 ·	21 21	09	(1	<u>لا ۲</u>	'	•	•	•
C13	N8	C1	4	106	g	ι 5 (17	、.		• •	ç
C13	N8	Fe	1 .	111	2) (4 (14))	•	•	• ?
C14	N8	Fe	1 ·	141	8	1 (14	ì	•	•	• ?
C29	N9	C2	<u>т</u> .	116	.0	1 (16))	•	•	• ?
C29	N9	Fe	2	121	- 5	- (9 (13))	•	•	• ?
C20	N9	Fe	2 .	121	. 5	9 (9 (13))	•	•	• ?
C18	N1		22	10	6	2 (8 0	(1	, 8)	•	•	• ?
C18	N1	00 700	<u>е</u> 1	11	1	28	(1	4)		••	。 ?
C22	N1	1 0 7 0	ст е1	14	1	92	(1	4)		••	。 ?
C32	N1	1 C	33	10	6.	75	(1	$\frac{1}{7}$		•	。 ?
C32	N1	- 0 1 F	e2	11	0.	40	(1	3)		•	。 ?
C33	N1	 1 ፑ	e2	14	2	83	(1	3)			。 ?
C37	N1	2 C	38	10	7	10	(1	9)		•	。 ?
C37	N1	2 E	e2	11	0	37	(1	3)		•	。 ?
C38	N1	2 F	e2	14	2	41	(1	6)		•	。 ?
N7	C.8	C 9	12:	2.2	(2)	(-	• /	? `	•••	•
N7	C.8	C13	1	11.	16	, (1	• 7)	•	•	2)
C9	C8	C13	1	26.	- 0	2)	• ,	•	-		
C8	C9	C10	1	19.	5 (2)	•	•		2	
C8	C 9	н4	120	0.3	- ('	- /	?	•			
C10	C.9	H4	1:	20.	3	•		?			
C11	C1	0 C	9	119	.3)			?	
						·	1	-	-	~	
C11 C10 H5 120.4 . . ? C9 C10 H5 120.4 . . ? C10 C11 C12 119.5(2) . . ? С10 С11 Н6 120.3 . . ? С12 С11 Н6 120.3 . . ? N7 C12 C11 122.3(2) . . ? N7 C12 C18 111.15(17) . . ? C11 C12 C18 126.5(2) . . ? N8 C13 O2 117.4(2) . . ? N8 C13 C8 121.02(18) . . ? O2 C13 C8 121.5(2) . . ? N8 C14 C15 108.9(2) . . ? N8 C14 C17 101.0(2) . . ? C15 C14 C17 112.1(3) . . ? N8 C14 C16 111.4(2) . . ? C15 C14 C16 109.9(2) . . ? C17 C14 C16 113.2(2) . . ? C14 C15 H23 109.5 . . ? C14 C15 H24 109.5 . . ? H23 C15 H24 109.5 . . ? C14 C15 H25 109.5 . . ? H23 C15 H25 109.5 . . ? H24 C15 H25 109.5 . . ? C14 C16 H26 109.5 . . ? C14 C16 H27 109.5 . . ? H26 C16 H27 109.5 . . ? C14 C16 H28 109.5 . . ? H26 C16 H28 109.5 . . ? H27 C16 H28 109.5 . . ? 02 C17 C14 104.3(2) . . ? O2 C17 H7 110.9 . . ? C14 C17 H7 110.9 . . ? O2 C17 H8 110.9 . . ? С14 С17 Н8 110.9 . . ? H7 C17 H8 108.9 . . ? N10 C18 O1 118.8(2) . . ? N10 C18 C12 120.96(18) . . ? 01 C18 C12 120.3(2) . . ? Si4 C19 H35 109.5 . . ? 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 . . ? C26 C20 N9 122.8(2) . . ? C26 C20 C32 125.50(19) . . ? N9 C20 C32 111.75(17) . . ? O1 C21 C22 105.4(2) . . ?

01	C21 H	H9 11	0.7 ?	
C22	C21	H9 1	10.7 ?	
01	C21 F	H10 1	10.7 ?	
C22	C21	H10	110.7 ?	
Н9	C21 F	H10 1	.08.8 ?	
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) ?	
C22	C23	Н29	109.5 ?	
C22	C23	Н30	109.5 ?	
H29	C23	Н30	109.5 ?	
C22	C23	H31	109.5 ?	
H29	C23	Н31	109.5 ?	
Н30	C23	Н31	109.5 ?	
C22	C24	Н32	109.5 ?	
C22	C24	Н33	109.5 ?	
Н32	C24	Н33	109.5 ?	
C22	C24	Н34	109.5 ?	
Н32	C24	Н34	109.5 ?	
Н33	C24	Н34	109.5 ?	
Si4	C25	Fe1	119.56(10) ?	
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 1	.20.3 ?	
C31	C26	H1 1	20.3.?	
Si4	C27	H38	109.5 ?	
Si4	C27	H39	109.5 ?	
H38	C27	H39	109.5 ?	
S14	C27	H40	109.5 ?	
H38	C27	H40	109.5 ?	
H39	C27	H40	109.5 ?	
S14	C28	H41	109.5 ?	
S14	C28	H4Z	109.5 ?	
H41	C28	H4Z	109.5 ?	
514	CZ	H43	100 5 0	
H41	028	H43	100 5 0	
п42 мо	020 020	П43 ¬2∩ 1	103.0 · · · ·	
NIQ NIQ		- つし I - つつ 1	22.0(2) · · :	
С З О К NT	C29 (ンノ I でつつ	125 A(2)	
C3U	C29	C31	123.4(2) · · :	
COL	000	629	IIJ.U(Z) · · :	

C31	C30	H3 1	L20	.2	•	•	?			
C29	C30	H3 1	L20	.2	•	•	?			
C30	C31	C26	11	9.()(2) .	•	•	?	
C30	C31	H2 1	L20	.5	•	•	?			
C26	C31	H2 1	L20	.5	•	•	?			
N11	C32	05 1	L18	. 82	2(1	9)	•	•	:)
N11	C32	C20	12	1.4	42 (17)		•	•	?
05	C32	C20 1	L19	.75	5(1	8)	•	•	:)
N11	C33	C36	11	0.	77 (19)		•	•	?
N11	C33	C35	10	9.2	24 (19)		•	•	?
C36	C33	C35	11	0.2	2(2)	•	•	?	
N11	C33	C34	10	2.()6(18)		•	•	?
C36	C33	C34	11	2.4	4(2) .	•	•	?	
C35	C33	C34	11	1.8	3(2) .	•	•	?	_
05	C34	C33]	L05	.94	4(1	8)	•	•)
05	C34	HIL		.5	•	•	:			
C33	C34	HII HII		0.5	. כ	•	?			
05	C34	HIZ J		.5 ^ '	•	•	:			
C33	C34	HIZ		0.:	. C	•	: 2			
HII GDD	C34	HIZ	1 0	о. о г	-	•	:			
C33	C35	HOO	1 O	9.3	5.	•	: 0			
160	C35	ноэ	10	9.0 0 [). 5	•	ຳ ໂ			
C33	C35	п09 1170	10	9 0. [, .	•	: ว			
ч68	C35	н70 н70	10	9 9. [5.	•	: ?			
н69	C35	H70	10	9	5.	•	• ?			
C33	C36	н71	10	9.5	5.	•	?			
C33	C36	н72	10	9.5	5.		?			
H71	C36	Н72	10	9.5	5.		?			
C33	C36	Н7З	10	9.5	5.	•	?			
H71	C36	Н7З	10	9.5	5.		?			
Н72	C36	Н7З	10	9.5	5.		?			
N12	C37	06 1	L18	.6	(2)	•		?		
N12	C37	C29	12	1.2	25(18))	•	•	?
06	C37	C29 1	L20	.1	(2)	•	•	?		
C52	C38	N12	11	0.4	4(2) .	•	•	?	
C52	C38	C40	11	0.8	3 (3) .	•	•	?	
N12	C38	C40	10	9.8	3 (2) .	•	•	?	
C52	C38	C39	11	2.	7(3) .	•	•	?	
N12	C38	C39	10	1.9	9(2) .	•	•	?	
C40	C38	C39		1.()(3) .	•	•	?	
06	C39	C38]		.3	(2)	•	•	2		
06	C39	HI3 J		.2	•	•	:			
538 06	039 020	н⊥3 ⊔1и 1		ບ•2 ົ	∠ •	•	:			
00	53 550	п14] 111/	L⊥U 11	• ∠	•	•	:			
с J О Ц 1 Э	C 3 0	п⊥4 ц1Л	⊥⊥ 1∩	∪•∠ Q ⊑	- • 5	•	・ つ			
C 3 8	C39	нт4 Н74	⊥0 1∩	9 . 9 .		•	: ?			
-	010	TT / T	- U	~ • ·	- •	•	•			

C38	C40	Н75	109.	5			?		
Н74	C40	H75	109.	5			?		
C38	C40	H76	109.	5			?		
H74	C40	H76	109.	5			?		
Н75	C40	Н76	109.	5			?		
Si6	C41	H62	109.	5			?		
Si6	C41	Н63	109.	5			?		
Н62	C41	Н63	109.	5			?		
Si6	C41	Н64	109.	5			?		
Н62	C41	H64	109.	5			?		
Н6З	C41	H64	109.	5			?		
Si6	C42	H65	109.	5			?		
Si6	C42	Н66	109.	5			?		
Н65	C42	H66	109.	5			?		
Si6	C42	H67	109.	5			?		
Н65	C42	Н67	109.	5			?		
H66	C42	H67	109.	5			?		
Si6	C43	Fe2	120.	98	(1	1)			?
Si6	C43	H15	107.	1		•	?		
Fe2	C43	H15	107.	1			?		
Si6	C43	H16	107.	1			?		
Fe2	C43	H16	107.	1			?		
H15	C43	H16	106.	8			?		
Si3	C44	H44	109.	5			?		
Si3	C44	H45	109.	5			?		
H44	C44	H45	109.	5			?		
Si3	C44	H46	109.	5			?		
H44	C44	H46	109.	5			?		
H45	C44	H46	109.	5			?		
Si3	C45	H47	109.	5			?		
Si3	C45	H48	109.	5			?		
H47	C45	H48	109.	5			?		
Si3	C45	Н49	109.	5			?		
H47	C45	H49	109.	5			?		
H48	C45	H49	109.	5			?		
Si3	C46	Н50	109.	5			?		
Si3	C46	H51	109.	5			?		
Н50	C46	H51	109.	5			?		
Si3	C46	Н52	109.	5			?		
Н50	C46	H52	109.	5			?		
Н51	C46	Н52	109.	5			?		
Si3	C51	Fe1	119.	44	(1	0)			?
Si3	C51	Н19	107.	5	•	•	?		
Fe1	C51	Н19	107.	5			?		
Si3	C51	H20	107.	5			?		
Fe1	C51	H20	107.	5			?		
Н19	C51	H20	107.	0			?		
Si5	C50	Fe2	122.	72	(1	0)	-		?

Si5	C50	H17	106.6	•	•	?					
Fe2	C50	H17	106.6	•	•	?					
Si5	C50	H18	106.6	•	•	?					
Fe2	C50	H18	106.6	•	•	?					
H17	C50	H18	106.6	•	•	?					
Si5	C47	H53	109.5	•	•	?					
Si5	C47	H54	109.5	•	•	?					
H53	C47	H54	109.5	•	•	?					
Si5	C47	H55	109.5	•	•	?					
H53	C47	H55	109.5	•	•	?					
H54	C47	H55	109.5	•	•	?					
Si5	C48	H56	109.5	•	•	?					
Si5	C48	H57	109.5			?					
H56	C48	H57	109.5			?					
Si5	C48	H58	109.5			?					
H56	C48	H58	109.5			?					
H57	C48	H58	109.5			?					
Si5	C49	H59	109.5			?					
Si5	C49	H60	109.5			?					
H59	C49	H60	109.5			?					
Si5	C49	H61	109.5			?					
H59	C49	H61	109.5			?					
H60	C49	H61	109.5			?					
238	C52	H77	109.5			?					
238	C52	H78	109.5			?					
H77	C52	H78	109.5			?					
C38	C52	H79	109.5			?					
H77	C52	H79	109.5			?					
H78	C52	H79	109.5			?					
Si6	C53	H80	109.5			?					
Si6	C53	H81	109.5			?					
Н80	C53	H81	109.5			?					
Si6	C53	H82	109.5			?					
H80	C53	H82	109.5			?					
H81	C53	H82	109.5	•	•	?					
dif	ffrn	meas	sured f	Ēra	act	cion	th	eta	max	k 1.(000
_ dif	ffrn ⁻	_ ref]	lns the	eta	a í	Eull			25	5.50	
_ dif	ffrn ⁻	- meas	sured f	Ēra	act	cion	th	eta	ful	11 1.	.000
_ ref	fine	dif	f densi	_tv	, n	nax	_		- 0.	.323	
_ ref	fine	dif	f_densi	t	 7 n	nin			-0).193	3
_ ref	fine	dif	f_densi	t	 / 1	rms			0.	.061	
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CIF file:(zd10.cif):

data zd10

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(Bruker) '
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computing structure solution
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computing molecular graphics
computing publication material
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refine special details
Refinement of F^2^ against ALL reflections. The weighted R-
factor wR and
goodness of fit S are based on F^{2^{\prime}}, 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
on F^2 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 site disorder group
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N1 N 0.7346(4) 0.1924(2) 0.16948(19) 0.0594(9) Uani 1 1 d . . .
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C18 C 0.5903(4) 0.2585(3) 0.2424(3) 0.0608(12) Uani 1 1 d . . .
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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)
C14 0.1321(16) 0.237(3) 0.0887(12) -0.0290(16) -0.0063(12)
0.0377(18)
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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)
treatment of cell esds is used for estimating esds involving
l.s. planes.
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N1 C17 1.379(6) . ?
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C11 H111 0.9600 . ?
C11 H112 0.9600 . ?
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C16 C17 1.380(7) . ?
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C42 C47 1.395(9) . ? C43 C44 1.404(9) . ? C43 H43 0.9300 . ? C44 C45 1.373(10) . ? C44 H44 0.9300 . ? C45 C46 1.346(10) . ? C45 Cl4 1.738(8) . ? C46 C47 1.387(11) . ? C46 H46 0.9300 . ? C47 H47 0.9300 . ? loop geom angle atom site label 1 _geom_angle_atom_site label 2 geom angle atom site label 3 geom angle _geom_angle_site_symmetry 1 geom angle site symmetry 3 geom angle publ flag N4 Col N1 178.1(2) . . ? N4 Col N2 98.79(19) . . ? N1 Co1 N2 81.46(17) . . ? N4 Co1 N3 98.52(17) . . ? N1 Co1 N3 81.23(17) . . ? N2 Col N3 162.69(17) . . ? C17 N1 C13 120.1(4) . . ? C17 N1 Co1 120.4(3) . . ? C13 N1 Co1 119.5(3) . . ? C12 C11 H111 109.5 . . ? C12 C11 H112 109.5 . . ? H111 C11 H112 109.5 . . ? C12 C11 H113 109.5 . . ? H111 C11 H113 109.5 . . ? H112 C11 H113 109.5 . . ? N2 C12 C13 113.2(4) . . ? N2 C12 C11 124.4(5) . . ? C13 C12 C11 122.4(5) . . ? N1 C13 C14 119.6(5) . . ? N1 C13 C12 109.7(4) . . ? C14 C13 C12 130.7(5) . . ? C15 C14 C13 119.0(5) . . ? C15 C14 H14 120.5 . . ? C13 C14 H14 120.5 . . ? C16 C15 C14 121.7(5) . . ? C16 C15 H15 119.1 . . ? C14 C15 H15 119.1 . . ? C15 C16 C17 118.9(5) . . ?

C42 C43 1.386(8) . ?

C15 C16 H16 120.6 . . ? C17 C16 H16 120.6 . . ? N1 C17 C16 120.8(5) . . ? N1 C17 C18 108.7(4) . . ? C16 C17 C18 130.5(5) . . ? N3 C18 C17 112.8(4) . . ? N3 C18 C19 124.7(5) . . ? C17 C18 C19 122.5(4) . . ? C18 C19 H191 109.5 . . ? C18 C19 H192 109.5 . . ? H191 C19 H192 109.5 . . ? C18 C19 H193 109.5 . . ? H191 C19 H193 109.5 . . ? H192 C19 H193 109.5 . . ? C12 N2 C21 119.9(4) . . ? C12 N2 Co1 116.2(3) . . ? C21 N2 Co1 123.9(3) . . ? C26 C21 C22 120.5(6) . . ? C26 C21 N2 121.3(5) . . ? C22 C21 N2 117.9(4) . . ? C23 C22 C21 118.2(7) . . ? C23 C22 C27 121.1(7) . . ? C21 C22 C27 120.7(5) . . ? C24 C23 C22 120.9(9) 4 745 . ? C24 C23 H23 119.5 4 745 . ? C22 C23 H23 119.5 . . ? C25 C24 C23 119.7(9) . 4 755 ? C25 C24 H24 120.2 . . ? C23 C24 H24 120.2 4 755 . ? C24 C25 C26 120.0(9) . 4_755 ? C24 C25 H25 120.0 . . ? C26 C25 H25 120.0 4 755 . ? C21 C26 C25 120.7(8) . 4 745 ? C21 C26 C28 119.3(7) . . ? C25 C26 C28 120.0(8) 4 745 . ? C22 C27 H271 109.5 . . ? C22 C27 H272 109.5 . . ? H271 C27 H272 109.5 . . ? C22 C27 H273 109.5 . . ? H271 C27 H273 109.5 . . ? H272 C27 H273 109.5 . . ? C26 C28 H281 109.5 . . ? C26 C28 H282 109.5 . . ? H281 C28 H282 109.5 . . ? C26 C28 H283 109.5 . . ? H281 C28 H283 109.5 . . ? H282 C28 H283 109.5 . . ? C18 N3 C31 117.5(4) . . ?

C18	NЗ	Co1	1	16	.8	(3)	•	•	?
C31	NЗ	Co1	12	25	.6	(3)			?
C36	C31	С3	2	12	2.	0	(5)			?
C36	C31	N3	1	19	. 9	(5)			?
C32	C31	N3	1	18	.2	(4)			?
C33	C32	2 C3	1 :	11	8.	1	(6)			?
C33	C32	2 C3	7	12	2.	7	(6)			?
C31	C32	2 C3	7	11	9.	0	(5)			?
C34	C33	3 C3	2	12	1.	5	(7)			?
C34	C33	3 НЗ	3	11	9.	2	•		?	-
C32	C33	3 НЗ	3	11	9.	2			?	
C33	C34	1 C3	5	12	1.	8	(7)	-		?
C33	C34	1 НЗ	4	11	9.	1	•		?	-
C35	C34	і н3	4	11	9.	1			?	
C34	C35	5 C.3	6	12	0.	2	(7)	•	•	?
C34	C 35	5 н3	5	11	9	9	(' '		· ·	•
C36	C35	5 H.3	5	 1 1	9.	9			?	
C31	C36	5 C.3	5	 1 1	6.	3	(6)	•	•	?
C31	C36	5 C3	8	12	1.	2	(6)			?
C35	C36	5 C3	8	12	2.	5	(7)			?
C32	C37	7 НЗ	71	1	09		5.		. ?)
C32	C37	7 НЗ	72	1	09		5.		. ?)
H371	C3	37 H	372	2	10	9	.5		•	?
C32	C37	7 НЗ	73	1	09		5.	-	. ?)
Н371	. C3	37 H	37	3	10	9	.5			?
Н372	2 C3	37 H	37	3	10	9	.5			?
C36	C38	3 НЗ	81	1	09	•	5.		. ?)
C36	C38	3 НЗ	82	1	09	•	5.		. ?)
Н381	. C3	38 H	382	2	10	9	.5			?
C36	C38	3 НЗ	83	1	09	•	5.		. ?)
Н381	. C3	38 H	38	3	10	9	.5			?
Н382	2 C3	38 H	38	3	10	9	.5			?
C41	N4	Co1	1	69	.9	(5)			?
N4 C	241	C42	12	24	.3	(6)			?
N4 C	241	H41	1	17	.9		• •		?	
C42	C41	Н4	1 :	11	7.	9			?	
C43	C42	2 C4	7	11	7.	7	(6)			?
C43	C42	2 C4	1 :	11	9.	8	(6)			?
C47	C42	2 C4	1 :	12	2.	5	(5)			?
C42	C43	3 C4	4	12	0.	6	(7)			?
C42	C43	3 Н4	3	11	9.	7	•		?	
C44	C43	3 H4	3	11	9.	7			?	
C45	C44	1 C4	3	11	9.	7	(7)			?
C45	C44	1 Н4	4	12	Ο.	2	•		?	
C43	C44	1 Н4	4	12	0.	2			?	
C46	C45	5 C4	4	12	0.	4	(8)			?
C46	C45	5 Cl	4	12	0.	8	(8)			?
C44	C45	5 Cl	4	11	8.	7	(6)			?

C45 C46 C47 120.7(9) . . ? C45 C46 H46 119.6 . . ? C47 C46 H46 119.6 . . ? C46 C47 C42 120.8(7) . . ? C46 C47 H47 119.6 . . ? C42 C47 H47 119.6 . . ? diffrn_measured_fraction_theta_max 1.000 _diffrn_reflns_theta_full 25.50 _diffrn_measured_fraction_theta_full 1.000 _refine_diff_density_max 0.421 _refine_diff_density_min -0.350 _refine_diff_density_rms 0.053