

THE UNIVERSITY OF MANITOBA

**SYNTHESIS AND COMPLEXATION STUDIES OF ACYCLIC
TRIDENTATE THIOETHER LIGANDS**

BY

JAMES ROBERT MANSFIELD

A THESIS

**SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FUFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE**

DEPARTMENT OF CHEMISTRY

WINNIPEG, MANITOBA

1990



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ISBN 0-315-71793-9

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JAMES ROBERT MANSFIELD

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
of the degree of

MASTER OF SCIENCE

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ABSTRACT

This thesis describes the synthesis, characterization, complexation and subsequent reactivity studies of some acyclic, tridentate thioether ligands. Thioether ligands have long been thought to be poor donor ligands, however, recent advances in macrocyclic thioether complexation have led to the conclusion that thioethers can, in fact, be good ligands.^{1,5} The bonding analogy between thioethers and phosphines, and the usefulness of tris(phosphine) complexes, such as $\text{Rh}(\text{PPh}_3)_3\text{Cl}$,⁷⁴ leads to the hypothesis that a tris(thioether) coordination of platinum group metals might induce useful or unusual reactivity.

Three thioether ligands were synthesized: 3,7,11-trithiatridecane (TTTD); 1,9-diphenyl-1,5,9-trithianonane (DPTN) and 2,12-dimethyl-3,7,11-trithiatridecane (DMTT). The halide complexes, $[\text{M}(\text{L})\text{X}][\text{BF}_4]$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{L} = \text{TTTD}, \text{DPTN}, \text{DMTT}$; $\text{X} = \text{I}, \text{Cl}$), synthesized serve as tools to probe the effects of a meridional tris(thioether) coordination. $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ is resistant to the oxidative addition of H_2 , HCl , Br_2 and MeI . The halide ligands of the platinum(II) complexes are readily abstracted, leaving a coordination site vacant which can be filled by various ancillary ligands such as PPh_3 or $\text{P}(\text{OMe})_3$. Reaction of DPTN with $[\text{RhCl}(\text{COD})]_2$ in the presence of Ag^+ formed the five coordinate complex $[\text{Rh}(\text{DPTN})(\text{COD})][\text{BF}_4]$ and the reaction of DMTT with $[\text{IrCl}(\text{COE})_2]_2$ in the presence of Ag^+ formed the five coordinate complex $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$. The η^4 -COD ligand in $[\text{Rh}(\text{DPTN})(\text{COD})][\text{BF}_4]$ was inert to substitution by other Lewis base ligands, while one of the η^2 -COE ligands in $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$ can be replaced with either CO or PPh_3 . Both $[\text{Rh}(\text{DPTN})(\text{COD})][\text{BF}_4]$ and $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$ are inert to oxidative addition of common reagents such as H_2 , MeI and HCl . Reaction of DMTT

and $[\text{RhCl}(\text{CO})_2]_2$ in the presence of Ag^+ formed the square-planar complex $[\text{Rh}(\text{DMTT})(\text{CO})][\text{BF}_4]$. These compounds were studied through the use of $^{195}\text{Pt}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR, infrared and mass spectroscopy, and X-ray crystallography.

**If you can fill an unforgiving minute
with sixty seconds worth of distance run,
then yours is the earth and all that's in it.**

Kipling

ACKNOWLEDGEMENTS

I would like, first of all, to thank Steve Loeb for accepting me as a graduate student and making it possible, both through his friendship and advice, for me to realize my goals. I would also like to thank the staff and faculty in the Chemistry Department of the University of Winnipeg for their assistance and support. I also thank Kirk Marat and Terry Wolowiec at the University of Manitoba for their advice and assistance with the NMR spectra and Doug Stephan at the University of Windsor for collecting the X-ray diffraction data. Thanks also to Broer de Groot for his assistance throughout these last two years.

I am eternally grateful to my parents, without whom I would have had neither the opportunity nor the inclination to undertake these studies. Finally, a special thanks to Karen for being there when I needed her most.

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KEY TO ABBREVIATIONS

NMR	Nuclear Magnetic Resonance
MSD	Mass Selective Detector
GCMS	Gas Chromatography-Mass Spectroscopy
IR	Infra Red
ORTEP	Oak Ridge Thermal Ellipsoid Plot
COD	1,5-cyclooctadiene
COE	cyclooctene
Me	methyl
Et	ethyl
<i>i</i> -Pr	<i>iso</i> -propyl
<i>t</i> -Bu	<i>tertiary</i> -butyl
Ph	phenyl
PPh ₃	triphenylphosphine
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,1-bis(diphenylphosphino)methane
ttp	bis(diphenylphosphinopropyl)phenylphosphine
etp	bis(diphenylphosphinoethyl)phenylphosphine
DMA	dimethylacetamide
DMAC	dimethylacetylenedicarboxylate
ETM	1,1-bis(ethylthio)methane
TTN	2,5,8-trithianonane
9S3	1,4,7-trithiacyclononane or TTCN
14S4	1,4,8,11-tetrathiacyclotetradecane
18S6	1,4,7,10,13,16-hexathiacyclooctadecane

TTOB	2,5,8-trithia[9]- <i>ortho</i> -benzenophane
HTOB	2,5,8,13,16,19-hexathia[9.9]- <i>ortho</i> -benzenophane
TTUD	2,6,10-trithiaundecane
TTTD	3,7,11-trithiatridecane
DPTN	1,9-diphenyl-1,5,9-trithianonane
DMTT	2,12-dimethyl-3,7,11-trithiatridecane

CHAPTER ONE

INTRODUCTION

1.1 Preamble.

It has long been known that thioethers can donate two electrons from a lone pair and coordinate to a metal centre.¹ Much of this early work was done using monodentate thioethers as ligands, $S(CH_3)_2$ being a common example.² At this time, it was believed that the poor stability of thioether-metal complexes was solely due to the lower σ -donor/ π -acceptor abilities of thioethers as compared to phosphines. However in the late 1960's and early 1970's, the use of macrocyclic thioether ligands such as 1,4,7,10,13,16-hexathiacyclooctadecane (18S6),^{3,4} which help to stabilize complexes through both the chelate effect and the macrocyclic effect, allowed an exploration of the donating properties of thioethers. The synthesis of these macrocyclic ligands was a major problem until the 1980's when an improved synthetic method was developed.^{5,23} Since then, a variety of thioether complexes have been synthesized, most of which appear to be quite stable. It would appear that the observed instability of monodentate thioether ligands is kinetic rather than thermodynamic in nature.

There are several factors which have contributed to the growth of thioether coordination chemistry. First, the realization that the unusual electrochemical and optical properties of blue copper proteins were a result of the coordination of the Cu centre to the thioether linkage of methionine.⁵ A second factor was the bonding analogy between phosphines (PR_3) and thioethers (SR_2). Both have orbitals of the proper symmetry to allow both σ -donation and π -backbonding with a metal.^{1,48} The extensive catalytic properties of metal-phosphine complexes would imply, if the analogy is strict enough, that metal thioether complexes might also have potential

applications. The π -acceptor ability of thioethers is less than that of phosphines but greater than that of amines.^{1,5} It is therefore proposed that thioethers will stabilize low oxidation states better than nitrogen donors but not as well as phosphorous donors, perhaps creating complexes of unusual reactivity.⁵ A third factor is the improved synthetic methods for macrocyclic thioethers, the synthesis of which, although not yet trivial, is far easier than prior to 1980.^{5,23,24}

Many of the compounds studied to date have been homoleptic thioether complexes and much of the emphasis has been on the scope of the coordination chemistry of thioethers. However, in order to determine the effect of coordinated thioethers on the reactivity of a metal, the ligand design must allow for at least one coordination site which is not occupied by a sulfur atom. This thesis describes investigations into the effect of tris(thioether) coordination on the reactivities of several of the platinum group metals.

1.2 Simple Mono and Bidentate Thioether Ligands.

Simple thioethers, such as SMe_2 or SEt_2 , can coordinate to a metal centre in a manner analogous to phosphines. An excellent review on the subject has recently been published.¹ Complexes of the general formulae *trans*- $MX_2(SR_2)_2$, $[MX(SR_2)_3]^+$ and $[MX_3(SR_2)]^-$ ($M = Pt, Pd$; $X = \text{halide}$; $R = \text{alkyl or aryl}$) have been synthesized.¹ Rhodium(III) and iridium(III) complexes of monodentate thioether ligands, such as $RhCl_3(SR_2)_3$, have also been synthesized.⁷¹ In addition to simple monodentate thioether ligands, many complexes of bidentate thioether ligands have been synthesized.¹ These ligands include 2,5-dithiahexane and 3,7-dithianonane,⁴⁶ which are usually complexed in a chelating mode, however, they may also be employed in a bridging mode.¹

1.3 Coordination Chemistry of 9S3.

Perhaps the most common macrocyclic thioether ligand is 1,4,7-trithiacyclononane (9S3 or TTCN).^{6,7} This ligand is unique in that the conformation of the free ligand, as shown by X-ray crystallography and conformational NMR studies, is nearly identical to the conformation of the ligand while complexed.^{6,7} 9S3 forms stable ML_2 complexes with a variety of metals in a range of oxidation states. Some examples of these are: Ni(II);⁸ Cu(II);⁸ Co(II);⁸ Co(III);⁹ Fe(II);¹⁰ Fe(III);¹¹ Pd(III);¹² Rh(III)¹³ and Ru(II).¹⁴⁻¹⁶ In all of these complexes, the metal is "sandwiched" between two ligand moieties (Figure 1.3). Some sandwiched metal complexes display unusual properties and reactivities. For example, bis(9S3) complexes of rhodium(III) and cobalt(III) possess unusually low reduction potentials.⁵¹⁻⁵³

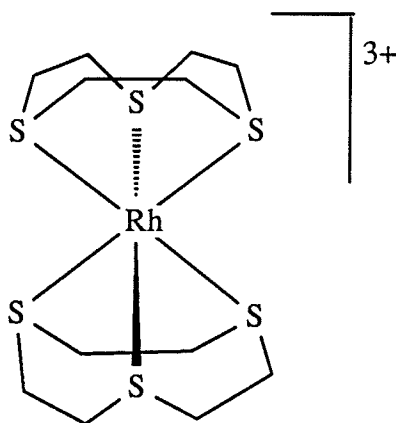


Figure 1.1 $[Rh(9S3)_2]^{3+}$, Sandwiched Metal Cation.

9S3 can also form 1:1 complexes with metal ions, leaving a coordination site, or sites, occupied by ancillary ligands. Examples of 1:1 coordination include $Mo(9S3)(CO)_3$, $[Mn(9S3)(CO)_3]^+$, $Cu(9S3)I$, $[Fe(9S3)(Cp)][BPh_4]$ and

$\text{Pd}(\text{9S3})\text{Br}_2$.¹⁷⁻²⁰ In addition to this, 9S3 can form complexes in which only two of the three sulfurs coordinate to the metal. Examples of this variety include $[\text{Pt}(\text{9S3})_2][\text{PF}_6]_2$ ²¹ and $[\text{Pd}(\text{9S3})_2][\text{ClO}_4]_2$.^{22,20} In both the Pt(II) and Pd(II) bis(9S3) complexes, four of the six donor sulfurs are coordinated in a square planar geometry. As well, in the platinum complex, one of the "dangling" sulfurs is bound in an apical interaction while both of the remaining sulfurs in the palladium complex show weak metal-sulfur interactions.²⁰⁻²²

1.4 Coordination Chemistry of Macrocyclic Thioethers

Much of the initial work on thioether complexes was done using macrocyclic "crown" thioethers. The discovery of the cesium mediated cyclization reaction in 1981^{23,24} dramatically increased yields for the synthesis of these ligands; from 5% for the synthesis of 18S6²⁵ before this discovery to 89% using the Cs_2CO_3 mediated cyclization.²⁴ The synthesis is general and can be used to prepare a large variety of macrocyclic thioethers in good yields.

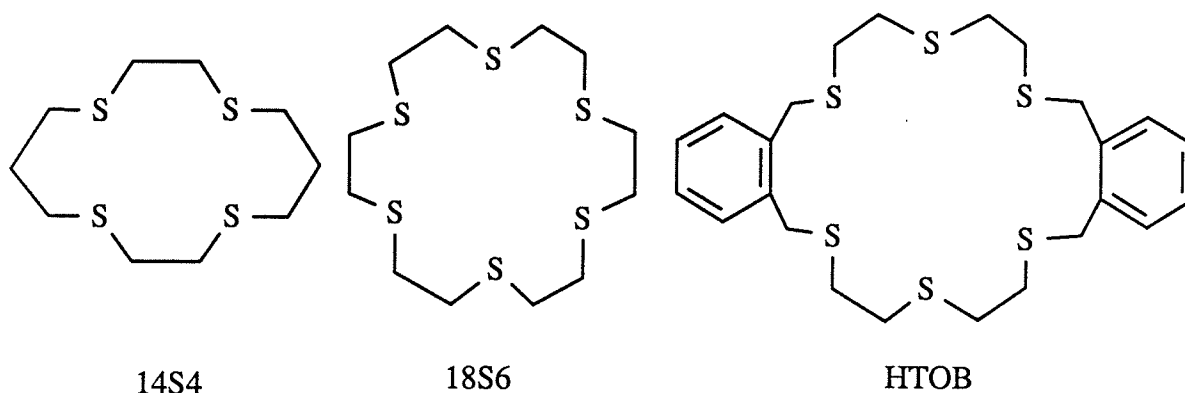


Figure 1.2 Macrocyclic Thioethers.

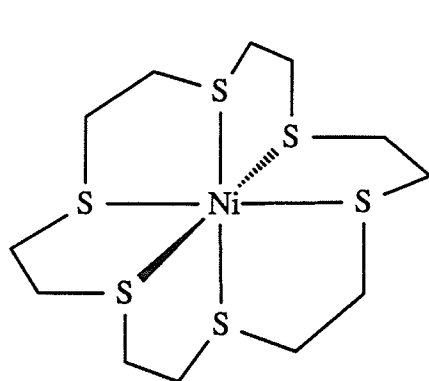
A large number of macrocyclic thioether complexes of a variety of 1st, 2nd and 3rd row transition metals have been characterized, most of which have been published

since 1981. Complexes of Ni(II),^{4,8,28,29,32,33} Fe(II),^{8,10,11,19,34} Co(II) and Co(III),^{8,9,26,29} Cu(I) and Cu(II),^{8,18,26,52} Rh(I) and Rh(III),^{13,36,72,88} Ir(III),⁸⁹ Pd(II) and Pd(III),^{12,22,90} Ag(I)^{18,91} and Pt(II)²¹ have been fully characterized by X-ray crystallography.

There are three major influences on the binding mode of a macrocyclic thioether. The number of sulfur atoms in the ring, the ring or cavity size and the length of the carbon backbone linking two consecutive sulfurs. Large crown thioethers such as 18S6 are capable of encapsulating a metal ion while small ring thioethers such as 9S3 are capable only of capping a metal ion. It has been found, using a series of Cu(II) complexes,^{26,27} that the minimum ring size necessary to accommodate a first row transition-metal ion within the cavity of the ligand, is fourteen. 14S4 has also been complexed with a large number of other transition metal ions such as Rh(I)³⁶ and Ni(II),³² in which the metal ion lies approximately in the square plane defined by the four sulfurs. An exception is the octahedral *cis*-[Ir(14S4)Cl₂][BPh₄], for which the chloride ligands occupy *cis* positions and the sulfurs of the 14S4 ligand occupy the remaining four sites.⁸⁹

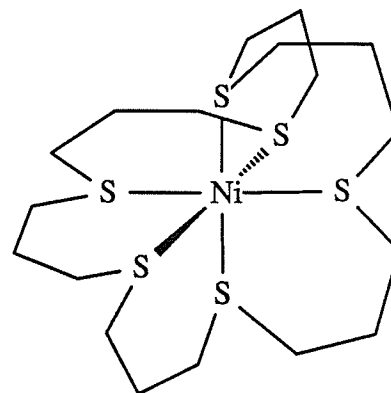
The length of the carbon backbone connecting the sulfurs has a large effect on the coordination modes of the ligand and on the reactivity and properties of the complex. It has been found in numerous polyphosphine, polyaza and polythia ligands, both cyclic and acyclic, that three heteroatoms connected by two carbon atoms prefer a facial orientation while three heteroatoms connected by a three carbon linkage prefer a meridional coordination.^{28-30,65} Coordination of the macrocycles 18S6 and 24S6 to Ni(II) reveals the preference of facial versus meridional coordination (Figure 1.3).^{28,29} In [Ni(18S6)]²⁺, where the sulfur atoms are linked by ethylene groups, each group of three consecutive sulfur atoms occupies a trigonal face while in [Ni(24S6)]²⁺, in which the sulfurs are joined by propylene groups, there are two sets of three sulfurs bound in a meridional configuration. Also, in

$[\text{Ru}\{\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SMe})_2\}\text{Cl}_3]$, the acyclic tridentate ligand is coordinated in a meridional geometry.⁶⁵



$[\text{Ni}(18\text{S}6)]^{2+}$

all sets of 3 sulfur atoms
coordinated facially.



$[\text{Ni}(24\text{S}6)]^{2+}$

2 sets of 3 sulfur atoms
coordinated meridionally.

Figure 1.3 Examples of Coordination Modes.

Similar results have been found for acyclic polyphosphine ligands. $[\text{Co}(\text{ttp})(\text{CO})\text{L}]^+$ (ttp = bis(diphenylphosphinopropyl)phenylphosphine; $\text{L} = \text{PR}_3$), in which the phosphorus atoms joined by propylene linkages, is square-pyramidal with the tridentate phosphine ligand bound meridionally. Conversely, $[\text{Co}(\text{etp})(\text{CO})\text{L}]^+$ (etp = bis(diphenylphosphinoethyl)phenylphosphine) is trigonal bipyramidal with the tridentate ligand adopting facial coordination.³⁰ In both the cyclic and acyclic cases the preference for meridional coordination can be attributed to the increase in the chelate bite angle of the ligand as one moves from a five membered (ethylene linkages) to a six membered (propylene linkages) chelate ring.^{30,31}

1.5 Acyclic Thioether Ligands.

Most of the effort put into synthesizing thioether complexes of transition metals has gone into the study of the complexation properties of cyclic crown thioethers.^{1,5} In spite of this, much work has been done on bidentate, acyclic thioether complexes of platinum(II).⁴⁶ The work in this area focused mainly on the inversion of coordinated sulfur in these compounds and the factors which affect this inversion process.^{45,46} It was not until relatively recently that complexes of acyclic tridentate thioether ligands were synthesized.

One of the few well studied acyclic tridentate thioether ligands is TTN (TTN = 2,5,8-trithianonane).⁴⁸ This compound, having ethylene linkages between sulfurs, prefers to coordinate facially to transition metals. As such, it is generally used to prepare complexes analogous to previously prepared 9S3 compounds, in order to show that the properties imparted by 9S3 are caused by thioether coordination, not the macrocyclic effect.^{48,51-53} The first, and, to the author's knowledge, only, X-ray structure of a complex containing an acyclic thioether of more than two sulfurs was a complex containing TTN, (TTN)Mo(CO)₃.⁴⁸ There is one example of an acyclic tridentate thioether ligand containing propylene linkages between sulfurs, TTUD (TTUD = 2,6,10-trithiaundecane).⁶⁵ Complexes of this ligand include Ru(TTUD)Cl₃, Os(TTUD)Cl₃ and Os(TTUD)Br₃. In all of these complexes the ligand is coordinated in a meridional fashion, but none have been structurally characterized by X-ray diffraction.

1.6 Bonding Considerations.

In all thioether complexes, the bond angles about the sulfur are approximately tetrahedral. This is consistent with the sulfur being sp³ hybridized and having two

filled lone pairs, one or both of which can be donated to a metal centre.¹ Alternatively, the two lone-pair orbitals of thioethers may be viewed as an "s-type" and a "p-type" lone pair.^{1,47}

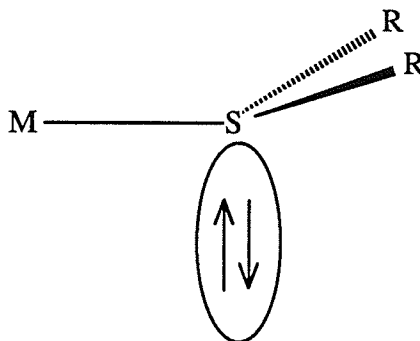


Figure 1.4 Depiction of Sulfur sp^3 Hybridization.

However, neither the sp^3 nor the "s and p" description of free thioethers can fully account for the coordination chemistry of thioethers. Recent theoretical and structural studies indicate that thioethers possess two donor orbitals.⁴⁸⁻⁵⁰ One, the highest occupied molecular orbital (HOMO), is primarily sulfur 3p in character and is located perpendicular to the R-S-R plane. The other, of slightly lower energy, is also primarily of sulfur 3p character and is located along the bisector of the R-S-R angle. In C_{2v} symmetry, these belong to the $1b_1$ and $2a_2$ representations respectively. After coordination, the sulfur belongs to point group C_s , both donor orbitals belong to representations a' and are free to mix. The amount of mixing of the two orbitals is reflected in the tilt angle α . If there is no mixing then the tilt angle, α , would be 90° , while if the two orbitals contributed equally there would be a tilt angle of 135° . For an idealized sp^3 hybridized orbital, one would expect a tilt angle of 125.25° .⁴⁸ Crystallographic data for transition metal-thioether complexes^{1,50} show tilt angles between 105 and 120° , typically around 115° . This would indicate that the HOMO

($1b_1$) of the free thioether ligand is the more important ligand donor orbital.⁵⁰

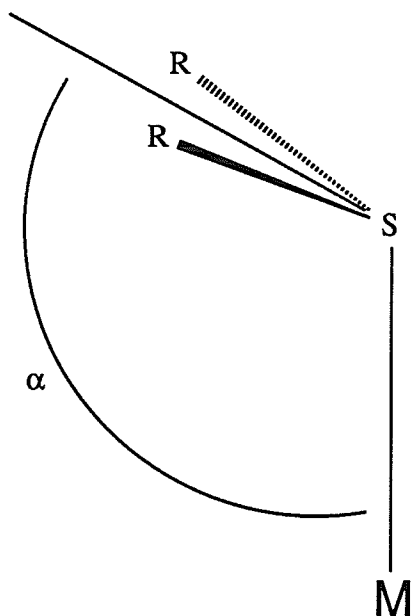


Figure 1.5 Depiction of Coordinated Thioether Hybridization.

1.7 Electronic Effects.

Homoleptic thioether coordination is known to cause unusual electronic effects and reactivity. Examination of the X-ray structures of $[\text{Co}(\text{9S3})_2]^{2+}$, $[\text{Co}(\text{TTN})_2]^{2+}$ (TTN = 2,5,8-trithianonane) and $[\text{Co}(\text{18S6})]^{2+}$ revealed that these structures resembled those of low-spin, Jahn-Teller distorted Cu(II) systems.^{8,51-53} This type of distortion could be seen in Co(II), as it is a d^7 ion, but only if it were low spin and octahedral. Most strong field ligand complexes of Co(II) are seen to lose ligands in order to adopt four or five coordination and hence be incapable of exhibiting Jahn-Teller distortion. However, magnetic measurements revealed that these cobalt thioether complexes are indeed examples of enforced, octahedral, d^7 , Jahn-Teller distorted cobalt(II) complexes.

Thioethers are thought to exert a ligand field roughly comparable to that of

ammonia (NH_3),⁵ and $[\text{Co}(\text{NH}_3)_6]^{2+}$ is a high spin complex. As TTN is an acyclic thioether ligand and is seen to form low spin complexes of Co(II), the origin of low spin Co(II) complexes cannot be attributed to the macrocyclic effect, but rather must be attributed simply to the effect of a hexakis(thioether) coordination. This implies that the hexakis(thioether) coordination does not induce spin-pairing by way of a large ligand field, a one electron term, but rather through a lowering of the electron spin-pairing energy, a two electron term.⁵

Low spin complexes of a relatively weak field ligand are possible as a result of the delocalization of t_{2g} electron density from the metal onto the ligand, most likely into S-C σ^* orbitals.⁵⁴ Thus, the low spin state in the $[\text{Co}(\text{SR}_2)_6]^{2+}$ complexes is a result of the π -acidity, or π -acceptor ability, of thioethers.⁵

Thioethers have the ability to stabilize low oxidation states in metals, an ability generally attributed to their π -acidity. This effect is most clearly seen in electrochemical behaviour. For all $\text{Co}(\text{SR}_2)_6$ complexes, the Co(II/III) couple not only approaches electrochemical reversibility but occurs at strongly oxidizing potentials, both of which are rarities in cobalt complexes.⁵ $[\text{Co}(\text{18S6})]^{2+}$ and $[\text{Co}(\text{TTN})_2]^{2+}$ undergo oxidation at +844 to +864 mV versus NHE,⁵³ while $[\text{Co}(\text{9N3})_2]^{2+}$ (9N3 being the amine analog of 9S3) undergoes oxidation at -410 mV versus NHE; a difference of over 1200 mV.^{5,58} This is a significant difference in light of the similar ligand field strengths of amines and thioethers and must reflect the ability of thioethers to induce unusual electronic states in metal ions.

1.8 σ -Donor/ π -Acceptor Abilities of Thioether Ligands

There is a definite relationship between ν_{CO} and the amount of electron density on the metal. In the past there have been attempts to use this relationship as a yardstick against which to measure the relative π -acceptor abilities of ligands.^{62,63} It

is, however, nearly impossible, either theoretically or empirically, to separate π -acceptor properties from σ -donor properties. It was originally thought that d- π back donation was the most important facet of late transition metal chemistry.⁶³ It is, however, also possible to explain all of the data using a σ only model, without contributions from d- π backbonding.⁸⁵ The true situation likely lies somewhere between the two extremes, with both the σ -donor and π -acceptor aspects being important. It is, therefore, quite reasonable to speak of σ -donor/ π -acceptor ability as a single entity corresponding roughly to the Lewis basicity of the donor.

Regardless of the mechanism, coordination of a strong Lewis base to a metal will result in there being a higher electron density residing on the metal than if a weaker Lewis base were coordinated. The more electron density on the metal, the more is available for backbonding to a coordinated CO ligand. This increases the bond order of the metal-carbon bond and decreases the bond order of the carbon oxygen bond, hence reducing ν_{CO} .⁶⁴

<u>Compound</u>	<u>ν_{CO} (cm⁻¹)</u>
(Cl ₃ P) ₃ Mo(CO) ₃	2040, 1991
(PPh ₃) ₃ Mo(CO) ₃	1949, 1835
(PEt ₃) ₃ Mo(CO) ₃	1937, 1841
(TTOB)Mo(CO) ₃	1935, 1818
(TTN)Mo(CO) ₃	1927, 1815
(dien)Mo(CO) ₃	1898, 1758

Table 1.1 Comparison of π -Backbonding Abilities.^{48,64,85,86}

In Table 1.1 a comparison of the varying σ -donor/ π -acceptor abilities of some

phosphine, thioether and amine complexes is made (TTOB = 2,5,8-trithia[9]-*ortho*-benzenophane; dien = ethylenetriamine). It can be seen that the Lewis basicity of thioethers is much closer to that of trialkylphosphines than it is to that of amines. It would seem from this type of analysis that the bonding analogy between thioethers and trialkylphosphines is quite valid in terms of σ -donor/ π -acceptor ability. Is this analogy also seen in the reaction chemistry imparted by these ligands?

1.9 Reaction Chemistry.

It has been found that increasing the basicity of the ligands coordinated to a metal can greatly alter the relative stability of the complex towards oxidative addition, in particular towards their reaction with alkyl halides.³⁵ Many common square planar rhodium(I) compounds such as $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $[\text{Rh}(\text{CN}t\text{-Bu})_4]^+$ will oxidatively add methyl iodide and yet are quite inert to CH_2Cl_2 or CHCl_3 . In contrast to this, the more basic alkyl phosphine analogs, $\text{Rh}(\text{PMe}_3)_3\text{Cl}$ and $[\text{Rh}(\text{PMe}_3)_4]^+$, rapidly react with CH_2Cl_2 .³⁵ A similar rhodium(I)-thioether complex, $[\text{Rh}(14\text{S}4)]^+$, a square planar complex with tetrakis(thioether) coordination, undergoes oxidative addition of CH_2Cl_2 at room temperature affording *trans*- $[\text{RhCl}(\text{CH}_2\text{Cl})(14\text{S}4)]^+$.³⁶ In both the rhodium-phosphine and rhodium-thioether cases, the rhodium is surrounded by basic, good σ -donor/poor π -acceptor ligands which increase the nucleophilicity of the metal centre.

Another thioether complex which exhibits reactivity patterns similar to its phosphine analog is $[\text{RhCl}(\text{CO})(\text{ETM})_2]$ (ETM = 3,5-dithiaheptane).⁵⁵ The carbonyl stretching frequency in this compound is 1965 cm^{-1} as compared to 1968 cm^{-1} in the *dppm* analog³⁷ (*dppm* = 1,1-bis(diphenylphosphino)methane), indicating a similar electron density on the rhodium atoms in both molecules.

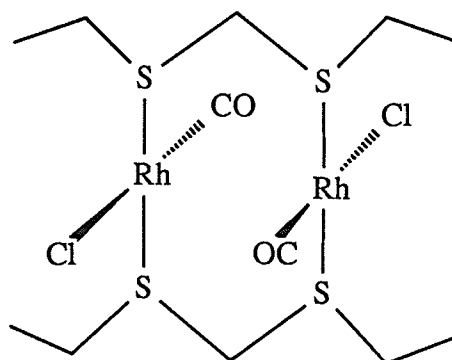


Figure 1.6 $[\text{RhCl}(\text{CO})(\text{ETM})]_2$ Molecule.

There are many similarities and differences in the reactions of $[\text{RhCl}(\text{CO})(\text{ETM})]_2$ and $[\text{RhCl}(\text{CO})(\text{dppm})]_2$ with CO and alkynes. Both compounds catalytically cyclotrimerize acetylene, although the dppm complex will not catalyze the reaction of non-activated alkynes. Both will react with DMAC (DMAC = dimethylacetylenedicarboxylate) to form an adduct.^{37,55} However, unlike its phosphine analog, the ETM-DMAC complex will undergo further cyclotrimerization reactions with acetylene to form substituted benzenes. The coordinatively unsaturated ETM complex will, under an atmosphere of CO, add two equivalents of CO to form $[\text{RhCl}(\text{CO})_2(\text{ETM})]_2$, a coordinatively saturated compound while the dppm complex does not react with CO.^{55,37} The ability to add CO leads to another unique property of the ETM complex; under an atmosphere of CO/acetylene (approximately 1:1) in wet acetonitrile the ETM complex undergoes a reaction under ambient conditions with end products identified as *p*-hydroquinones.⁵⁵ The catalytic synthesis of hydroquinones from acetylene, CO and water had been accomplished before but only under extreme conditions *ie.* over 100 atmospheres pressure and 200°C.^{56,57}

Even though there are rather striking differences in the reaction chemistry observed in analogous thioether and trialkylphosphine compounds, the overall

similarity between the reaction chemistries of these complexes is even more striking. It appears that the similarity in reaction chemistry of analogous thioether and trialkylphosphine compounds implies that the bonding analogy between thioethers and phosphines is valid.

CHAPTER TWO

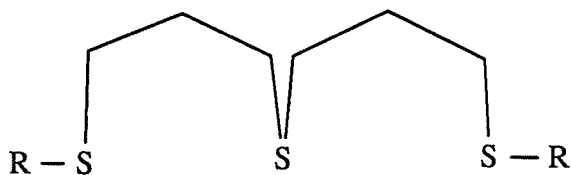
LIGAND SYNTHESIS

2.1 Introduction

Thioether ligands which enforce a homoleptic environment on a metal centre are ideal for studying the electronic effects of coordinated thioethers. However, if one wishes to study the effect of a coordinated thioether on the reaction chemistry of a metal, then at least one coordination site must remain unoccupied or contain a labile ancillary ligand.

In the past two decades, much research has been done investigating the substitution and catalytic properties, redox chemistry and reaction mechanisms of square planar, d^8 , platinum group metal complexes of tertiary phosphines. Perhaps the best known and understood of these complexes is Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$.⁷⁴⁻⁷⁹

In an attempt to mimic the tris(phosphine) substitution of Wilkinson's catalyst we have synthesized a series of acyclic thioether ligands containing three sulfur donors which are capable of coordinating to a metal centre in a meridional fashion. The sulfur donors can occupy three coplanar coordination sites of a metal in a square planar, trigonal bipyramidal, square pyramidal or octahedral coordination environment. In each case, this leaves at least one coordination site filled by an ancillary ligand, which would then be free to undergo substitution. In order to best stabilize a meridional substitution pattern, propylene linkages were incorporated between sulfur atoms. Three different terminal organic groups were used (Figure 2.1) in order to vary both the steric bulk of the ligand and the solubility properties of the complexes.



R = phenyl, *iso*-propyl, ethyl

Figure 2.1 Ligand Design.

These ligands have a strict phosphine analog in ttp (ttp = bis(3-diphenylphosphinopropyl)phenylphosphine) which induces in its complexes different reaction properties than a simple tris(monophosphine) substitution. Rh(tpp)Cl is more basic and hence more nucleophilic than Rh(PPh₃)₃Cl as a result of the alkyl substituents on the phosphines.^{30,60,61,79,101}

The acyclic, tridentate thioether ligands used herein are designed to be the thioether analogs of ttp and, hence, mimic the tris(phosphine) coordination of Wilkinson's catalyst Rh(PPh₃)₃Cl.

2.2 Experimental

(i) General

Pt(COD)Cl₂,⁸¹ Pt(COD)I₂,⁸¹ [RhCl(COD)]₂,⁸² (COD = 1,5-cyclooctadiene), PdCl₂(PhCN)₂,⁸⁴ and [IrCl(COE)₂]₂,⁸³ (COE = cyclooctene) were prepared by literature methods. 1-bromopropanol, sodium sulfide nonahydrate, *p*-toluenesulfonyl chloride, thiophenol, 2-propanethiol, ethanethiol, 1,5-cyclooctadiene, K₂PtCl₄, cyclooctene, IrCl₃ hydrate, RhCl₃ hydrate, benzonitrile, Na₂PdCl₄ and [RhCl(CO)₂]₂ were purchased from Aldrich and used as received. Absolute ethanol, CH₃CN and

CH_2Cl_2 were purified by distillation from CaH_2 under N_2 . Pyridine was pre-dried over NaOH and distilled from BaO . THF was distilled from benzophenyl-ketyl/Na under N_2 . Reactions under N_2 were performed using standard Schlenk line techniques and all solvents were degassed before use. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra were recorded at 300.1, 75.4, 121.49 and 64.52 MHz, respectively, on a Bruker AM300 spectrometer locked to the deuterated solvent. Variable temperature ^{13}C NMR line shape fitting calculations were performed using a modified version of the program DNMR3.⁹² Infrared spectra were recorded on a Perkin-Elmer 781 grating spectrometer. GC-MS experiments were performed on Hewlett-Packard HP 5970 Series MSD coupled to an HP 5890a gas chromatograph. Elemental analyses were performed by Canadian Microanalytical Service Ltd., New Westminster, B.C., Canada.

(ii) Preparation of 4-Thiaheptane-1,7-diol.

This compound was prepared using a modification of a preparative method found in the literature.⁴ 3-Bromopropanol (64.9 g, 476 mmol) and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (54.8 g, 228 mmol) were refluxed in anhydrous ethanol (750 mL) for 18 h. The mixture was cooled, filtered and the ethanol removed *in vacuo*. The remaining liquid was extracted with CH_2Cl_2 , filtered and the solvent removed *in vacuo*. The resulting clear, oily liquid was vacuum distilled (bp. 134-138 °C, 1 mmHg). Yield: 23.3 g (65 %). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 60.91 (CH_2OH), 31.88 (SCH_2), 28.36 (CH_2). ^1H NMR (CDCl_3): δ 3.64 (s, 2H, OH), 3.61 (t, 4H, OCH_2) ($^3\text{J} = 6.19$ Hz), 2.54 (t, 4H, SCH_2) ($^3\text{J} = 7.18$ Hz), 1.74 (q, 4H, CH_2).

Preparation of 4-Thia-1,7-heptaneditosylate-CH₂Cl₂ (1).

4-Thiaheptane-1,7-diol (22.65 g, 151 mmol) was dissolved in freshly distilled, dry pyridine at 0 °C and *p*-toluene sulfonyl chloride (57.50 g, 302 mmol) added over a 2 h period. This mixture was left to stir at 0 °C for 14 h. The reaction mixture was then poured over ice (900 g) and left to melt. The resulting sticky white solid was filtered off and redissolved in CH₂Cl₂ (300 mL). The CH₂Cl₂ solution was washed with 0.1N HCl (2 x 160 mL) and water (2 x 100 mL). The aqueous fractions were collected, washed with fresh CH₂Cl₂ (100 mL) and the organic portions combined. The organic portion was dried over MgSO₄, treated with activated charcoal, filtered and the solvent removed *in vacuo*. The resulting liquid was dissolved in an equal volume of diethylether and cooled to -10 °C for 12 h. The crystallized white solid was collected and washed with anhydrous ethanol (50 mL) and dried *in vacuo*. Yield: 38.42 g (59 %). ¹³C{¹H} NMR (CDCl₃): δ 127.81, 129.84, 132.86, 144.83 (aromatic), 68.64 (CH₂O), 28.75 (SCH₂), 27.77 (CH₂), 21.61 (CH₃). ¹H NMR (CDCl₃): δ 7.78 (d, 4H, aromatic), 7.34 (d, 4H, aromatic) (³J = 8.00 Hz), 4.10 (t, 4H, OCH₂) (³J = 6.03 Hz), 2.46 (t, 4H, SCH₂) (³J = 7.09 Hz), 2.44 (s, 6H, CH₃), 1.86 (q, 4H, CH₂). Analysis calculated for C₂₁H₂₈O₄S₃Cl₂: C, 49.31; H, 5.51; S, 18.80. Found: C, 51.59; H, 5.58; S, 20.14

(iv) Preparation of 3,7,11-Trithiatridecane (TTTD) 2.

Na metal (1.55 g, 67.4 mmol) was dissolved in anhydrous ethanol (700 mL) and ethanethiol (4.9 mL, 4.11 g, 66.2 mmol) added. This solution was then added drop-wise over 2 h to a slurry of 4-thiaheptane-1,7-ditosylate (14.21 g, 33.3 mmol) in anhydrous ethanol (200 mL). The mixture was stirred overnight at 40 °C. The solvent was removed *in vacuo* and the residue redissolved in CH₂Cl₂ (200 mL). The CH₂Cl₂

solution was washed with water (130 mL), dried over MgSO_4 , filtered and the solvent removed *in vacuo*. The resulting clear, viscous liquid was vacuum distilled (bp. 115-122 °C, 1 mmHg). Yield: 6.16g (78 %). MS: m/e 238. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 30.45 (EtSCH_2), 29.96 (CH_2SCH_2), 28.90 (SCH_2CH_2), 25.24 (CH_3CH_2), 14.41 (CH_3). ^1H NMR (CDCl_3): δ 2.47 (t, 4H, EtSCH_2) ($^3\text{J} = 7.16$ Hz), 2.47(t, 4H, CH_2SCH_2), 2.38 (q, 4H, CH_3CH_2) ($^3\text{J} = 7.41$ Hz), 1.70 (q, 4H, SCH_2CH_2), 1.10 (t, 6H, CH_3). Analysis calculated for $\text{C}_{10}\text{H}_{22}\text{S}_3$: C, 50.37; H, 9.30; S, 40.33. Found: C, 50.20; H, 9.21; S, 39.40.

(v) Preparation of 1,9-Diphenyl-1,5,9-trithianonane (DPTN) 3.

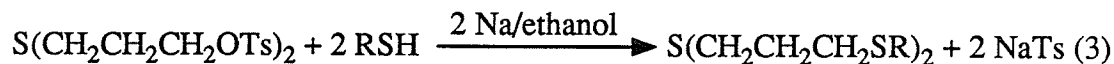
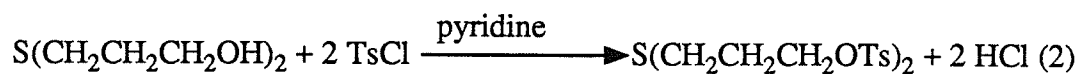
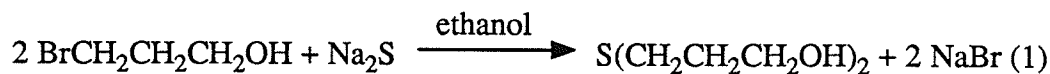
Na metal (1.25 g, 54.4 mmol) was dissolved in anhydrous ethanol (600 mL) and to this was added thiophenol (5.4 mL, 5.74 g, 52.1 mmol). This was then added drop-wise over a period of 3 h to a slurry of 4-thiaheptane-1,7-ditosylate (11.11 g, 26.0 mmol) in anhydrous ethanol (100 mL). This was stirred overnight at room temperature, and the ethanol removed *in vacuo*. The residue was redissolved in CH_2Cl_2 (160 mL) and filtered. The filtrate was washed with water (2 x 100 mL), dried over MgSO_4 , treated with activated charcoal and filtered. The solvent was removed *in vacuo* and the remaining dark oil was vacuum distilled (bp. 209-212 °C, 1 mmHg). Yield: 5.99 g (69 %). MS: m/e 334. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 125.74, 128.67, 128.99, 135.98 (aromatic), 32.16 (CH_2SCH_2), 30.51 (CH_2SPh), 28.55 (SCH_2CH_2). ^1H NMR (CDCl_3): δ 7.38 (m, 4H, aromatic), 7.23 (m, 6H, aromatic), 3.04 (t, 4H, CH_2SPh), 2.63 (t, 4H, CH_2SCH_2) ($^3\text{J} = 7.09$ Hz), 1.92 (q, 4H, SCH_2CH_2). Analysis calculated for $\text{C}_{18}\text{H}_{22}\text{S}_3$: C, 64.62; H, 6.63; S, 28.75. Found: C, 64.54; H, 6.51; S, 27.84.

(vi) Preparation of 2,12-Dimethyl-3,7,11-trithiatridecane (DMTT) 4.

Na metal (1.23 g, 53.5 mmol) was dissolved in anhydrous ethanol (550 mL), and to this was added 2-propanethiol (4.60 mL, 3.77 g, 49.53 mmol). This solution was added drop-wise over a period of 4 h to a slurry of 4-thiaheptane-1,7-ditosylate (10.46 g, 24.52 mmol) in anhydrous ethanol (50 mL). The mixture was stirred overnight at 40 °C. The ethanol was removed *in vacuo* and the residue redissolved in CH₂Cl₂ (160 mL). The CH₂Cl₂ was washed with water (2 x 100 mL), dried over MgSO₄, treated with activated charcoal, filtered and the solvent removed *in vacuo*. The remaining dark, viscous liquid was vacuum distilled (bp. 122-129 °C, 1 mmHg). Yield: 4.62 g (71 %). MS: m/e 266. ¹³C{¹H} NMR (CDCl₃): δ 34.73 (CH), 30.94 (*i*-PrSCH₂), 29.46 (CH₂SCH₂), 29.24 (SCH₂CH₂), 23.32 (CH₃). ¹H NMR (CDCl₃): δ 2.87 (m, 2H, CH) (³J = 6.70 Hz), 2.58 (t, 4H, CH₂SCH₂) (³J = 7.19 Hz), 2.57 (t, 4H, *i*-PrSCH₂) (³J = 7.16 Hz), 1.81 (q, 4H, SCH₂CH₂), 1.22 (d, 12H, CH₃). Analysis calculated for C₁₂H₂₆S₃: C, 54.08; H, 9.83; S, 36.09. Found: C, 54.37; H, 10.15; S, 35.55.

2.3 Results.**(i) Synthesis.**

The ligands were all easily prepared using the same basic synthetic route:



Here: R = *i*-propyl, phenyl, ethyl

Ts = *p*-toluenesulfonate (tosyl)

4-Thiaheptane-1,7-diol was prepared by refluxing 3-bromopropanol and Na₂S hydrate in ethanol. The diol cleanly distilled in good yield (65 %). The tosylation of the diol in distilled, dry pyridine at 0°C also occurred cleanly. The ditosylate thus formed, **1**, was recrystallized from CH₂Cl₂/diethylether. Substitution of the tosylate group for an [RS]⁻ anion was accomplished by a slow addition of NaSR in ethanol to a slurry of **1** in ethanol. The ligands, **2** to **4**, are all clear, colourless, viscous oils which cleanly vacuum distil at reasonable temperatures (under 220°C) at a pressure of 1 mmHg. The ligands were shown to be greater than 97% pure by MS, elemental analysis and NMR after one such distillation.

(ii) NMR of Ligands.

The ¹H and ¹³C{¹H} NMR of these ligands were all simple and first order. Tabulated chemical shifts and coupling constants are listed in Tables 2.1 to 2.3. The only unusual feature is the accidental overlap of protons H1 and H3 in the ligand TTTD at δ = 2.468. The ¹³C{¹H} NMR of this ligand shows two distinct peaks for the corresponding C1 and C3 nuclei.

Table 2.1 $^{13}\text{C}\{^1\text{H}\}$ NMR Data for Ligands, δ (ppm).

Compound	C1	C2	C3	C4	C5
TTTD	29.96	28.90	30.45	25.24	14.41
DMTT	29.46	29.24	30.94	34.73	23.32
DPTN ^a	30.15	28.55	32.16	125.74	128.67
				128.99	135.98

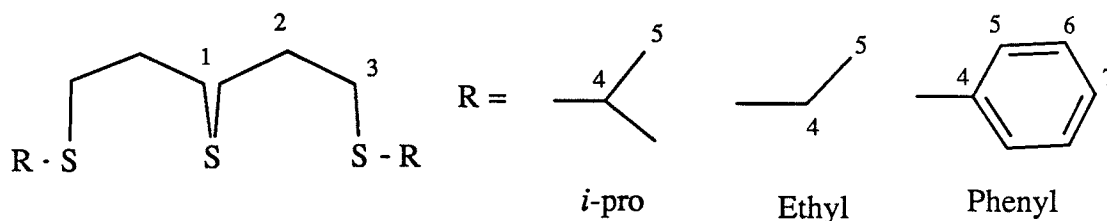
^afour shifts given for C4 and C5 are the phenyl carbons, C4, C5, C6, C7.

Table 2.2 Ligand ^1H NMR Data, δ (ppm).

Compound	H1	H2	H3	H4	H5
TTTD	2.468	1.703	2.468	2.380	1.100
DMTT	2.581	1.806	2.568	2.868	1.215
DPTN	2.632	1.920	3.036		

Table 2.3 Ligand Coupling Constants (Hz).

Compound	$J_{H1,H2}$	$J_{H2,H3}$	$J_{H4,H5}$
TTTD	7.16	7.16	7.41
DMTT	7.19	7.16	6.70
DPTN	7.09	7.09	multiplet



The IR spectrum of DMTT (4) showed the characteristic peaks of an *iso*-propyl group at $\nu = 1370$ and 1390 cm^{-1} , which were to prove useful for identification purposes in later complexation studies. The mass spectra of all of these ligands were obtained, each of which showed a parent M^+ ion at the appropriate m/e value. The fragmentation patterns of these compounds in the mass spectrometer were also consistent with the structures assigned.

2.4 Summary and Conclusions

The ease of preparation and relatively high yields obtained in the synthesis of these ligands makes them readily available for studying the effect of a tris(thioether) coordination on transition metal complexes.

CHAPTER THREE

PLATINUM(II) AND PALLADIUM(II) COMPLEXES

3.1 Introduction

The tridentate phosphine ligand ttp (ttp = bis(diphenylphosphinopropyl)-phenylphosphine), when coordinated in a meridional fashion to metals of the Platinum group greatly alters the reaction chemistry of the metal, as compared to three triphenylphosphine ligands analogously bound.^{30,60,61} For this reason, and because little is known about the properties of non-homoleptic thioether complexes of the Platinum group metals, it was decided to first complex the ligands 2-4 with a metal known to form stable sulfur compounds: platinum.

The complexes thus formed, through reaction with $\text{PtX}_2(\text{COD})$, have the general structure:

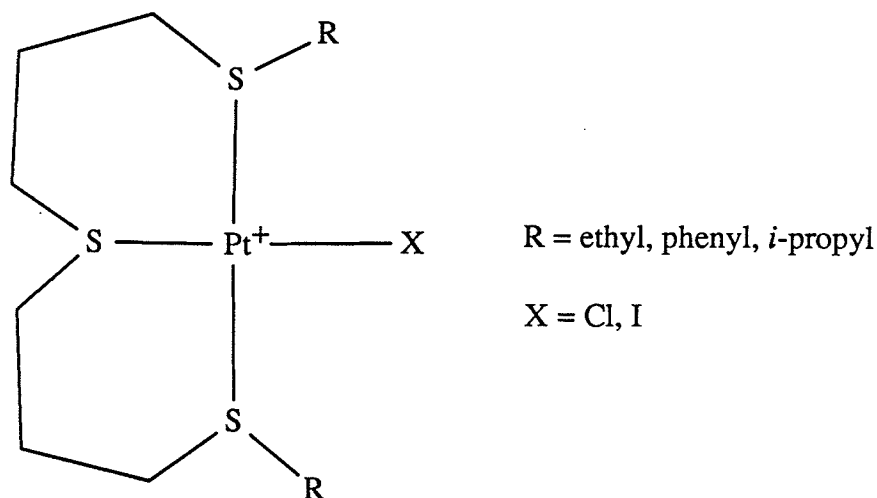


Figure 3.1 $[\text{Pt}(\text{L})\text{X}]^+$ General Structure

These ligands were also reacted with *cis*- $\text{PdCl}_2(\text{PhCN})_2$ to form the analogous Pd(II)

complexes. The platinum(II) halide complexes were studied to determine their susceptibility to oxidative addition and the ease with which the halide might undergo substitution by another donor ligand.

3.2 Platinum and Palladium Thioether Complexes

The coordination chemistries of platinum and palladium with thioethers are very similar.¹ Although there were, as of 1981, no Pt(0) or Pd(0) thioether complexes in the literature, the chemistry of Pt(II) and Pd(II) with thioethers dates back to the beginning of coordination chemistry.^{1,66,67} Much of this historical work was done on monodentate thioether ligands, forming complexes of the type *trans*-M(SR₂)₂X₂, *cis*-M(SR₂)₂X₂ and [M(SR₂)₄]²⁺ (M = Pd, Pt; R = alkyl or aryl; X = halide).¹ There have also been numerous studies on acyclic bidentate and tetradentate thioether complexes of palladium and platinum.^{1,68} In the case of tetradentate thioether complexes, there is a tendency to form five coordinate complexes, if the anion is a halide.¹

The cyclic thioether ligand 9S3 can form platinum(II) and palladium(II) complexes of either 1:1 or 2:1 stoichiometry *ie.* five coordinate MCl₂(9S3) or six coordinate [M(9S3)₂]²⁺ (M = Pd, Pt).^{20-22,12} Both the palladium(II) and platinum(II) complexes of bis(9S3) can, in strongly acidic media, be electrochemically oxidized to [M(9S3)₂]³⁺ cations which are stable enough to have been characterized by X-ray crystallography.^{12,22}

3.3 Experimental

(i) General

In order to avoid repetition, the reader is directed to section 2.2(i) in chapter two.

(ii) Preparation of [PtI(DPTN)][BF₄] (5).

1,9-Diphenyl-1,5,9-trithianonane (DPTN, 5) (0.603g, 1.80 mmol) was dissolved in degassed acetone (6 mL), and this added to a slurry of PtI₂(COD) (1.000g, 1.80 mmol) in acetone (20 mL) under N₂. One equivalent of AgBF₄ (0.375g, 1.83 mmol) was added and the solution stirred for 3 h. This was filtered through Celite to remove AgCl_(s), the volume reduced to *ca.* 10 mL *in vacuo* and the solution cooled to -10 °C for twelve hours. The resulting yellow microcrystals (0.835g) were isolated and washed with diethylether. Orange-yellow crystals suitable for X-ray diffraction were grown by slow diffusion of diethylether into the mother liquor, acetone solution. Yield: 0.936g (70 %). Analysis calculated for C₁₈H₂₂S₃PtIF₄B: C, 29.08; H, 2.98; S, 12.94. Found: C, 29.86; H, 3.09; S, 12.73.

(iii) Preparation of [PtCl(TTTD)][BF₄] (6).

3,7,11-Trithiatridecane (TTTD, 3) (0.616 g, 2.583 mmol) was dissolved in CH₂Cl₂ (20 mL) and this was added to a flask containing Pt(COD)Cl₂ (0.787 g, 2.103 mmol) and AgBF₄ (0.419 g, 2.152 mmol) under N₂, stirred for 2 h and then filtered through Celite to remove the AgCl_(s). The volume was reduced *in vacuo* to *ca.* 4 mL

and small portions of diethylether added until a light yellow precipitate formed. The mixture was then cooled to $-10\text{ }^{\circ}\text{C}$ for 12 h. The pale yellow microcrystals formed were collected and washed with diethylether. Yield: 0.919 g (79 %). A satisfactory elemental analysis could not be obtained.

(iv) Preparation of $[\text{PtCl}(\text{DPTN})][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ (7).

1,9-Diphenyl-1,5,9-trithianonane (DPTN, **5**) (0.560g, 1.67 mmol) was dissolved in 5 mL of CH_2Cl_2 and added to $\text{Pt}(\text{COD})\text{Cl}_2$ (0.624g, 1.67 mmol) under N_2 . CH_2Cl_2 (15 mL) was added and the solution stirred for 30 m. AgBF_4 (0.324g, 1.67 mmol) was added and after 1 h stirring, the solution was filtered through Celite to remove the $\text{AgCl}_{(s)}$. The solvent was removed *in vacuo* and the residue left *in vacuo* for 12 h to remove the residual COD. The residue was redissolved in a minimum of CH_2Cl_2 and small portions of diethylether added until a light yellow powder precipitated. This was collected and washed with diethylether. Yield: 724 mg (67 %). Analysis calculated for $\text{C}_{19}\text{H}_{24}\text{S}_3\text{PtCl}_3\text{F}_4\text{B}$: C, 30.97; H, 3.28; S, 13.05. Found: C, 30.85; H, 3.32; S, 10.29.

(v) Preparation of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ (8).

2,12-Dimethyl-3,7,11-trithiatridecane (DMTT, **4**) (1.456 g, 5.463 mmol) in CH_2Cl_2 (15 mL) under N_2 was added to a flask containing $\text{Pt}(\text{COD})\text{Cl}_2$ (2.006 g, 5.361 mmol) and AgBF_4 (1.066 g, 5.476 mmol) under N_2 . CH_2Cl_2 (10 mL) was added and the solution stirred for 2 h, during which time a white precipitate formed. The resulting pale yellow solution was filtered through Celite to remove the $\text{AgCl}_{(s)}$, and the solvent removed *in vacuo*. The residue was left *in vacuo* for 4 h to remove residual COD. A minimum of CH_2Cl_2 (4 mL) was added, the volume reduced *in*

vacuo, and small portions of diethylether added until a light yellow precipitate formed. This mixture was then cooled to -10 °C for 12 h. The yellow microcrystals that formed were collected and washed with diethylether. Yield: 2.856 g (91 %). Analysis calculated for $C_{12}H_{26}S_3PtClF_4B$: C, 24.69; H, 4.49; S, 16.47. Found: C, 24.69; H, 4.61; S, 16.60.

(vi) Preparation of $[PdCl(DPTN)][BF_4] \cdot \frac{1}{2}CH_2Cl_2$ (9).

To a slurry of $PdCl_2(PhCN)_2$ (1.009 g, 2.63 mmol) in acetone (15 mL) was added 1,9-diphenyl-1,5,9-trithianonane (DPTN, **3**) (0.896 g, 2.68 mmol) in acetone (5 mL). This mixture was stirred for 4 hours but no visible change was observed. The acetone was removed *in vacuo* and the oily residue redissolved in CH_2Cl_2 (20 mL). $AgBF_4$ (0.521 g, 2.68 mmol) was added and a white precipitate formed immediately. The solution was then filtered through Celite to remove the $AgCl_{(s)}$, and the volume of the solution reduced to *ca.* 4 mL. This was then stored at -10°C for 16 hours, during which time an orange precipitate formed. This was collected and washed with diethylether. Yield: 0.889 g (60 %). Analysis calculated for $C_{18}H_{22}S_3PdClF_4B \cdot \frac{1}{2}CH_2Cl_2$: C, 36.69; H, 3.83; S, 15.88. Found: C, 37.59; H, 4.02; S, 16.11.

(vii) Reactions of **8 with H_2 , $HCl \cdot DMA$, MeI and Br_2 .**

In a typical reaction $[PtCl(DMTT)][BF_4]$ (**8**) (*ca.* 250 mg) was dissolved in CH_2Cl_2 (10 mL) and one equivalent of reactant added. The mixture was then stirred for several hours, the solvent removed *in vacuo* and the residual solid recrystallized from CH_2Cl_2 /diethylether. In the case of HCl and MeI , the reaction was also attempted with a ten-fold excess of reactant. In none of the reactions attempted was

any platinum(IV) complex detected. In the case of reaction with Br₂, the chloride was partially replaced with bromide forming a mixture of [PtCl(DMTT)][BF₄] and [PtBr(DMTT)][BF₄].

(viii) Preparation of [Pt(DMTT)(PPh₃)](BF₄)₂ (10).

A flask containing [PtCl(DMTT)][BF₄] (8) (0.297 g, 0.509 mmol) and triphenylphosphine (0.134 g, 0.511 mmol) was stirred in CH₂Cl₂ (15 mL) under N₂ for one hour. AgBF₄ (0.100 g, 0.514 mmol) was added and the mixture stirred for an additional hour during which time a white precipitate formed. The solution was then filtered to remove the AgCl_(s), and the solvent removed *in vacuo*. The resulting clear, colourless oil was redissolved in CH₂Cl₂ and diethylether added slowly in increments until a white powder precipitated. This was then collected and washed with diethylether (2 x 5 mL). Crystals were grown by slow diffusion of diethylether into a 2:1 CH₃CN/CH₂Cl₂ solution of the product. Yield: 0.334 g (73 %). Analysis calculated for C₃₀H₄₁S₃PtPF₈B₂: C, 40.15; H, 4.60; S, 10.71. Found: C, 39.95; H, 4.70; S, 10.23.

(ix) Preparation of [Pt(DMTT){P(OMe)₃}](BF₄)₂ (11).

Method A: [PtCl(DMTT)][BF₄] (8) (0.325 g, 0.557 mmol) and P(OMe)₃ (0.07 mL, 0.59 mmol) were stirred in CH₂Cl₂ under N₂ for 30 minutes. AgBF₄ (0.111 g, 0.57 mmol) was added and the mixture stirred for another 2 hours, during which time a white precipitate formed. The solution was filtered to remove the AgCl_(s) and the solvent removed *in vacuo*. The resulting clear, colourless oil was redissolved in CH₂Cl₂ and diethylether added in increments until the first appearance of a solid. The solution was then stored at -10°C for three days during which time a white precipitate

formed. Yield: 0.178 g (42 %). A satisfactory elemental analysis could not be obtained.

Method B: [PtCl(DMTT)][BF₄] (**8**) (0.323 g, 0.553 mmol) and P(OMe)₃ (0.075 mL, 0.64 mmol) were stirred in CH₂Cl₂ (10 mL) for 2 hours. NaBF₄ (0.064 g, 0.58 mmol) was then added and the mixture stirred for an additional hour. The solution was filtered to remove the NaCl_(s), the solvent removed *in vacuo* and the residue washed with diethylether (2 x 10 mL). The resulting clear oil was never solidified but ³¹P{¹H} NMR showed that all of the P(OMe)₃ remaining in the sample was bound to the platinum.

(x) General X-Ray Diffraction Data Collection, Solution and Refinement

Diffraction experiments were performed at the University of Windsor by D.W. Stephan on a four-circle Syntex P2₁ diffractometer with graphite monochromatized MoK α radiation. The initial orientation matrices were obtained from 15 machine-centred reflections selected from rotation photographs. Partial rotation photographs around each axis were used to determine the crystal system. Finally, 30 high-angle reflections were used to obtain the final lattice parameters and orientation matrices. Machine parameters, crystal data, and data collection parameters are detailed in Tables 3.1 and 3.2. The intensities of three standard reflections were recorded every 197 reflections and showed no statistically significant changes over the duration of the data collection. The data were processed using the SHELX-76 program package on the computing facilities at the University of Manitoba. The absorption coefficients were large and psi-scans recorded showed significant absorption effects. These scans (three for both [PtCl(DMTT)][BF₄] and [Pt(DMTT)(PPh₃)]₂ and four for [Pt(DPTN)][BF₄]) were used in absorption

corrections which were applied to the data. Refinement was carried out using full-matrix least-squares techniques on F minimizing the function $\sum w(F_o - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are observed and calculated structure factors respectively. Atomic scattering factors⁹⁴ and anomalous dispersion⁹⁵ terms were taken from the usual sources. Fixed H-atom contributions were included with C-H distances of 0.95 Å and thermal parameters equal to 1.1 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

(xi) Structure Determination of [PtI(DPTN)][BF₄], (5).

Crystals of **5** were grown by slow diffusion of diethylether into an acetone solution of the compound. Preliminary photography was consistent with a monoclinic crystal system. Observed extinctions were consistent with space group $P2_1/n$. Intensity data ($\pm h, +k, +l$) were collected in one shell ($4.5^\circ < 2\theta < 45^\circ$). A total of 3023 data were collected and 2172 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The platinum position was determined using a Patterson synthesis. The remaining non-hydrogen atoms were located using successive difference Fourier map calculations. In the final cycles of refinement, the phenyl groups were defined as rigid groups. The six carbon atoms of the phenyl group were arranged in an idealized hexagon with bond lengths of 1.395 Å and isotropic thermal parameters. The platinum, iodine, fluorine, sulfur, boron and remaining carbon atoms were assigned anisotropic thermal parameters. This resulted in $R = \sum ||F_o| - k|F_c|| / \sum |F_o| = 0.0519$ and $R_w = (\sum w(|F_o| - k|F_c|)^2 / \sum F_o^2)^{1/2} = 0.0590$ at final convergence.

The Δ/σ value for any parameter in the final cycle of refinement was less than 0.017 (0.002 excluding the BF₄ anion). A final difference Fourier map showed no peaks of chemical significance; the largest was 1.61 electrons/Å³ and was associated

with the platinum atom. Atomic positional parameters are summarized in the appendix in Table A1, selected bond distances and angles in Table 3.3, anisotropic thermal parameters in Table A3 and hydrogen atom parameters in Table A2.

(xii) Structure Determination of [PtCl(DMTT)][BF₄], (8).

Crystals of **8** were obtained from slow diffusion of diethylether into a CH₂Cl₂ solution of the compound. Preliminary photography was consistent with a monoclinic crystal system. Observed extinctions were consistent with space group P2₁/c. Intensity data ($\pm h, +k, +l$) were collected in one shell ($4.5^\circ < 2\theta < 45^\circ$). A total of 2376 reflections were collected and 1970 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The platinum atom was located using a Patterson synthesis and the remaining non-hydrogen atoms located from successive difference Fourier map calculations. In the final cycles of refinement, all non-hydrogen atoms were assigned anisotropic thermal parameters. This resulted in $R = \Sigma||F_o| - k|F_c|| / \Sigma|F_o| = 0.0527$ and $R_w = (\Sigma w(|F_o| - k|F_c|)^2 / \Sigma w F_o^2)^{1/2} = 0.0550$ at final convergence.

The Δ/σ value for any parameter in the final cycle was less than 0.116 (0.017 excluding the BF₄ anion). A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 2.58 electrons/Å³ and was associated with the platinum atom. Atomic positional parameters are summarized in the appendix in Table A4, selected bond distances and angles in Table 3.4, anisotropic thermal parameters in Table A6 and hydrogen atom parameters in Table A5.

Table 3.1 Crystallographic Data for [PtI(DPTN)][BF₄] (5) and [PtCl(DMTT)][BF₄] (8).

Chemical formula	C ₁₈ H ₂₂ S ₃ PtIBF ₄	C ₁₂ H ₂₆ S ₃ PtClBF ₄
Crystal colour	orange-yellow	pale yellow
Crystal form	tabular	acicular
Formula weight	743.35	651.90
<i>a</i> , Å	13.415(4)	10.409(6)
<i>b</i> , Å	12.350(5)	14.180(4)
<i>c</i> , Å	14.316(5)	13.726(8)
β, deg	107.48(3)	104.49(4)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c
Vol, Å ³	2262.2(14)	1961.5(17)
ρ(calcd), g/cm ⁻³	2.18	2.21
Z	4	4
μ, abs coeff, cm ⁻¹	75.21	73.18
Radiation (λ, Å)	MoKα (.71069)	
Temp, °C	24	
Scan speed, deg/min	2.0-5.0 (θ-2θ scan)	
Scan range, deg	1.0 below Kα ₁ and 1.0 above Kα ₂	
Bkgd/scan time ratio	0.5	
2θ	4.5 to 45°	
<i>hkl</i> range	± <i>h</i> ,+ <i>k</i> ,+ <i>l</i>	
Data collected (2θ)	3023	2376
Unique data (F _o ² >3σF _o ²)	2172	1970
No. of variables	169	199

$R(F_o^2)$, %	5.19	5.27
$R_w(F_o^2)$, %	5.90	5.50

(xiii) Structure Determination of $[Pt(DMTT)(PPh_3)]_2[BF_4]_2$, (10).

Crystals of **10** were grown by slow diffusion of diethylether into a 2:1 CH_2Cl_2 /acetonitrile solution of the compound. Preliminary photography was consistent with a triclinic crystal system. Calculations were initially performed in space group P1, which was, by successful convergence of the least-squares calculations, verified (*vide infra*). Intensity data ($\pm h, \pm k, +l$) were collected in one shell ($4.5^\circ < 2\theta < 45^\circ$). A total of 5260 intensity data were collected and 4606 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The platinum position was determined using a Patterson synthesis. The remaining non-hydrogen atoms were located using successive difference Fourier map calculations. In the final cycles of refinement, the phenyl groups were defined as rigid groups. All of the non-hydrogen atoms in the $[Pt(DMTT)(PPh_3)]^{2+}$ cation were refined anisotropically except for carbons C4, C5 and C6, which were refined isotropically, and the eighteen carbon atoms of the phenyl groups, which were fixed in rigid, idealized hexagons with bond lengths of 1.395 Å and given isotropic thermal parameters. The atoms of one of the $[BF_4]^-$ anions were refined anisotropically while the atoms of the second $[BF_4]^-$ anion were refined isotropically. The atoms of the solvent of crystallization were all given isotropic thermal parameters.

Carbon C5 was disordered over two positions, each with an occupancy factor of 0.50. For this reason, there are four calculated hydrogen atoms attached to carbons C4 and C6, with occupancy factors each of 0.50, to account for this disorder. The two positions of carbon C5 were each assigned two calculated hydrogen atoms of 0.50

occupancy factor. The $[\text{BF}_4]^-$ anion with isotropic thermal parameters was input with fixed bond lengths of 1.36 Å and fixed to an idealized tetrahedral geometry. The solvent of crystallization was input with a fixed geometry and an occupancy factor of 0.74, with unfixed isotropic thermal parameters. This resulted in $R = \Sigma||F_o|-k|F_c||/\Sigma|F_o| = 0.0515$ and $R_w = (\Sigma w(|F_o|-k|F_c|)^2/\Sigma F_o^2)^{\frac{1}{2}} = 0.0579$ at final convergence.

The Δ/σ value for any parameter in the final cycle of refinement was less than 0.006 (0.003 excluding the $[\text{BF}_4]^-$ anion). A final difference Fourier map showed no peaks of chemical significance; the largest was 1.92 electrons/Å³ and was associated with the platinum atom. Atomic positional parameters are summarized in Table A7, selected bond distances and angles in Table 3.5, anisotropic thermal parameters in Table A9 and hydrogen atom parameters in Table A8.

Table 3.2 Crystallographic Data for $[\text{Pt}(\text{DMTT})(\text{PPh}_3)][\text{BF}_4]_2$ (10).

Chemical formula	$\text{C}_{30}\text{H}_{41}\text{S}_3\text{PPtB}_2\text{F}_8 \cdot 0.74\text{CH}_2\text{Cl}_2$
Crystal colour	white
Crystal form	blocks
Formula weight	960.35
a , Å	13.266(3)
b , Å	11.315(2)
c , Å	13.970(2)
α , deg	106.038(15)
β , deg	84.948(15)
γ , deg	86.559(18)
Crystal system	triclinic

Space group	P1
Vol, Å ³	1999.7(22)
ρ(calcd), g/cm ⁻³	1.59
Z	2
μ, abs coeff, cm ⁻¹	37.19
Radiation (λ, Å)	MoKα (.71069)
Temp, °C	24
Scan speed, deg/min	2.0-5.0 (θ-2θ scan)
Scan range, deg	1.0 below Kα ₁ and 1.0 above Kα ₂
Bkgd/scan time ratio	0.5
2θ	4.5 to 45°
<i>hkl</i> range	± <i>h</i> , ± <i>k</i> , + <i>l</i>
Data collected (2θ)	5260
Unique data (F _o ² > 3σF _o ²)	4591
No. of variables	241
R(F _o ²), %	5.15
R _w (F _o ²), %	5.79

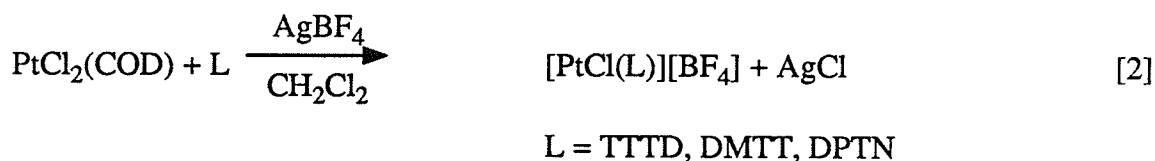
3.4 Results

(i) Synthesis

The orange-yellow complex [PtI(DPTN)][BF₄], **5**, is easily prepared by reacting an acetone or CH₂Cl₂ slurry of PtI₂(COD) with one equivalent of the ligand DPTN, **3**, and one equivalent of AgBF₄. Once the AgI has been filtered off, the complex can be isolated by recrystallization from acetone or CH₂Cl₂ and diethylether.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR show no peaks resulting from COD.

The platinum and palladium-chloride compounds, 6-9, analogous to 5 are readily prepared by the reaction of a stoichiometric amount of the appropriate ligand (2-4) in CH_2Cl_2 with a mixture of $\text{PtCl}_2(\text{COD})$, or *cis*- $\text{PdCl}_2(\text{PhCN})_2$, and AgBF_4 in CH_2Cl_2 according to reaction [2].



The AgCl is filtered off and the pale yellow or orange complexes recrystallized from CH_2Cl_2 /diethylether. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of the complexes show no peaks resulting from COD, either free or complexed, or from benzonitrile in the case of palladium. The platinum and palladium halide complexes are soluble in CH_2Cl_2 , CH_3CN , and hot ethanol, are slightly soluble in acetone and chloroform and are insoluble in diethylether and benzene.

In all of the platinum(II) and palladium(II) complexes synthesized, the ligand occupies three of the four coordination sites on the square planar metal leaving the fourth site free to undergo substitution or reaction. It is known that the analogous phosphorous ligand, ttp, will displace both the COD and one of the chlorides from $\text{PtCl}_2(\text{COD})$ to form $[\text{PtCl}(\text{ttp})]\text{Cl}$.⁹⁹ The ligands 2-4 will not do this, due perhaps to the lower trans influence and increased basicity of thioethers as compared to phosphines. Many attempts were made to substitute a η^1 alkyl or aryl group for the halide in the platinum complexes 5-8, using either Grignard or lithium reagents. However, all of these attempts resulted in either no reaction or decomposition of the starting material. There is precedence for instability in certain η^1 -alkyl and aryl platinum complexes, *viz.* in the attempted synthesis of $[\text{Pt}(\text{ttp})(\text{R})][\text{BF}_4]$, for which

repeated attempts were found to be unsuccessful.⁹⁹

The dicationic complexes **10-13** were all prepared similarly. $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$, **8**, and the appropriate ligand were stirred in CH_2Cl_2 for approximately 1 hour and then one equivalent of AgBF_4 added. The AgCl was filtered off and the product recrystallized from CH_2Cl_2 or $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ and diethylether. If the reaction of **8** with PPh_3 is attempted, substituting NaBF_4 in place of AgBF_4 , no reaction is observed to occur. However, if **8** is stirred with $\text{P}(\text{OMe})_3$ and NaBF_4 is added a reaction will occur. The product thus formed, $[\text{Pt}(\text{DMTT})\{\text{P}(\text{OMe})_3\}][\text{BF}_4]_2$, appears clean by $^{31}\text{P}\{^1\text{H}\}$ NMR but not by $^{13}\text{C}\{^1\text{H}\}$ NMR. It appears that the reaction will not go to completion, but rather that an equilibrium is established. $\text{P}(\text{OMe})_3$, a better π -acceptor than PPh_3 ,⁶⁴ is, in this case, a better ligand than PPh_3 . As a result of the tris(thioether) coordination on the platinum there is an increased electron density on the metal which is available for π -backbonding to the phosphorous ligand.

(ii) Stereochemical Considerations

For a system with three chiral centres and a potential internal plane of symmetry, there are three theoretically possible pairs of diastereomers which could be present, although not necessarily in equal proportions.⁷³

When coordinated to the platinum atom, the two terminal sulfur atoms (S_1 and S_3) are chiral centres; and, depending on which lone pair is coordinated to the metal, can be in either the R or S configuration. The central sulfur (S_2) will be a chiral centre only if the two terminal sulfurs are of opposite configuration *viz.* if one is in the S configuration and the other in the R configuration (or *vice versa*).

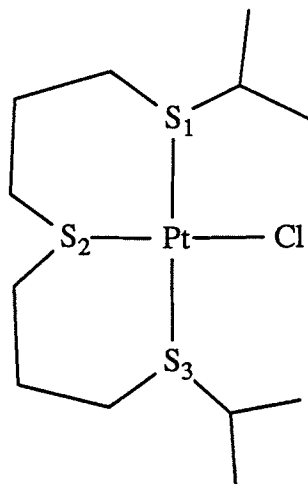


Figure 3.2 [PtCl(DMTT)]⁺ Cation.

When all of the uncoordinated sulfur lone pairs are on the same side of the metal square plane, the molecule is in the *Meso-A* conformation with an SSR or RRS configuration at the sulfurs. When the two terminal sulfur's lone pairs are on the same side of the square plane, and the central sulfur's lone pair is on the opposite side, the molecule is in the *Meso-B* conformation with an SRR or RSS configuration at the sulfurs. If the lone pairs of the terminal sulfurs are on opposite sides of the square plane then there is only one possible configuration as the central sulfur is achiral; this is the *racemic* conformation with an S-S or R-R configuration at the S1 and S3 sulfur atoms.

(iii) X-Ray Structure of [PtI(DPTN)][BF₄] (5).

A perspective view of **5** showing the atom numbering scheme can be seen in Figure 3.3. The unit cell contains four discrete cations of **5** and four discrete BF₄ anions. The closest non-bonded intermolecular contact between cations is 2.59 Å between H15 and H2B. The closest intramolecular anion to cation approach is 2.43 Å,

between F3 and H26.

The complex cation exhibits slightly distorted square planar coordination geometry at the Pt(II) centre while the ligand, DPTN, is in the *Meso-B* conformation, with the phenyl groups mutually *syn*. The sulfur atoms are seen to be approximately tetrahedral and, as such, one can infer the positions of the free lone pair of electrons on each sulfur from the arrangement of the other three substituents. In **5** the lone pair electrons of the terminal sulfurs are on the opposite side of the square plane as the lone pair electrons of the sulfur *trans* to the iodine, with the phenyl groups being mutually *syn*. The Pt atom is bonded to the three sulfurs of the ligand as well as to the I atom. The Pt-I bond distance is 2.603(1) Å, the Pt-S1 and Pt-S3 distances are equal within experimental error at an average value of 2.293(4) Å and the Pt-S2 distance is 2.280(4) Å. The two six membered chelate rings of the tridentate ligand impose a slightly strained geometry on the platinum. The bond angles I-Pt-S1 and I-Pt-S3 are 83.9(1) and 85.9(1) respectively. There is a slight distortion towards tetrahedral geometry. The largest deviation from the least squares plane formed by the Pt, I, S1 and S3 atoms is 0.038 Å, while the S2 atom lies 0.42 Å above this plane. Complete listings of bond distances and angles can be found in Table 3.3.

Table 3.3 Selected Bond Distances and Angles for [PtI(DPTN)][BF₄] (5**).**

Distances (Å)			
Pt-I	2.603(1)	S1-C11	1.776(11)
Pt-S1	2.296(4)	S3-C21	1.739(12)
Pt-S2	2.280(4)	C21-C22	1.395
Pt-S3	2.290(4)	S2-C4	1.784(20)

S1-C1	1.734(20)	C4-C5	1.540(25)
C1-C2	1.514(27)	C5-C6	1.552(22)
C2-C3	1.494(27)	C6-S3	1.816(14)
C3-S2	1.812(17)		

Angles (°)

S1-Pt-I	83.9(1)	C6-S3-C21	100.8(7)
S3-Pt-I	85.9(1)	C6-S3-Pt	111.3(7)
S1-Pt-S2	97.3(2)	C21-S3-Pt	107.5(4)
S2-Pt-S3	93.2(2)	S1-C11-C16	122.2(3)
I-Pt-S2	170.0(1)	S1-C11-C12	117.8(3)
S1-Pt-S3	169.4(2)	S3-C21-C26	118.3(3)
C1-S1-Pt	113.5(7)	S3-C21-C22	121.2(3)
C2-C1-S1	120.6(14)	C1-S1-C11	100.7(8)
C3-C2-C1	114.0(17)	C11-S1-Pt	108.4(4)
S2-C3-C2	115.4(14)	C5-C4-S2	115.1(13)
C4-S2-C3	97.4(9)	C6-C5-C4	113.4(15)
S3-C6-C5	115.3(12)		

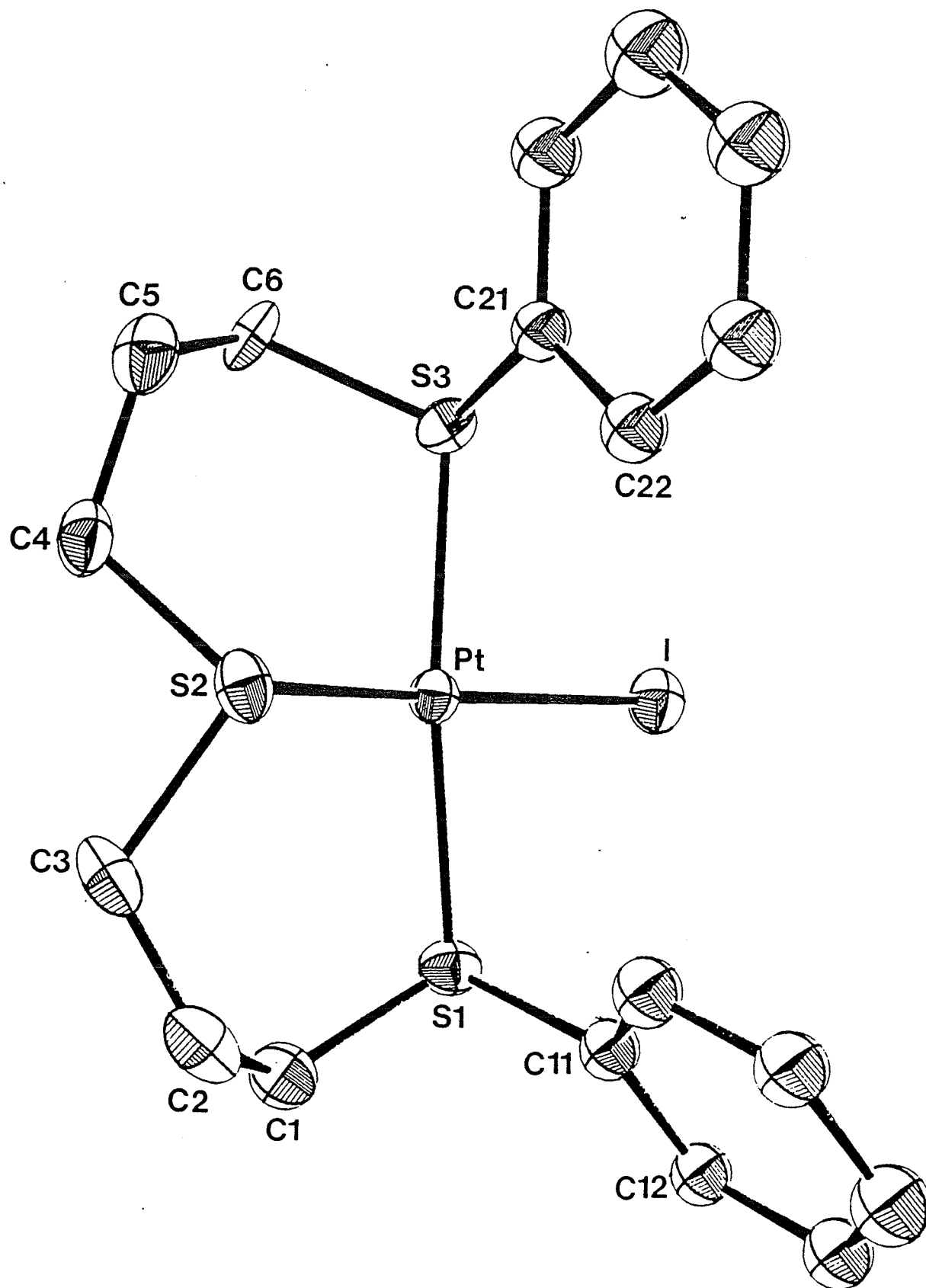


Figure 3.3 Perspective ORTEP Diagram of [PtI(DPTN)]⁺ Cation.

20% Thermal Ellipsoids are Shown.

(iv) X-Ray Structure of [PtCl(DMTT)][BF₄] (**8**).

A perspective view of **8** giving the atom numbering scheme is shown in Figure 3.4. The unit cell contains four discrete cations of **8** and four discrete BF₄ anions. The closest intermolecular contact between cations is 2.36 Å between H12A and H32B. The closest intermolecular cation to anion approach is 2.51 Å between F2 and H4B, the closest metal to anion approach is 3.97 Å between F4 and the Pt. Complete listings of intramolecular distances and angles may be found in Table 3.4.

The complex cation exhibits slightly distorted square planar coordination geometry at the Pt(II) centre while the ligand, DMTT, is in the *Meso-B* conformation, with the *iso*-propyl groups mutually *syn*. The sulfur atoms are seen to be approximately tetrahedral and, as such, one can infer the positions of the free lone pair of electrons on each sulfur from the arrangement of the other three substituents. In **8** the lone pair electrons of the terminal sulfurs are on the opposite side of the square plane as the lone pair electrons of the sulfur *trans* to the chloride, with the *iso*-propyl groups being mutually *syn*. The Pt atom is bonded to three sulfurs of the ligand as well as to the Cl atom. The Pt-Cl bond distance is 2.327(3) Å, The Pt-S1 and Pt-S3 distances are equal within experimental error at an average value of 2.306(4) Å and the Pt-S2 distance is 2.254(4) Å. The two six membered chelate rings of the tridentate ligand impose a slightly strained geometry on the platinum. The bond angles Cl-Pt-S1 and Cl-Pt-S3 are 87.6(1) and 85.9(1) respectively. There is a slight distortion towards tetrahedral geometry about the platinum; the S2 sulfur is 0.36 Å above the least squares plane defined by the Pt, Cl, S1 and S3 atoms. The largest deviation of any of the defining atoms from the plane is 0.08 Å.

Table 3.4 Selected Bond Distances and Angles for [PtCl(DMTT)][BF₄] (8).

Distances (Å)			
Pt-Cl	2.327(3)	C4-C5	1.601(25)
Pt-S1	2.303(4)	C5-C6	1.434(22)
Pt-S2	2.254(4)	C6-S3	1.806(13)
Pt-S3	2.308(3)	S3-C31	1.836(12)
S1-C1	1.768(22)	S1-C11	1.804(17)
C1-C2	1.439(25)	C11-C12	1.490(23)
C2-C3	1.239(22)	C11-C13	1.535(20)
C3-S2	1.782(15)	C31-C32	1.497(19)
S2-C4	1.821(17)	C31-C33	1.606(18)
Angles (°)			
S1-Pt-Cl	87.6(1)	C6-S3-C31	104.7(7)
S3-Pt-Cl	85.9(1)	C6-S3-Pt	106.2(5)
S1-Pt-S2	97.2(1)	C31-S3-Pt	107.1(4)
S2-Pt-S3	89.9(1)	S1-C11-C12	117.5(13)
Cl-Pt-S2	173.2(1)	S1-C11-C13	110.9(12)
S1-Pt-S3	171.0(1)	S3-C31-C32	108.0(10)
C1-S1-Pt	112.0(11)	S3-C31-C33	107.1(9)
C2-C1-S1	117.3(17)	C1-S1-C11	101.8(11)
C3-C2-C1	126.0(24)	C11-S1-Pt	110.9(5)
S2-C3-C2	132.4(15)	C5-C4-S2	109.6(10)

C4-S2-C3	98.6(12)	C6-C5-C4	112.8(14)
S3-C6-C5	118.5(10)		

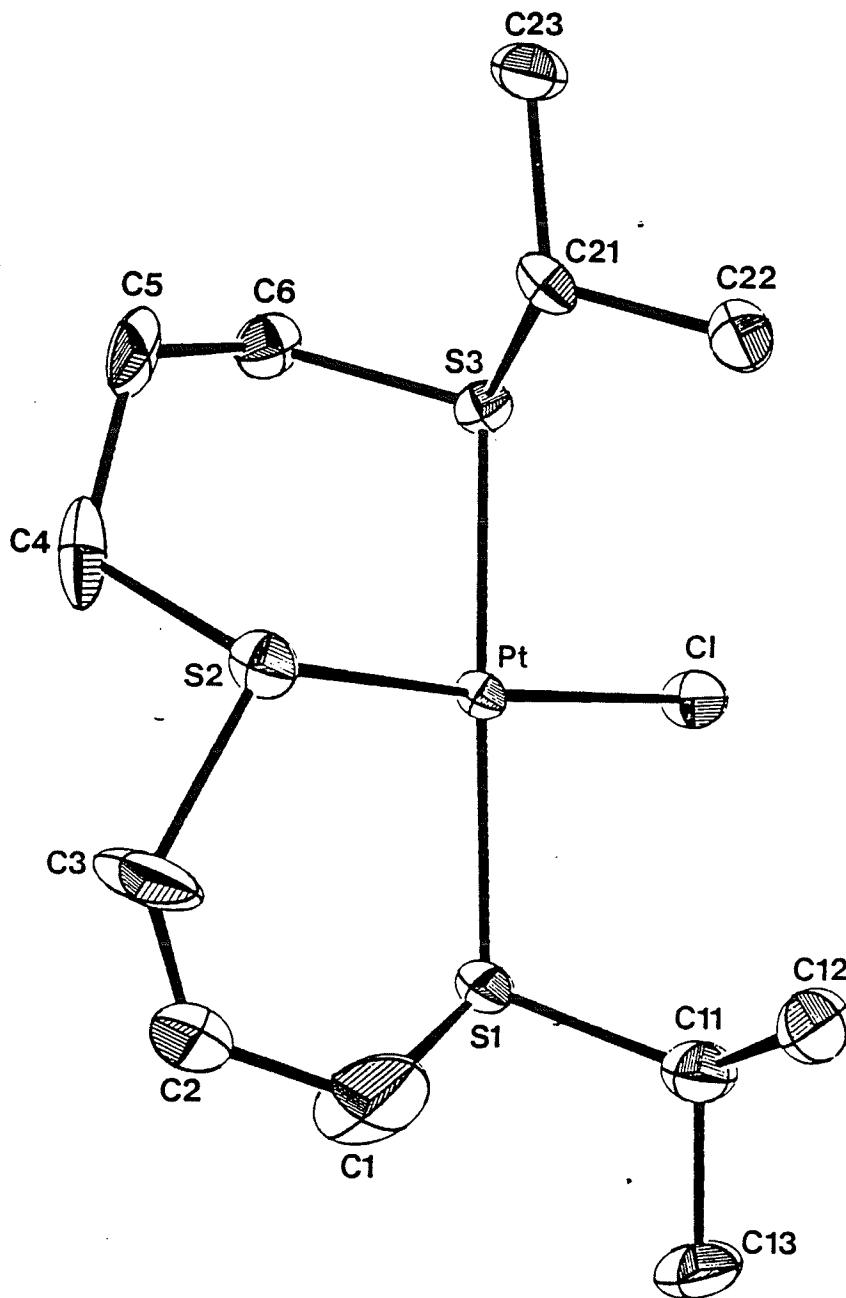


Figure 3.4 Perspective ORTEP Diagram of $[\text{PtCl}(\text{DMTT})]^+$ Cation.

20% Thermal Ellipsoids are Shown.

(v) X-Ray Structure of [Pt(DMTT)(PPh₃)]₂[BF₄]₂ (**10**).

A perspective view of **10** giving the atom numbering scheme is shown in Figure 3.5. The unit cell contains two discrete cations of **10** and four discrete BF₄ anions and two CH₂Cl₂ molecules of crystallization with 74% site occupancy. The closest intermolecular contacts between cations are 2.51 Å between H11A and H5Bd and 2.55 Å between H34 and H13A. The closest intermolecular cation to anion #1 (F1 to F4) approach is 2.33 Å between F1 and H5B, the closest intermolecular cation to anion #2 (F5 to F8) approaches are 2.02 Å between F7 and H4Bd and 2.38 Å between F5 and H3B, the closest intermolecular cation to solvent (CH₂Cl₂) approach is 2.96 Å between CL1 and H54, and the closest Pt to anion approach is 3.57 Å to F8. Complete listings of intramolecular distances and angles may be found in Table 3.5.

The complex cation displays a slightly distorted square planar geometry at the Pt(II) centre and the ligand DMTT is arranged in the *racemic* conformation; the *i*-propyl groups being mutually *anti* and the sulfur *trans* to the triphenylphosphine being achiral. The Pt atom is bonded to three sulfurs of the ligand as well as to the phosphorous atom. The Pt-P bond distance is 2.331(2) Å, while the Pt-S1 and Pt-S3 distances are found to be 2.338(2) Å and 2.329(2) Å respectively. The two six membered chelate rings of the tridentate ligand impose a slightly strained geometry on the platinum. The bond angles P-Pt-S1 and P-Pt-S3 are 85.9(1) and 90.8(1) respectively. There is a slight distortion towards tetrahedral geometry about the platinum; the S2 sulfur is 0.15 Å above the least squares plane defined by the Pt, Cl, S1 and S3 atoms. The largest deviation of any of the defining atoms from the plane is 0.01 Å.

Table 3.5 Selected Bond Distances and Angles for [Pt(DMTT)(PPh₃)](BF₄)₂ (10).

Distances (Å)			
Pt-P	2.331(2)	C4-C5	1.503
Pt-S1	2.338(2)	C5-C6	1.535
Pt-S2	2.340(3)	C6-S3	1.833(2)
Pt-S3	2.329(2)	S3-C21	1.873(11)
S1-C1	1.840(9)	S1-C11	1.848(10)
C1-C2	1.520(15)	C11-C12	1.490(16)
C2-C3	1.544(16)	C11-C13	1.532(16)
C3-S2	1.824(11)	C21-C22	1.521(17)
S2-C4	1.767(3)	C21-C23	1.554(17)
C31-C32	1.395	C4-C5d	1.526
C5d-C6	1.508		
Angles (°)			
S1-Pt-P	85.9(1)	C6-S3-C21	102.1(4)
S3-Pt-P	90.8(1)	C6-S3-Pt	114.8(1)
S1-Pt-S2	85.6(1)	C21-S3-Pt	108.0(4)
S2-Pt-S3	97.8(1)	S1-C11-C12	109.1(8)
P-Pt-S2	171.0(1)	S1-C11-C13	108.8(8)
S1-Pt-S3	176.3(1)	S3-C21-C22	114.4(9)
C1-S1-Pt	106.1(3)	S3-C21-C23	108.1(9)
C2-C1-S1	117.7(7)	C1-S1-C11	104.4(5)

C3-C2-C1	115.8(9)	C11-S1-Pt	110.0(3)
S2-C3-C2	112.5(7)	C5-C4-S2	118.4(1)
C4-S2-C3	103.0(4)	C6-C5-C4	112.9
S3-C6-C5	116.7(1)	Pt-P-C31	110.2(2)
Pt-P-C41	116.0(2)	Pt-P-C51	112.5(3)
C6-C5d-C4	113.1		

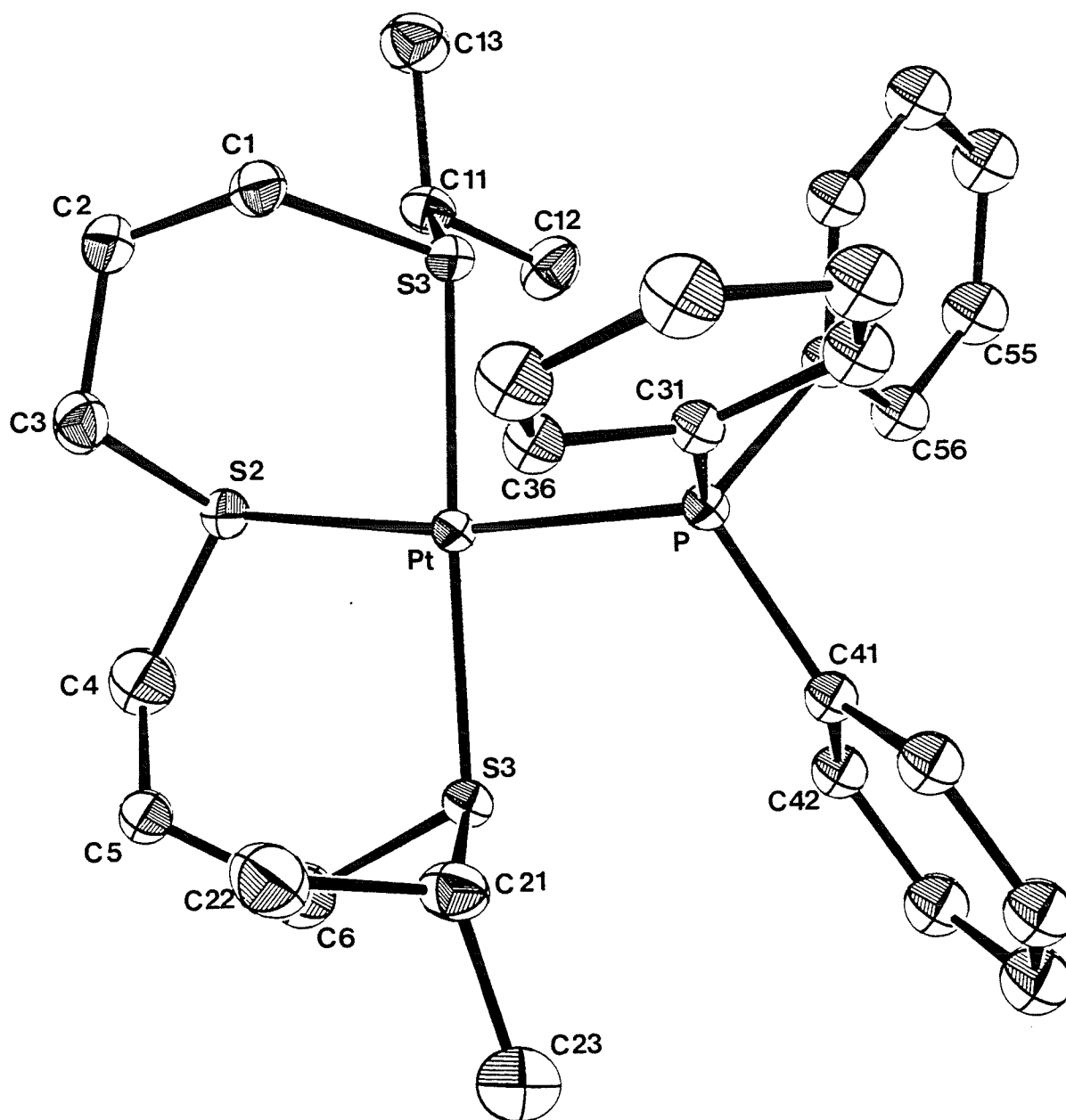


Figure 3.5 Perspective ORTEP Diagram of [Pt(DMTT)(PPh₃)]²⁺ Dication.

20% Thermal Ellipsoids are Shown.

(vi) Comparison of the Crystal and Molecular Structures of 5, 8 and 10.

Both of the platinum halide complexes, [PtI(DPTN)][BF₄] (**5**) and [PtCl(DMTT)][BF₄] (**8**), crystallized in what is essentially the same space group (P2₁/c), with their ligands in the same configuration (*Meso-B*). Replacement of the anionic halide ligand with the neutral, bulky PPh₃ ligand results in large changes in the crystal structure. The ligand DMTT in **10** is in the *racemic* conformation, and the molecule is in space group P1.

Table 3.6 Comparison of Crystallographic Data for 5, 8 and 10.

Measurement (Å)	5	8	10
Space Group:	P2 ₁ /n	P2 ₁ /c	P1
Conformation of Ligand:	<i>Meso-B</i>	<i>Meso-B</i>	<i>Racemic</i>
Pt-S2 distance:	2.280(4)	2.254(4)	2.340(3)
S2 distance above Pt-L-S1-S3 plane: ^a	0.42	0.36	0.15
Average Pt-S1, S3 distance:	2.293	2.306	2.336

^aHere L = I, Cl or PPh₃, accordingly.

As can be seen in Table 3.6 there is a general trend in certain measurements in complexes **5**, **8** and **10** with changes in the ancillary ligand, L. The ancillary ligands Cl, I, PPh₃ follow a *trans* effect trend of PPh₃ > Cl > I.⁸⁵ The trend in bond distance from the platinum to the sulfur *trans* to the ancillary ligand, the trend towards planarity and the trend in average platinum to S1 and S3 distances can all be seen to follow the pattern of *trans* effects. It is likely that the increase in π -acceptor ability as one moves from I to PPh₃ is a factor in the trends observed in Table 3.6. The PPh₃ ligand removes electron density from the platinum, reducing the amount available for donation to the three bound sulfurs. This would increase the length of all of the sulfur-metal interactions.

(vii) Fluxional Behaviour of Thioether Ligands

Nuclear Magnetic Resonance (NMR) has long been used as a tool to evaluate exchange rates and energy barriers in chemical systems. In 1956 the Bloch equations, derived in 1946 and describing the precessional motion of a dipole in a magnetic field,³⁸ were first modified to account for chemical exchange.^{39,40} The modified Bloch equations, being based on a classical model, break down in the presence of spin-spin coupling.⁴¹ The calculation of a theoretical spectrum in the presence of spin-spin coupling requires the use of the quantum mechanical density matrix theory.⁵⁹ Using either of these systems of equations it is possible to determine the thermodynamic activation parameters (ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger) of the chemical system of interest by fitting calculated spectra to experimentally determined spectra.⁴¹⁻⁴⁴

At low temperatures, when the rate of exchange from one conformer to another is slow compared to the chemical shift difference between the two nuclei on the conformers, the molecule can be considered to be rigid and peaks from all

conformers can be observed. As the temperature is raised, and the rate of exchange increases, the peaks in the spectra are broadened and move together. At high temperatures, and fast rates of exchange as compared to the frequency difference, only a single, narrow, averaged peak was observed.

The inversion of a coordinated sulfur centre was first demonstrated in 1966 using the chelate compound $\text{PtCl}_2(2,5\text{-dithiahexane})$.⁴⁵ Variable temperature NMR, of this and other similar compounds, was used to show that diastereomers could be interconverted by the inversion of a chiral sulfur centre and that the process proceeded via a non-dissociative mechanism, as ^{195}Pt coupling was retained in the high temperature, averaged spectra.⁴⁶

(viii) Analysis of the Fluxional Behaviour of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ (10).

The room temperature ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR show spectra characteristic of a system which is exchanging on the NMR time-scale. Each coordinated sulfur is in a tetrahedral environment as seen from the X-ray analysis, and as such has two lone pairs with which it could potentially bind to the metal. The exchange of the lone pair bound to the metal, or inversion of the coordinated sulfur centre, has been invoked in many platinum-sulfur compounds to explain observations in the NMR spectra.^{43,45,46}

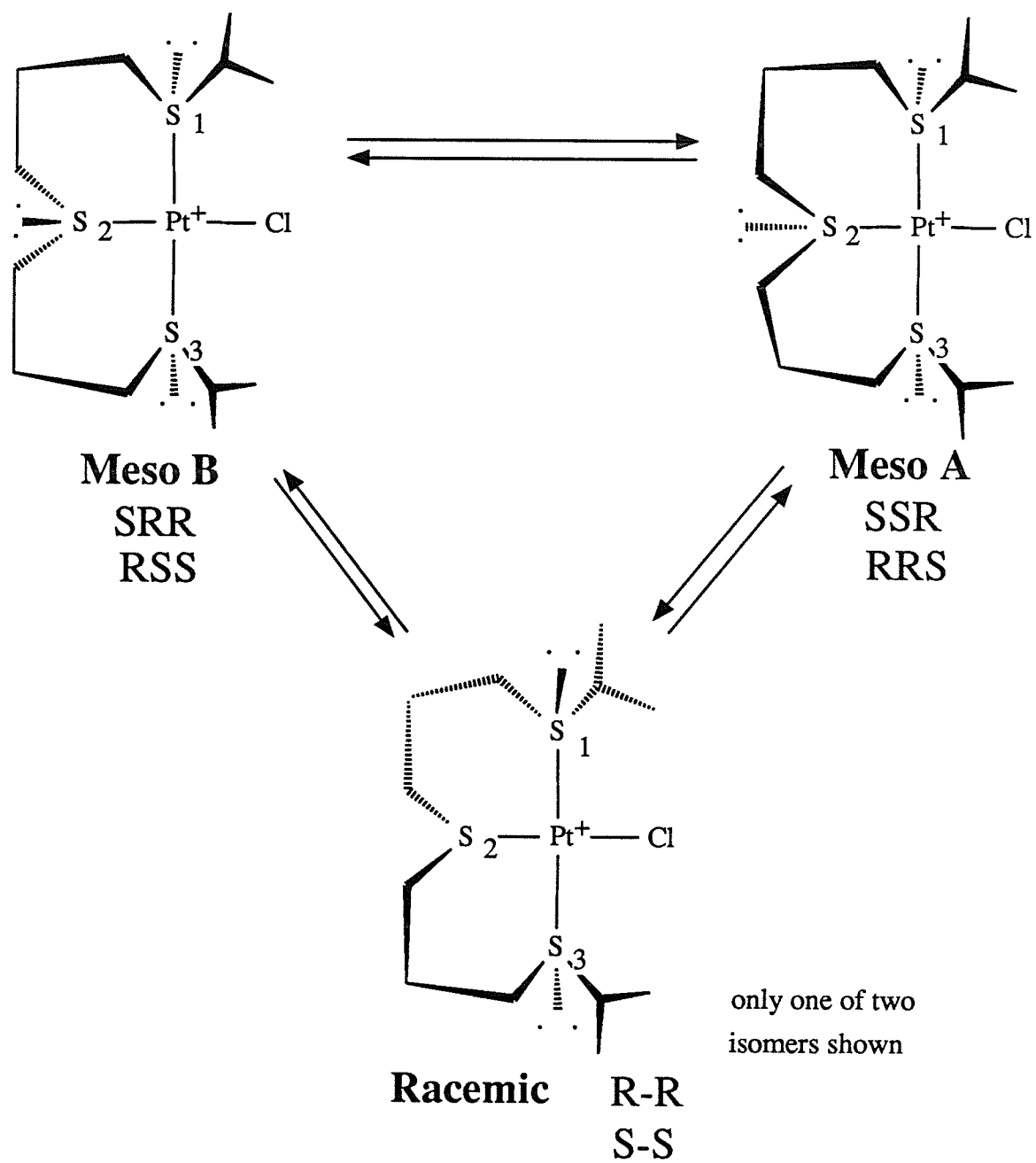


Figure 3.6 Interconversion Scheme for the Isomers of $[\text{PtCl}(\text{DMTT})]^+$.

The three possible isomers, *Meso-A*, *Meso-B* and *Racemic*, can be interconverted by the inversion of one of their sulfurs as shown in Figure 3.6. At elevated temperatures (380K) the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of the complex $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$, **8**, are simple and first order. A doublet due to the methyl protons, at 380 K, is seen at $\delta = 1.526$ ppm as well as a single peak in the ^{13}C NMR at $\delta = 21.14$ ppm. This is indicative of equivalent methyl groups. The $^{13}\text{C}\{^1\text{H}\}$ NMR at 380 K shows five peaks (Figure 3.7), some of which show satellites from coupling with ^{195}Pt . At this temperature the sulfurs can be considered to be in an "averaged planar" conformation as a result of the rapid inversion of the coordinated sulfur centre on the NMR timescale. As the temperature is lowered, these peaks broaden and collapse in turn

At low temperatures, a complex spectrum is seen in the $^{13}\text{C}\{^1\text{H}\}$ NMR. The single peak of the methyl group has become a six line system and all of the other peaks, which at high temperatures were single peaks, have split into three separate resonances. The three peaks seen for the backbone and methine carbons can be assigned to the three possible isomers: *Meso-A*; *Meso-B* and *Racemic*. The existence of six methyl resonances is due to the prochiral nature of the *iso*-propyl group. Prochiral groups attached to a chiral centre are inequivalent and, barring chance overlap, anisochronous. At low temperatures, the chirality of each sulfur can be considered fixed on an NMR timescale and, as a result, the methyl carbons of each *iso*-propyl group become inequivalent. We see, therefore, two separate methyl resonances for each configurational isomer, giving a six line pattern overall.

A full line-shape fitting calculation was performed on the methine carbon of **8** using a locally modified program based on DNMR3.⁹² Spectra at nine temperatures (230, 240, 250, 260, 270, 280, 300, 320 and 340 K) were fitted and the corresponding exchange coefficients (k , listed in Table 3.7) used in an Arrhenius-type plot to calculate the thermodynamic parameters. The methine carbon was chosen as it had



Figure 3.7 Variable Temperature $^{13}\text{C}\{^1\text{H}\}$ NMR of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$.

the smallest $^1J_{Pt,C}$ coupling of all of the carbons in the spectrum, appearing as nearly imperceptible shoulders on the central resonance. This was important, as the program used for the calculations (DNMR3) was only capable of handling three configurations, and not the six that would have been required to include the effects of platinum coupling.

The populations used in the calculations were 0.107, 0.775 and 0.118 for the peaks at $\delta = 39.53$, 42.09 and 44.13 ppm, respectively. The relaxation time (T_2), which was used in the calculations, was $T_2 = 0.088$ s and was calculated from the peak width at half-height of the largest methine peak at 230 K. The chemical shifts used in the calculations were empirically adjusted for temperature dependence by extrapolating their chemical shift temperature dependence, from below the coalescence point, to all temperatures used in the calculation.

Table 3.7 Arrhenius Plot Data for Thermodynamic Calculations.

Temperature (K)	Exchange Coefficient (k)
230	0.52
240	0.90
250	10.5
260	25.0
270	75.0
300	800
320	3000
340	7800

A plot of $\ln(k/T)$ versus $1/T$ of the data shown in Table 3.5 yielded a straight line of the form $y = mx + b$, where:

$$\Delta H^\ddagger = -mR \quad \text{and} \quad \Delta S^\ddagger = R[b - \ln(k_B/h)]$$

The thermodynamic values thus calculated were:

$$\Delta G^\ddagger_{300} = 56.6 \pm 4.2 \text{ kJ mol}^{-1}$$

$$\Delta H^\ddagger = 56.2 \pm 3.6 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = -1.3 \pm 8.3 \text{ J K}^{-1}\text{mol}^{-1}.$$

This is in general agreement with values obtained for bidentate platinum(II) thioether complexes, such as $\text{PtCl}_2\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}$, for which a value of $\Delta G^\ddagger = 65.6 \text{ kJ mol}^{-1}$ was measured.⁴⁶

(ix) General NMR.

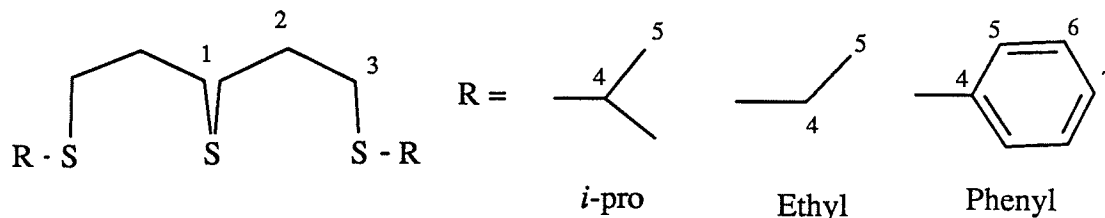
All of the platinum complexes synthesized, **5-13**, exhibit this type of fluxional behaviour, and as we will see, so do all of the complexes of **2-4** described herein. Once the complex nature of this fluxional process is understood it becomes relatively easy to assign peaks in the $^{13}\text{C}\{^1\text{H}\}$ NMR without the need to perform a full variable temperature experiment (Table 3.8).

Table 3.8 $^{13}\text{C}\{^1\text{H}\}$ NMR Data for Platinum and Palladium Complexes at 230 K, δ (ppm).

Compound	C1	C2	C3	C4	C5
$[\text{PdCl}(\text{DPTN})]^{+a}$					
Isomer 1 ^b	35.64	23.91	34.12	-	-
$[\text{PtI}(\text{DPTN})]^+$					
Isomer 1	35.57	22.85	34.24	-	-
Isomer 2	36.02	23.27	34.52	-	-
Isomer 3	35.00	21.60	33.86	-	-
$[\text{PtCl}(\text{DPTN})]^+$					
Isomer 1	36.10	31.05	33.86	-	-
Isomer 2	34.78	32.39	34.40	-	-
$[\text{PtCl}(\text{TTTD})]^{+c}$					
Isomer 1	33.76	23.02	31.99	28.94	13.07
Isomer 2	34.92	-	32.45	30.59	13.53
Isomer 3	33.32	-	31.05	28.28	12.56
$[\text{PtCl}(\text{DMTT})]^{+c,d}$					
Isomer 1	34.54	23.78	27.47	42.09	22.18, 21.00
Isomer 2	35.58	-	28.84	44.13	24.06, 22.59
Isomer 3	31.64	-	24.90	39.53	21.09, 19.75
$[\text{Pt}(\text{DMTT})(\text{PPh}_3)]^{2+}$					
Isomer 1 ^c	35.14	25.51	29.18	44.77	22.05, 20.91

^aat 300K. ^bisomer of highest population listed first; isomer peaks to high field grouped as one isomer, those to low field as another. ^cin some cases not all isomer peaks were

observed. ^ddue to prochiral *i*-propyl group, six peaks observed for methyl carbon.



At low enough temperatures, the interconversion of the three isomers for the platinum complexes will become slow enough that the individual isomers will be visible in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. In the case of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ and $[\text{PtCl}(\text{TTTD})][\text{BF}_4]$, the exchange of the middle carbon of the propylene chain was never slowed enough to observe separate isomers. This is likely due to another exchange process which is well documented for ethylene linkages;⁶⁴ there are several spacial conformations that the backbone can adopt, namely the boat and chair conformations (see Figure 3.8),⁹⁶ and interconversion of these isomers will broaden the peaks for C3 enough so that only the major isomer is observed.

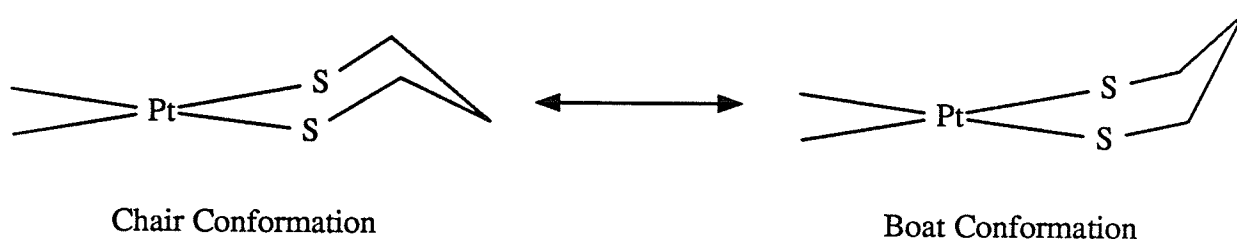


Figure 3.8 Boat-Chair Conformations of Six Membered Rings.

For the complexes $[\text{Pt}(\text{DMTT})(\text{PPh}_3)][\text{BF}_4]_2$ and $[\text{PdCl}(\text{DPTN})][\text{BF}_4]$, only one isomer is observed at low temperatures and for $[\text{PtI}(\text{DPTN})][\text{BF}_4]$ only two isomers are observed. There are two possible explanations for these observations:

first, the populations of the unobserved isomers are much smaller than the observed isomers, so, while the low temperature limit had been reached, it is impossible to observe the minor isomers; second, the low temperature limit had not yet been reached and, although the peaks of the major isomer appear sharp, the peaks of the minor isomers are still too broad to be observed against the baseline noise. Solubility limitations precluded the testing of these hypotheses.

The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ was recorded and the chemical shift of this compound determined to be $\delta = -3981.3$ ppm at 300K (all chemical shift given relative to H_2PtCl_6 at $\delta = 0$ ppm⁸⁷). At temperatures above 280K the spectrum consisted of a singlet with peak width at half height, $v_{\frac{1}{2}} \approx 30$ Hz. At lower temperatures the resonance began to broaden but it was not possible to reach a limiting spectrum, even at 230K.

$^{195}\text{Pt}\{^1\text{H}\}$ NMR was used to determine if oxidative addition had occurred during reactions of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$. The wide range of chemical shifts possible for platinum and the strong shift dependence on oxidation state of the metal makes this an ideal method.^{74,87} In only one case was any platinum compound other than starting material detected. The reaction of Br_2 with $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ did not produce any platinum(IV) complexes, but rather produced a mixture of $[\text{PtBr}(\text{DMTT})][\text{BF}_4]$ and $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$ in approximately a 2:1 ratio. The ^{195}Pt shift of $[\text{PtBr}(\text{DMTT})][\text{BF}_4]$ was determined to be $\delta = -4167.6$ ppm at 300K. The chemical shifts of these two DMTT complexes correlate closely to the shifts of their analogous $\text{S}(\text{Me})_2$ compounds. The chemical shift for $[\text{PtCl}(\text{SMe}_2)_3]^+$ is $\delta = -4002$ ppm and the shift for $[\text{PtBr}(\text{SMe}_2)_3]^+$ is $\delta = -4162$ ppm.^{74,87}

The $^{31}\text{P}\{^1\text{H}\}$ NMR of those complexes containing phosphorous, **10** and **11**, were simple and first order, consisting of a large peak and corresponding platinum satellites. The shift of $\delta = 73.41$ ppm with $^1J_{\text{Pt,P}} = 5709.2$ Hz observed for $[\text{Pt}(\text{DMTT})\{\text{P}(\text{OMe})_3\}][\text{BF}_4]_2$ is comparable to the values found for

$[\text{Pt}(\text{ttp})\{\text{P}(\text{OMe})_3\}][\text{BF}_4]_2$ ($\delta = 86.1$ ppm, $^1J_{\text{Pt,P}} = 4189$ Hz) and the values observed for $[\text{Pt}(\text{DMTT})(\text{PPh}_3)][\text{BF}_4]_2$, $\delta = 13.79$ ppm and $^1J_{\text{Pt,P}} = 2970.7$ Hz, are comparable to those found for $[\text{Pt}(\text{ttp})(\text{PEt}_3)][\text{BF}_4]_2$ ($\delta = 1.8$ ppm; $^1J_{\text{Pt,P}} = 2161$ Hz). The significantly larger Pt-P coupling constants for **10** and **11**, as compared to their ttp analogs, can be attributed to the higher electron density remaining on the platinum for thioether complexes, which reflects the increased σ -basicity/poorer π -acceptor ability of thioethers relative to triarylphosphines.

3.5 Summary and Conclusions

Platinum(II) and palladium(II) halide complexes of the type $[\text{MX}(\text{L})][\text{BF}_4]$ were easily prepared from $\text{PtCl}_2(\text{COD})$, L (M = Pd, Pt; L = TTTD, DPTN or DMTT; X = I, Cl) and AgBF_4 . These compounds are resistant to oxidative addition of a number of typical oxidants and are stable in the presence of dioxygen. The halide ligand can be replaced with a neutral Lewis base donor such as PPh_3 or $\text{P}(\text{OMe})_3$ with the use of AgBF_4 or NaBF_4 , forming the dicationic complexes $[\text{Pt}(\text{DMTT})(\text{L})][\text{BF}_4]_2$ (L = PPh_3 , $\text{P}(\text{OMe})_3$ or CNR). Understanding the fluxional behaviour of the tridentate thioether ligand is important in the characterization of these platinum and palladium complexes, and, as will be seen, in the characterization of the rhodium and iridium complexes of chapter four.

CHAPTER FOUR

IRIDIUM AND RHODIUM COMPLEXES OF DMTT

4.1 Introduction

After the initial success in synthesizing complexes of palladium and platinum, we turned our attention to the more reactive members of the platinum group. Iridium(I) and rhodium(I) are known to form a large number of complexes with tertiary phosphines. The chemistry of these compounds is complex and varied.⁶⁴ A classic example of rhodium(I) compounds is Wilkinson's catalyst,⁷⁵ $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, a neutral, d^8 , distorted square-planar complex which undergoes an enormous variety of reactions and catalyses numerous reactions.^{64,74} An important discovery in the study of the catalytic reaction of this compound was that the four coordinate complex is not the active species in the catalytic cycle; a prerequisite for catalysis to occur is the dissociation of the phosphine *trans* to the chloride. It is this three coordinate species which is active in the catalytic cycle.^{64,74-78}

It is not surprising, then, that the ttp analog of Wilkinson's catalyst, $\text{Rh}(\text{ttp})\text{Cl}$, will not act as a homogeneous hydrogenation catalyst as the phosphine *trans* to the chloride is the central phosphine in the chelate string.^{60,61} Indeed, instead of reacting reversibly with dihydrogen as does Wilkinson's catalyst, $\text{Rh}(\text{ttp})\text{Cl}$ reacts irreversibly, forming a stable Rh(III) dihydride species. The stability of this dihydride and the tendency of $\text{Rh}(\text{ttp})\text{Cl}$ to undergo oxidative-addition reactions is comparable to the more basic iridium(I)-triphenylphosphine and rhodium(I)-trialkylphosphine complexes. The combined inductive and chelate effects increase the nucleophilicity of $\text{Rh}(\text{ttp})\text{Cl}$ over that of $\text{Rh}(\text{PPh}_3)_3\text{Cl}$.^{30,61,80}

The complexation of the tridentate phosphine ligand ttp to iridium results in compounds with an increased tendency to be five-coordinate, as seen in the

complexes $\text{IrCl}(\text{ttp})(\text{CO})$ and $[\text{Ir}(\text{ttp})(\text{CO})_2]^+$, both of which are stable at room temperature.¹⁰¹ It is, however, still possible to utilize the complex of a chelating triphosphine compound and a planar d^8 metal in a catalytic cycle if the fourth site on the metal is an important ligand in the catalytic cycle.⁷⁹ For example, $\text{Rh}(\text{ttp})\text{H}$ is an excellent hydrogenation catalyst.⁷⁹ In light of this, and since thioethers are more σ -basic than triarylphosphines, one might hypothesize that a tris(thioether) substitution on rhodium(I) would result in a more basic complex which would also behave similarly to iridium(I) tris(triarylphosphines) complexes. The increased tendency of $[\text{Rh}(14\text{S}4)]^+$ to oxidatively add CH_2Cl_2 supports this hypothesis, and gives precedence to reactive, basic rhodium thioether complexes.³⁶

4.2 Rhodium and Iridium Thioether Complexes

In contrast to the large number of palladium and platinum thioether complexes known, only three examples of rhodium(I) and two iridium(I)thioether complexes had been reported as of 1981.^{1,69-71} Since then several rhodium(I) complexes have been synthesized, but no new iridium(I) complexes have been published. 20S6 (20S6 = 1,4,7,11,14,17-hexathiacycloicosane) will form a rhodium(I) complex with the formula $[\text{Rh}_2(20\text{S}6)(\text{COD})_2][\text{PF}_6]_2$.⁷² In this complex the metal centres are five coordinate with each rhodium coordinated to three sulfurs of the ligand and to four carbons of the COD. Rhodium(I) will also form mononuclear, tetrakis(thioether), square-planar complexes with 14S4 of the type $[\text{Rh}(14\text{S}4)]\text{Cl}$.³⁶

4.3 Experimental

(i) General

In order to avoid repetition the reader is directed to section 2.2(i) in Chapter Two. Many of the species in this chapter were characterized in solution only as they were not isolable as tractable solids suitable for elemental analysis.

(ii) Preparation of $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$ (13)

$[\text{IrCl}(\text{COE})_2]_2$ (2.000 g, 4.464 mmol) was stirred in CH_3CN (30 mL) for 30 minutes. AgBF_4 (0.880 g, 4.52 mmol) was added and then DMTT (1.223 g, 4.59 mmol)(4), dissolved in CH_3CN (30 mL), was quickly added. This mixture was stirred for 2 hours and then filtered to remove the $\text{AgCl}_{(s)}$. The solvent was removed *in vacuo* and the remaining residue washed with diethylether (3 x 10 mL) giving an orange-yellow powder. Yield: 2.872 g (87%). A satisfactory elemental analysis could not be obtained.

(iii) Preparation of $[\text{Ir}(\text{DMTT})(\text{COE})(\text{PPh}_3)][\text{BF}_4]$ (14).

To a flask containing $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$ (0.288 g, 0.390 mmol)(13) and PPh_3 (0.106 g, 0.404 mmol) was added CH_3CN (10 mL) and the mixture stirred for 4 hours. The solvent was removed *in vacuo* and the residue pumped on for four hours to remove excess COE. The residue was washed with diethylether (2 x 10 mL) and dried *in vacuo*.

(iv) Preparation of [Ir(DMTT)(dppe)][BF₄] (15).

To a flask containing [Ir(DMTT)(COE)₂][BF₄] (0.298 g, 0.404 mmol)(13) and 1,2-bis(diphenylphosphino)ethane, dppe, (0.164 g, 0.41 mmol) was added CH₃CN (13 mL) and the solution stirred for 3 hours. The solvent was removed *in vacuo* and the residue pumped on for three hours to remove excess COE. The residue was then washed with diethylether (2 x 10 mL) and dried *in vacuo*.

(v) Preparation of [Ir(DMTT)(COE)(CO)][BF₄] (16).

[Ir(DMTT)(COE)₂][BF₄] (0.275 g, 0.37 mmol)(13) was dissolved in CH₃CN (10 mL) and stirred under an atmosphere of CO for 2 hours. The solvent was removed *in vacuo* and the residue pumped on for 2 hours to remove the COE. The residue was then washed with diethylether (10 mL) and dried *in vacuo* giving a yellow-orange powder. Yield: 0.220 g (91 %). A satisfactory elemental analysis could not be obtained.

(vi) Preparation of [Rh(DPTN)(COD)][BF₄] (17).

To a slurry of [RhCl(COD)]₂ (0.512 g, 2.08 mmol of Rh) in CH₂Cl₂ (5 mL) was added first DPTN (0.721 g, 2.16 mmol)(3) and then AgBF₄ (0.408 g, 2.10 mmol). This was stirred for 1 hour and then filtered through Celite to remove the AgCl_(s). The solvent was removed *in vacuo* and the residue was crystallized from CH₂Cl₂/diethylether giving an orange-brown solid. Yield: 0.456 g (35 %). A satisfactory elemental analysis could not be obtained.

(vii) Preparation of [Rh(DMTT)(CO)][BF₄] (18).

DMTT (0.359 g, 1.35 mmol)(4) in CH₂Cl₂ (10 mL) was added to a flask containing [RhCl(CO)₂]₂ (0.241 g, 1.240 mmol of Rh) and AgBF₄ (0.249 g, 1.28 mmol). This mixture was stirred for 2 hours during which time a white precipitate formed. This was then filtered to remove the AgCl_(s), the solvent removed *in vacuo* and the residue pumped on for 1 hour. Attempts to crystallize this gummy solid failed. Analysis calculated for C₁₃H₂₆S₃RhF₄OB•CH₂Cl₂: C, 29.54; H, 4.96; S, 16.90. Found: C, 29.38; H, 5.37; S, 18.89.

(viii) Reactions of [Ir(DMTT)(COE)₂][BF₄] with H₂, MeI and DMA•HCl.

a) H₂

[Ir(DMTT)(COE)₂][BF₄] (0.258 g, 0.39 mmol)(13) was dissolved in CH₃CN (10 mL) and stirred at room temperature under an atmosphere of H₂ for 18 hours. The solvent was removed *in vacuo*, the residue washed with diethylether (2 x 5 mL) and the entire sample placed in an NMR tube. No evidence of oxidative-addition/reductive-elimination was observed *ie.* no hydride peaks in the ¹H NMR or change in the COE peaks in the ¹³C{¹H} NMR were observed.

b) MeI or DMA•HCl

For a typical reaction, [Ir(DMTT)(COE)₂][BF₄] (*ca.* 0.30 g)(13) was dissolved in CH₃CN (10 mL). To this was added appropriate stoichiometric amounts of either DMA•HCl or MeI and the resulting mixture stirred for three hours. In both cases, neither the solution state IR (in CH₂Cl₂) or NMR showed evidence of oxidative addition.

(ix) Reactions of [Ir(DMTT)(COE)(CO)][BF₄] with H₂ and CO.

In a typical reaction, [Ir(DMTT)(COE)(CO)][BF₄] (*ca.* 250 mg)(16) was dissolved in CH₃CN and stirred under an atmosphere of the appropriate gas for several hours. The product was then analysed by IR (in CH₂Cl₂, under an atmosphere of the appropriate gas). In both cases all that was observed was starting material.

(x) Reactions of [Rh(DPTN)(COD)][BF₄] with CO, P(CH₃)₂Ph, H₂ and DMA·HCl.

a) P(CH₃)₂Ph or DMA·HCl.

[Rh(DPTN)(COD)][BF₄] (*ca.* 150 mg)(17) was dissolved in acetone (10 mL) and one equivalent of the appropriate reactant (P(CH₃)₂Ph or DMA·HCl) added. The solution was then stirred for several hours and the solvent removed *in vacuo*. The residue was then analysed by both NMR and IR spectroscopy. In neither case was any reaction observed to occur.

b) H₂ or CO.

[Rh(DPTN)(COD)][BF₄] (*ca.* 150 mg)(17) was dissolved in CH₂Cl₂ (10 mL) and stirred under an atmosphere of the appropriate gas for several hours. An aliquot of this reactions was removed and the solution state IR (in CH₂Cl₂, under an atmosphere of the appropriate gas) was recorded. The solvent from the bulk of the sample was removed *in vacuo* and the NMR spectra of the sample were recorded. No evidence of a reaction was observed in either case.

(xi) Reaction of [Rh(DMTT)(CO)][BF₄] with CO.

[Rh(DMTT)(CO)][BF₄] (*ca.* 0.30 g)(**18**) was dissolved in CH₂Cl₂ (5 mL) and stirred under an atmosphere of CO for 6 h. An aliquot of this mixture was removed and the solution state IR (in CH₂Cl₂, under an atmosphere of CO) was recorded. No changes in the IR spectrum were observed.

4.4 Results

(i) Synthesis

In non-polar solvents, such as petroleum ether or diethylether, the thioether ligands **2-4** will displace the COE of [IrCl(COE)₂]₂ or the COD of [RhCl(COD)]₂ but will not break up the dimer to form a neutral mononuclear chloride complex as will reaction with three equivalents of PPh₃ or the analogous phosphine ligand ttp. It is hence necessary to synthesize cationic rhodium and iridium complexes by using AgBF₄ to strip the starting material of the bridging chlorides and allow complexation of the thioether to the metal. The inability of such thioether ligands to break up the chloride bridged dimers of these common starting materials is probably related to the lower *trans* effect of thioethers as compared to phosphines.

The yellow-orange complex [Ir(DMTT)(COE)₂][BF₄], **13**, was synthesized in a manner analogous to the platinum halide complexes, **5-9**. The IR, both solid state and solution, of this complex shows the characteristic *iso*-propyl bands at 1370 and 1390 cm⁻¹ as well as the broad peak of the [BF₄]⁻ anion at 1000 cm⁻¹. The fact that the iridium retains both COE groups is related to the low *trans* influence and higher σ -basicity of thioethers as compared to phosphines. There is a higher electron density remaining on the iridium, resulting in an increased amount of π -backbonding to the

COE groups and hence stronger bonds to the metal.

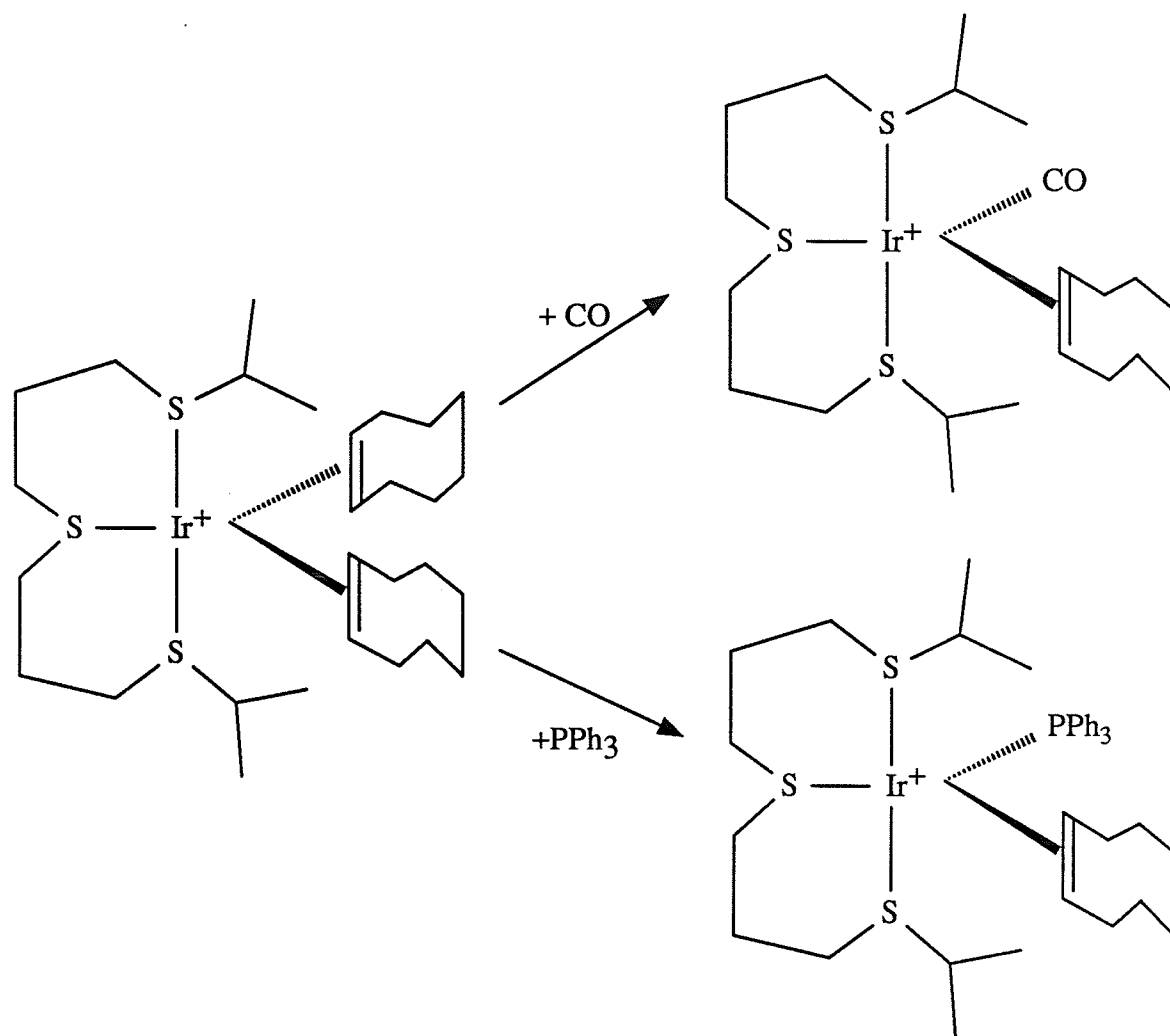


Figure 4.1 Reaction Scheme for $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$.

The reaction of $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$, **13**, with excesses of both CO and PPh_3 results in the displacement of only one of the COE groups (see Figure 4.1). The stability of rhodium and iridium bonds to alkenes in thioether complexes is well documented.^{71,72} The high ν_{CO} in $[\text{Ir}(\text{DMTT})(\text{COE})(\text{CO})][\text{BF}_4]$, **16**, (2044 cm^{-1} in CH_2Cl_2) is a result of the five coordinate and cationic nature of this compound. The carbonyl and COE are both competing for the electron density on the iridium,

resulting in a lower amount of π -backbonding to the CO as compared to compounds such as $[\text{Ir}(\text{CO})(\text{PMePh}_2)_3][\text{BF}_4]$, which has νCO of 2000 cm^{-1} .⁹⁷

The reaction of DPTN, $[\text{RhCl}(\text{COD})]_2$ and AgBF_4 in acetone results in the complex $[\text{Rh}(\text{DPTN})(\text{COD})][\text{BF}_4]$, **17**, in relatively high yield. In this complex, the η^4 -COD is inert to substitution by CO and PMe_2Ph . This is not surprising in light of the known stability of rhodium and iridium-alkene bonds in thioether complexes such as $[\text{Rh}_2(2\text{OS6})(\text{COD})_2][\text{BF}_4]_2$ and $[\text{Ir}\{\text{S}(\text{CH}_2\text{CH}_2\text{SPh})_2\}(\text{COD})][\text{BF}_4]$.^{71,72} The compound **18** is also inert to oxidative-addition reactions with H_2 and HCl . The rhodium and iridium chloride bridged alkene dimers, $[\text{RhCl}(\text{COD})]_2$ and $[\text{IrCl}(\text{COE})_2]_2$, are normally considered the starting materials of choice in the preparation of phosphine complexes, however, the organic groups appear to have insufficient lability in rhodium and iridium thioether complexes to be considered as useful.

The complex $[\text{Rh}(\text{DMTT})\text{CO}][\text{BF}_4]$, **18**, was synthesized in a manner analogous to the platinum halide complexes **5-8**. The solution state IR (in CH_2Cl_2) of this complex shows a single strong νCO band at 2021 cm^{-1} . This is indicative of a four coordinate monocarbonyl complex; if both carbonyl groups were retained, two peaks would be expected with an intensity ratio closely related to the OC-Rh-CO angle.⁶⁴ The νCO peak of 2021 cm^{-1} can be compared to those observed for similar rhodium-phosphine complexes (see Table 4.1).

It can be seen that νCO for **18** falls approximately midway between the values for tris(triarylphosphine) substitution and tris(alkyldiarylphosphine) rhodium substitution, and has very nearly the same value as a tris(triarylphosphine) iridium complex. The reaction of DMTT (**4**) with $[\text{RhCl}(\text{CO})_2]_2$ gives a square-planar complex. The lower νCO frequency corresponds to the higher Lewis basicity (poorer π -acceptor ability) of thioether ligands as compared to phosphine ligands. $[\text{Rh}(\text{DMTT})(\text{CO})]^+$ will not, under an atmosphere of CO, add a second CO group.

$[\text{Rh}(\text{ttp})(\text{CO})]^+$ will add a second CO group, and the resulting dicarbonyl complex is stable under an atmosphere of CO, while the analogous iridium complex, $[\text{Ir}(\text{ttp})(\text{CO})]^+$ is not known, this complex only being stable as the dicarbonyl species $[\text{Ir}(\text{ttp})(\text{CO})_2]^+$.^{61,101}

Complex	ν_{CO}
$[\text{Rh}(\text{PPh}_3)_3\text{CO}]^+$	2029 cm^{-1}
$[\text{Rh}(\text{ttp})\text{CO}]^+$	2026 cm^{-1}
$[\text{Rh}(\text{PMePh}_2)_3\text{CO}]^+$	2015 cm^{-1}
$[\text{Ir}(\text{PPh}_3)_3\text{CO}]^+$	2020 cm^{-1}
$[\text{Rh}(\text{DMTT})(\text{CO})]^+$	2021 cm^{-1}

Table 4.1 ν_{CO} for Some Rhodium(I) and Iridium(I) Phosphine Complexes.^{61,97,100}

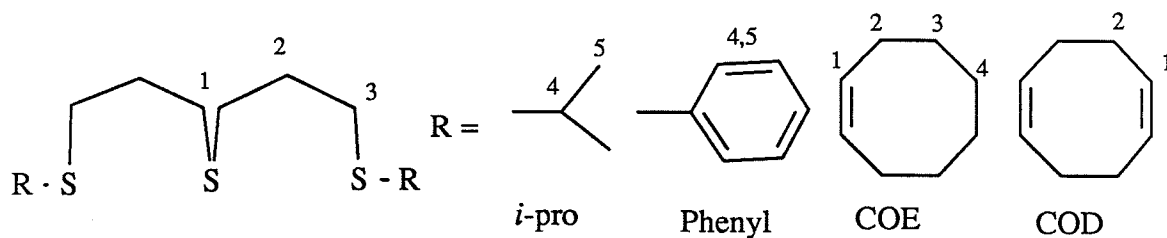
(ii) NMR

The $^{13}\text{C}\{^1\text{H}\}$ NMR of $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$, **13**, at 230K in CD_3CN shows 10 peaks (Figure 4.2), the number expected for such a compound. There is evidence of only one isomer, present in solution, of the expected three. As the line widths of the peaks are still quite large, even at 230K, it is quite possible that the lower limiting spectrum has not yet been reached. It can be seen from the variable temperature analysis of $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$, **8**, that even 15-20° above the limiting temperature only one isomer appears to be present. Solubility limitations prevented spectra for **13** from being accumulated at temperatures lower than 230K.

Table 4.2 $^{13}\text{C}\{^1\text{H}\}$ NMR Data for Rhodium and Iridium Complexes, δ (ppm).

Compound	C1	C2	C3	C4	C5
[Rh(DPTN)(COD)]^{+a}					
DPTN	34.06	25.29	31.94	-	-
COD	90.86 ^f	30.49			
[Rh(DMTT)(CO)]^{+b}					
DMTT	34.19	24.71	28.64	42.26	23.24, 22.24
CO	183.89 ^g				
[Ir(DMTT)(COE)₂]^{+c}					
DMTT:	34.46	25.87	32.97	37.78	21.18, 19.71
COE:	67.87	24.54	23.31	23.21	-
[Ir(DMTT)(COE)(CO)]^{+d}					
DMTT:	35.34	29.78	33.44	38.45	21.64, 20.19
COE:	-	25.33	23.70	23.70	-
[Ir(DMTT)(PPh₃)(COE)]^{+e}					
[Ir(DMTT)(dppe)]^{+e}					

^aat 300 K. ^bat 235 K. ^cat 240 K. ^dat 297 K. ^edue to fluxional processes of ligand, well resolved spectra could not be obtained. ^fbroad, unresolved doublet. ^gdoublet, $^1J_{\text{Rh,C}} = 73$ Hz.



The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{Ir}(\text{DMTT})(\text{COE})(\text{CO})]^+$ (**16**) shows six resonances for the ligand DMTT, as well as two resonances for the COE. The peak at $\delta = 23.70$ ppm appears, from peak intensities, to be an accidental overlap of carbons C3 and C4 of the COE ligand. Neither the olefinic carbon nor the carbonyl carbon are observed in this spectrum. These resonances indicate the presence of only a single configurational isomer, however, the broad peaks in the spectrum indicate that the low temperature limit has not yet been reached for this compound. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of both $[\text{Ir}(\text{DMTT})(\text{COE})(\text{PPh}_3)]^+$ (**14**) and $[\text{Ir}(\text{DMTT})(\text{dppe})]^+$ (**15**) show, at all temperatures from 235 to 340 K, only broad peaks. Well resolved spectra were not obtained for either of these compounds. Solubility limitations precluded study outside this range.

All of the iridium thioether complexes, **13-16**, and the rhodium complexes, **17** and **18**, have ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra which exhibit the same type of fluxionality as the platinum and palladium complexes, **5-12**, already discussed. At 25°C , the spectra show broad peaks which begin to narrow as the temperature of the sample is lowered.

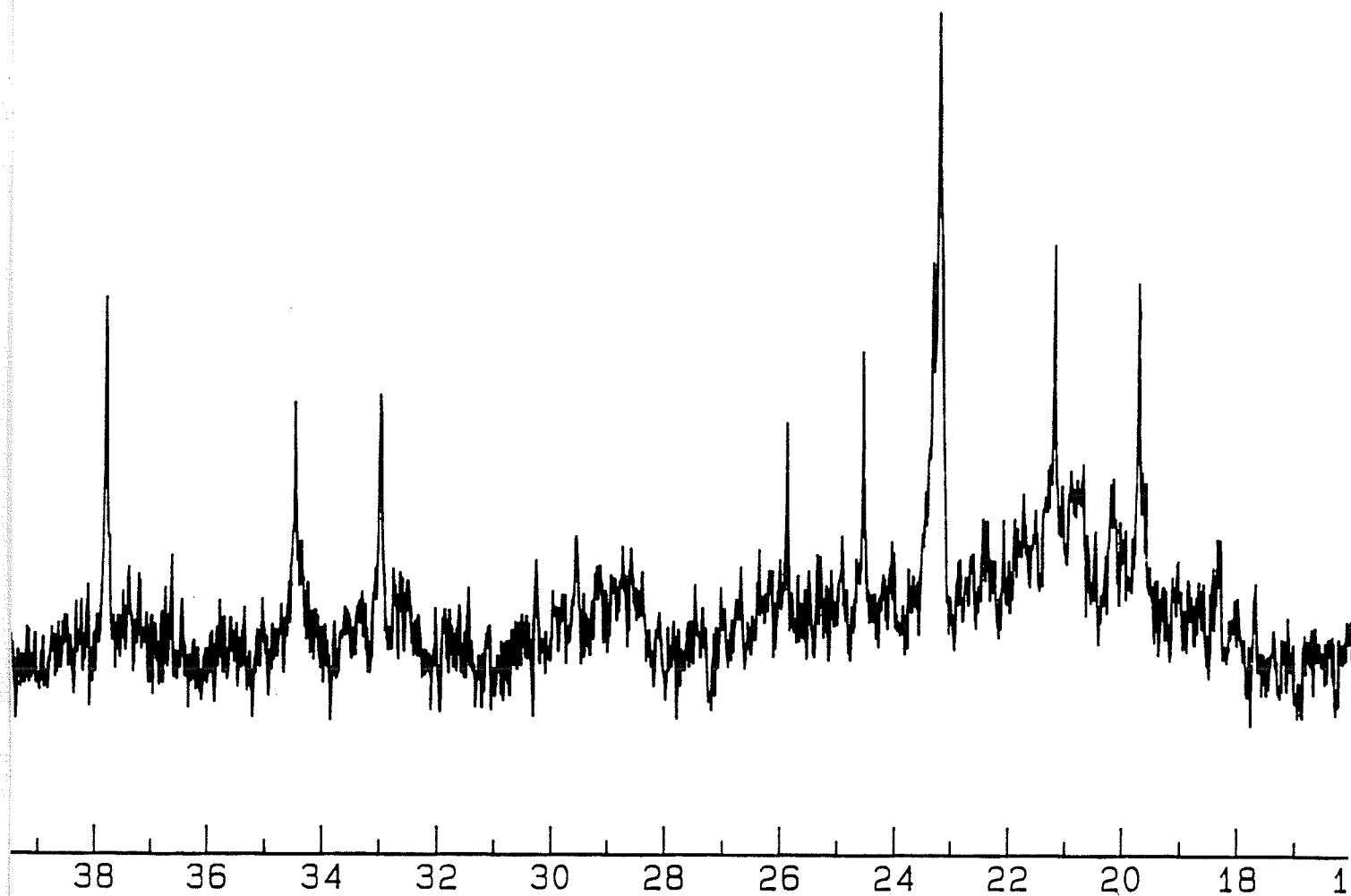


Figure 4.2 $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{Ir}(\text{DMTT})(\text{COE})_2]^+$ at 230 K.

Figure 4.2 $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{Ir}(\text{DMTT})(\text{COE})_2]^+$ at 230 K (ppm).

The complex $[\text{Rh}(\text{DMTT})(\text{CO})][\text{BF}_4]$, **18**, shows, at room temperature, a $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum consistent with a square-planar complex (Figure 4.4). At 230K five broad peaks in the alkyl region are seen as well as a doublet at 183.9 ppm due to the carbonyl group with $^1J_{\text{Rh,C}} = 73$ Hz. The magnitude of the coupling and the chemical shift seen for the carbonyl carbon is similar to other four coordinate rhodium(I) carbonyl cations, *viz.* $\delta = 181.3$ and 185.6 ppm, and $^1J_{\text{Rh,C}} = 73$ and 67 Hz for $\text{RhCl}(\text{py})(\text{CO})_2$.⁹⁸ At approximately 340K the process appears to reach coalescence; the carbonyl doublet is no longer visible and most other peaks nearly disappear into the baseline. The temperature dependence of the line shapes of the spectra for **18**, which were recorded for 235, 270, 300 and 340 K, closely match those seen in $[\text{PtCl}(\text{DMTT})][\text{BF}_4]$, **8**.

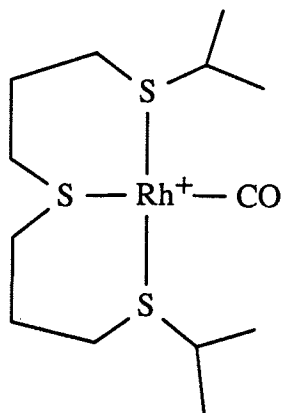


Figure 4.3 $[\text{Rh}(\text{DMTT})(\text{CO})]^+$ (**18**) Cation.

The five coordinate compound $[\text{Rh}(\text{DPTN})(\text{COD})]^+$ (**17**) showed, in its $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 30°C , seven peaks due to the ligand DPTN and two peaks due to the COD ligand. The olefinic COD peak, at $\delta = 90.86$ ppm, was a broad,

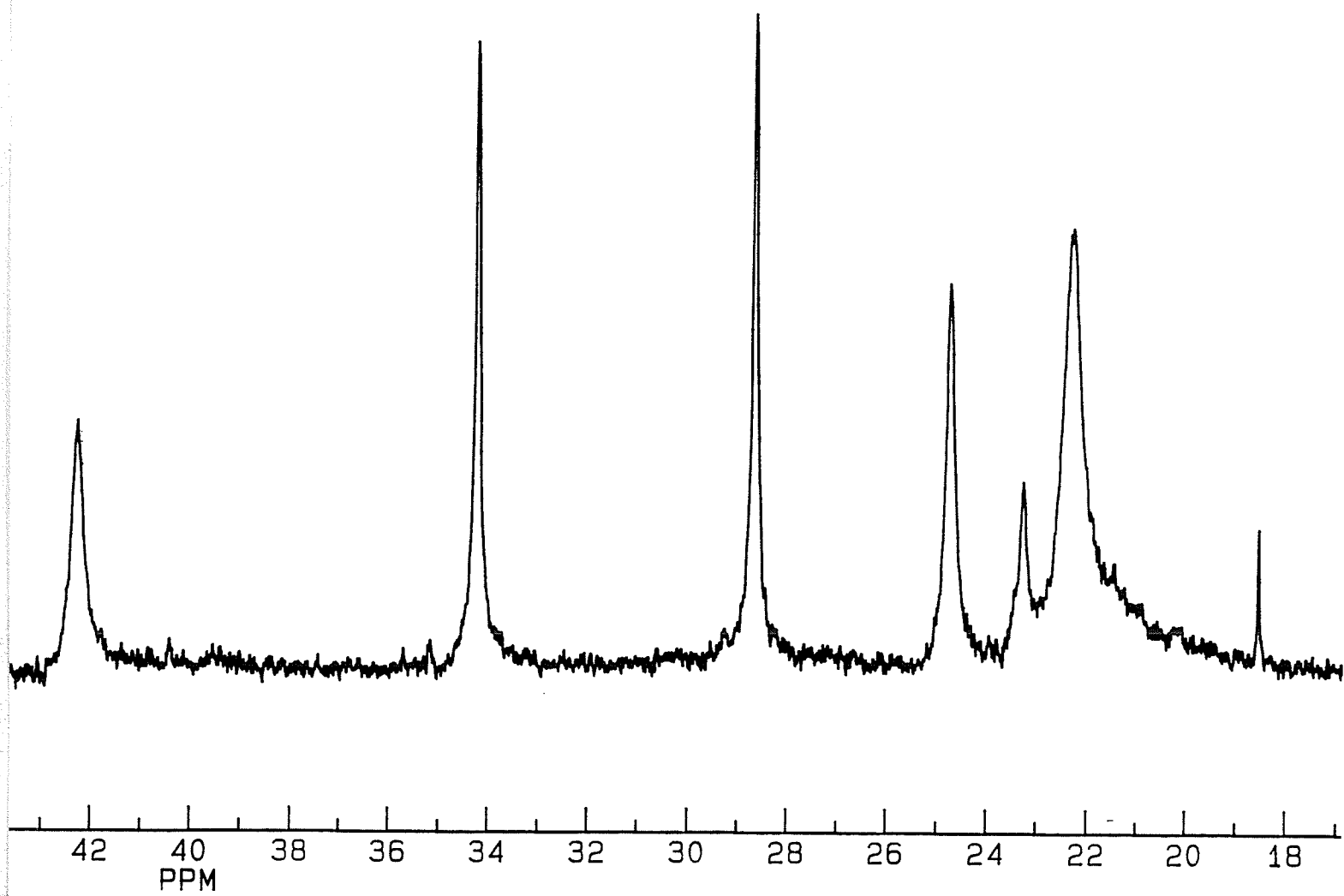


Figure 4.4 $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of $[\text{Rh}(\text{DMTT})(\text{CO})]^+$ at 230 K.

unresolved doublet typical of rhodium-COD compounds. As very little conformational information was available through $^{13}\text{C}\{^1\text{H}\}$ NMR, compared to $^{31}\text{P}\{^1\text{H}\}$ NMR, it was not possible to determine whether **17** is square-pyramidal or trigonal bipyramidal, or the configuration of the DPTN ligand within these geometries. The inertness of **17** to oxidative addition of H_2 and HCl shows the stability of this five coordinate, eighteen electron complex. If there were ligand dissociation processes occurring, exchanging between five and four coordinate species through dissociation of a sulfur group, one would expect a relatively facile oxidative addition process.

4.5 Summary and Conclusions

The tridentate thioether ligand DMTT forms five coordinate complexes of the formula $[\text{Ir}(\text{DMTT})(\text{COE})_2][\text{BF}_4]$ upon reaction with $[\text{IrCl}(\text{COE})_2]_2$ and AgBF_4 . One of the two COE ligands can be replaced with either CO or PPh_3 . The ligand DPTN forms a five coordinate complex, $[\text{Rh}(\text{DPTN})(\text{COD})][\text{BF}_4]$ upon reaction with $[\text{RhCl}(\text{COD})]_2$ and AgBF_4 . Both five coordinate iridium and rhodium complexes are inert to oxidative addition of common oxidants, and $[\text{Rh}(\text{DPTN})(\text{COD})][\text{BF}_4]$ is inert to substitution of the η^4 -COD ligand. The ligand DMTT will form a four coordinate square-planar complex, $[\text{Rh}(\text{DMTT})(\text{CO})][\text{BF}_4]$, upon reaction with $[\text{RhCl}(\text{CO})_2]_2$ and AgBF_4 . Although no crystals suitable for X-ray studies were grown, we believe that these complexes were synthesized as shown. Further studies on the four coordinate $[\text{Rh}(\text{DMTT})(\text{CO})][\text{BF}_4]$ are required to determine if the tris(thioether) coordination, by analogy to rhodium-phosphine complexes, has any effect on the reactivity and catalytic properties of the rhodium.

APPENDIX

Table A1. Positional Parameters^a for [PtI(DPTN)][BF₄].

Atom	x	y	z
Pt	-738(0)	1123(0)	559(0)
I	1284(1)	1289(1)	990(1)
S1	-354(3)	-141(3)	1792(3)
S2	-2493(3)	1215(3)	333(4)
S3	-805(3)	2349(3)	-659(3)
C1	-1418(16)	-924(14)	1817(16)
C2	-2470(18)	-405(17)	1706(17)
C3	-3014(14)	-16(15)	693(16)
C4	-3187(14)	1155(14)	-944(15)
C5	-2999(13)	2119(16)	1553(15)
C6	-1913(11)	2092(16)	-1731(11)
C11	-90(8)	548(8)	2929(8)
C12	694(8)	133(8)	3725(8)
C13	925(8)	641(8)	4636(8)
C14	372(8)	1562(8)	4751(8)
C15	-412(8)	1977(8)	3955(8)
C16	-643(8)	1469(8)	3044(8)
C21	-1156(10)	3593(8)	-284(8)
C22	-1100(10)	3781(8)	692(7)
C23	-1258(10)	4822(8)	998(7)

C24	-1470(10)	5676(8)	329(7)
C25	-1526(10)	5488(8)	-646(7)
C26	-1368(10)	4447(8)	-953(7)
B	4886(35)	1536(23)	1715(24)
F1	5946(14)	1753(16)	2133(14)
F2	4833(18)	1277(17)	742(14)
F3	4365(28)	861(22)	2058(16)
F4	4338(27)	2306(30)	1689(29)

^aMultiplied by 10^4

Table A2. Hydrogen Atom Parameters^a for [PtI(DPTN)][BF₄].

Atom	x	y	z	U ^b
H1A	-1224	-1291	2429	104
H1B	-1522	-1436	1302	104
H2A	-2368	195	2140	117
H2B	-2905	-924	1882	117
H3A	-2972	-571	248	74
H3B	-3726	111	647	74
H4A	-3913	1125	-1012	52
H4B	-2983	513	-1202	52
H5A	-3523	2110	-2170	54
H5B	-3052	2770	-1217	54

H6A	-1824	1395	-1977	53
H6B	-1911	2625	-2209	53
H12	1070	-494	3646	69
H13	1459	359	5177	82
H14	530	1908	5371	98
H15	-788	2604	4033	84
H16	-1177	1751	2502	81
H22	-1955	3200	1147	76
H23	-1220	4950	1662	91
H24	-1577	6385	537	97
H25	-1671	6070	-1102	111
H26	-1406	4319	-1617	83

^a Multiplied by 10⁴. ^b Multiplied by 10³.

Table A3. Thermal Parameters^a for [PtI(DPTN)][BF₄].

Atom	U11	U22	U33	U23	U13	U12
Pt	461(4)	460(4)	476(4)	-53(3)	131(3)	4(3)
I	653(8)	735(8)	786(9)	-73(7)	155(7)	2(6)
S1	701(28)	485(23)	611(26)	26(20)	232(22)	77(21)
S2	494(24)	609(27)	817(32)	-99(24)	230(23)	28(20)
S3	535(25)	628(25)	501(24)	30(21)	147(20)	91(20)
C1	946(157)	524(104)	868(143)	25(101)	204(118)	10(102)
C2	1064(172)	697(133)	1119(183)	-53(127)	570(150)	-222(125)

C3	675(122)	597(114)	1254(187)	-59(122)	381(126)	-197(97)
C4	475(100)	707(123)	882(140)	-103(107)	14(95)	-12(88)
C5	493(104)	842(136)	987(152)	-102(121)	94(103)	176(97)
C6	478(96)	948(134)	387(90)	-110(90)	-76(75)	163(93)
B	1812(370)	487(145)	910(223)	-93(145)	43(226)	-169(193)
F1	1362(141)	1612(160)	1667(164)	-589(132)	78(122)	-344(122)
F2	2006(191)	2251(232)	1279(152)	-674(136)	486(129)	-987(160)
F3	4747(455)	2358(254)	1305(168)	370(165)	-54(210)	-2469(294)
F4	3531(403)	2930(367)	4160(493)	-8(343)	2375(378)	1465(329)
C11	617(44)					
C12	624(45)					
C13	744(52)					
C14	893(62)					
C15	766(53)					
C16	740(52)					
C21	565(41)					
C22	693(50)					
C23	825(56)					
C24	887(61)					
C25	1012(72)					
C26	749(52)					

^a Multiplied by 10⁴.

Table A4. Positional Parameters^a for [PtCl(DMTT)][BF₄].

Atom	x	y	z
Pt	2538(0)	1970(0)	9190(0)
Cl	2429(4)	846(2)	-2063(2)
S1	1407(4)	2975(2)	-2048(3)
S2	2570(4)	2922(2)	511(3)
S3	3862(3)	900(2)	253(2)
C1	662(31)	3919(19)	-1549(25)
C2	1477(24)	4425(13)	-710(17)
C3	2027(35)	4086(12)	122(14)
C4	4298(18)	3186(13)	1115(15)
C5	5009(15)	2263(13)	1673(13)
C6	5253(12)	1563(11)	987(11)
C11	-18(16)	2397(12)	-2843(13)
C12	-975(18)	1941(11)	-2344(14)
C13	-835(21)	3089(12)	-3614(15)
C31	2950(13)	523(8)	1162(10)
C32	1737(14)	5(10)	601(12)
C33	3928(15)	-137(9)	1969(10)
B	-3073(75)	1586(20)	-5657(22)
F1	-3379(16)	2517(7)	5858(8)
F2	-3046(14)	1372(9)	-4747(10)
F3	-2728(20)	1141(11)	-6344(15)

F4 -4649(19) 1198(18) -6001(12)

^aMultiplied by 10⁴

Table A5. Hydrogen Atom Parameters^a for [PtCl(DMTT)][BF₄].

Atom	x	y	z	U ^b
H1A	-79	3674	-1343	283
H1B	363	4361	-2077	283
H2A	912	4903	-569	160
H2B	2166	4704	-953	160
H3A	2815	4450	325	397
H3B	1444	4240	531	397
H4A	4334	3675	1594	108
H4B	4734	3386	620	108
H5A	4474	1998	2070	51
H5B	5838	2452	2097	51
H6A	5663	1867	526	45
H6B	5851	1119	1375	45
H11	369	1901	-3138	80
H12A	-507	1506	-1807	86
H12B	-1639	1617	-2829	86
H12C	-1380	2407	-2021	86
H13A	-258	3395	-3952	102
H13B	-1241	3545	-3282	102

H13C	-1500	2756	-4090	102
H31	2676	1038	1505	68
H32A	1186	418	132	73
H32B	1264	-218	1064	73
H32C	1990	-514	253	73
H33A	4684	216	2307	97
H33B	4201	-658	1634	97
H33C	3475	-361	2445	97

^a Multiplied by 10⁴. ^b Multiplied by 10³.

Table A6. Thermal Parameters^a for [PtCl(DMTT)][BF₄].

Atom	U11	U22	U33	U23	U13	U12
Pt	393(4)	339(4)	370(4)	-11(2)	156(3)	55(2)
Cl	906(28)	551(20)	434(17)	-148(17)	90(17)	179(18)
S1	591(26)	463(20)	738(26)	196(16)	27(21)	-75(15)
S2	725(26)	527(20)	490(19)	-96(15)	238(19)	77(16)
S3	382(18)	486(17)	438(16)	-8(14)	116(14)	102(14)
C1	2125(355)	1608(247)	3123(434)	-1409(285)	-1395(328)	1412(247)
C2	1352(211)	624(112)	1503(207)	-80(127)	-458(159)	266(122)
C3	3591(430)	565(112)	662(120)	-40(97)	-262(179)	1020(180)
C4	852(139)	1097(146)	1059(153)	-563(119)	335(117)	-680(116)
C5	479(102)	984(121)	886(123)	-187(106)	-107(91)	-426(97)

C6	296(76)	890(106)	591(85)	107(82)	22(66)	-6(73)
C11	699(108)	721(96)	856(114)	232(92)	135(96)	-6(89)
C12	601(117)	983(114)	905(128)	300(93)	-41(100)	-219(85)
C13	807(155)	1201(170)	1048(157)	507(118)	-362(126)	-15(104)
C31	630(88)	385(66)	580(77)	90(62)	295(72)	-29(64)
C32	548(100)	552(87)	924(113)	57(81)	-45(83)	-125(75)
C33	788(107)	607(85)	635(91)	240(72)	148(81)	106(80)
B	6636(998)	567(162)	988(216)	-505(154)	1812(433)	-1395(356)
F1	2306(151)	645(70)	958(78)	87(57)	316(85)	291(83)
F2	1913(129)	1047(88)	1116(86)	206(74)	236(93)	190(88)
F3	3025(226)	999(96)	2606(200)	114(121)	2003(182)	426(120)
F4	2257(186)	2984(239)	1450(131)	-391(149)	808(132)	-1104(183)

^a Multiplied by 10⁴.

Table A7. Positional Parameters^a for [Pt(DMTT)(PPh₃)] [BF₄]₂.

Atom	x	y	z
Pt	3395(0)	2798(0)	2060(0)
P	1940(2)	3547(2)	3180(2)
S1	4173(2)	2600(2)	3452(2)
S2	4946(2)	1921(3)	1130(2)
S3	2544(2)	3089(2)	743(2)
C1	5294(7)	3489(9)	3496(8)
C2	6135(8)	3051(11)	2633(9)

C3	5836(9)	3060(10)	1592(9)
C4	5023	1808	-162
C5	4448	2792	-484
C5d	4112	1562	-761
C6	3306	2634	-481
C11	4705(8)	988(9)	3234(8)
C12	3865(10)	161(11)	3089(11)
C13	5279(11)	907(13)	4121(11)
C21	2260(9)	4790(10)	959(9)
C22	3184(11)	5471(13)	793(11)
C23	1428(12)	4983(16)	287(12)
C31	2092(4)	5089(5)	3983(5)
C32	1448(4)	5604(5)	4865(5)
C33	1539(4)	6808(5)	5439(5)
C34	2274(4)	7496(5)	5131(5)
C35	2918(4)	6981(5)	4249(5)
C36	2827(4)	5777(5)	3675(5)
C41	750(4)	3689(4)	2615(5)
C42	488(4)	2649(4)	1909(5)
C43	-423(4)	2687(4)	1501(5)
C44	-1089(4)	3763(4)	1789(5)
C45	-827(4)	4803(4)	2505(5)
C46	93(4)	4765(4)	2913(5)
C51	1685(5)	2581(5)	4035(5)
C52	2067(5)	2854(5)	4962(5)
C53	1915(5)	2088(5)	5581(5)
C54	1380(5)	1049(5)	5273(5)

C55	998(5)	776(5)	4346(5)
C56	1150(5)	1542(5)	3726(5)
B1	5877(10)	6546(12)	2891(12)
F1	5101(8)	6088(11)	2410(10)
F2	5903(8)	7794(7)	3013(8)
F3	5840(12)	6302(11)	3804(8)
F4	6743(7)	5933(10)	2324(9)
B2	2214(12)	9474(13)	448(12)
F5	2307(8)	8229(9)	173(8)
F6	1330(9)	9926(11)	223(9)
F7	3012(12)	9941(16)	86(14)
F8	2197(16)	9981(18)	1465(12)
Cl1	8373(11)	9984(13)	2389(12)
Cl2	9564(14)	7772(12)	1784(13)
Csol	9334	9134	1584

^aMultiplied by 10⁴

Table A8. Hydrogen Atom Parameters^a for [Pt(DMTT)(PPh₃)] [BF₄]₂.

Atom	x	y	z	U ^b
H1A	5062	4311	3527	

H1B	5062	4311	3527
H2A	6670	3571	2779
H2B	6370	2229	2579
H3A	5530	3857	1635
H3B	6433	2885	1131
H4A	4334	3267	1014
H4B	5808	910	-481
H4Ad	4545	3224	292
H4Bd	5769	924	-0493
H5A	3970	3426	-58
H5B	4704	3120	-1038
H5Ad	3824	870	-622
H5Bd	4329	1373	-1457
H6A	2658	1885	-767
H6B	2014	4104	830
H6Ad	2827	2056	-792
H6Bd	2134	4005	1791
H11	5172	731	2645
H12A	3531	241	2533
H12B	3392	384	3675
H12C	4135	-670	2968
H13A	5805	1447	4186
H13B	5565	84	4011
H13C	4822	1138	4718
H21	2469	5020	1613
H22A	3046	6322	114
H22B	3333	5382	98

H22C	3750	5136	1035
H23A	1428	5791	211
H23B	782	4881	592
H23C	1564	4393	-352
H32	984	5135	5075
H33	1100	7159	6039
H34	2336	8316	5522
H35	3419	7450	4039
H36	3266	5426	3074
H42	935	1916	1706
H43	-611	1979	1020
H44	-1716	3789	1520
H45	-1274	5536	2707
H46	272	5473	3394
H52	2432	3562	5172
H53	2176	2275	6213
H54	1277	527	5695
H55	633	68	4136
H56	889	1355	3094

^a Multiplied by 10^4 . ^b Multiplied by 10^3 .

Table A9. Thermal Parameters^a for [Pt(DMTT)(PPh₃)]₂[BF₄]₂.

Atom	U11	U22	U33	U23	U13	U12
Pt	385(3)	400(3)	400(3)	100(2)	-11(2)	-49(2)
P	391(12)	453(13)	367(12)	110(10)	-7(10)	-62(10)
S1	430(13)	502(13)	428(13)	115(11)	-62(10)	-49(11)
S2	458(14)	699(17)	493(15)	89(13)	48(11)	33(12)
S3	481(14)	640(16)	406(13)	185(12)	-28(11)	-57(12)
C1	537(58)	459(52)	626(64)	158(47)	-172(50)	-193(45)
C2	531(62)	716(70)	715(74)	208(58)	-82(55)	-236(53)
C3	608(67)	583(64)	787(79)	197(57)	40(58)	-171(53)
C4	948(42)					
C5	550(49)					
C5d	1145(105)					
C6	805(35)					
C11	659(66)	473(56)	498(59)	70(47)	-85(51)	29(48)
C12	674(77)	620(72)	1134(112)	172(73)	-204(75)	-112(60)
C13	989(101)	804(85)	889(97)	428(77)	-279(81)	-4(74)
C21	747(73)	535(61)	665(71)	232(54)	-236(59)	-75(54)
C22	1018(104)	887(91)	821(93)	351(77)	-87(80)	-220(81)
C23	1017(116)	1207(124)	1019(116)	514(101)	-250(95)	126(97)
C31	418(20)					
C32	609(27)					
C33	664(29)					
C34	751(33)					

C35	709(31)					
C36	512(23)					
C41	445(21)					
C42	531(24)					
C43	693(30)					
C44	758(33)					
C45	655(29)					
C46	577(26)					
C51	448(23)					
C52	546(24)					
C53	712(31)					
C54	806(35)					
C55	829(36)					
C56	619(27)					
B1	607(83)	545(75)	831(99)	98(67)	-82(74)	-45(62)
F1	970(67)	1477(87)	1836(112)	151(78)	-597(73)	-191(63)
F2	1692(90)	712(50)	1196(71)	254(47)	-342(66)	-68(53)
F3	2683(156)	1461(89)	813(69)	459(64)	-348(80)	-730(98)
F4	882(60)	1432(81)	1535(92)	607(70)	132(61)	60(57)
B2	963(50)					
F5	1263(51)					
F6	1509(41)					
F7	2461(80)					
F8	2644(92)					
Cl1	2773(69)					

Cl2 3161(87)

Csol 1657(120)

^a Multiplied by 10^4 .

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