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REACTIONS OF RUTHENIUM AND PLATINUM THIOLATES AND THE DEVELOPMENT OF NOVEL HOMOGENEOUS CATALYSTS OF CLAUS CHEMISTRY

by

Mohammad El-khateeb

A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for
the degree of Doctor of Philosophy.

Department of Chemistry
McGill University
Montreal, Quebec
Canada

February 1996

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REACTIONS OF RUTHENIUM AND PLATINUM THIOLATES AND THE DEVELOPMENT OF NOVEL HOMOGENEOUS CATALYSTS OF CLAUS CHEMISTRY

Ph.D. Mohammad El-khateeb Chemistry

Abstract

The complexes $CpRu(PPh_3)(L)SR$ ($Cp= \eta^5$-cyclopentadienyl; $R= CMe_3, CHMe_2$, 4-C_6H_4Me) reacted with $NOBF_4$ to give either $[CpRu(PPh_3)(NO)SR]BF_4$ ($L= PPh_3$) or complexes containing disulfide ligands (L= CO). The bisphosphine complexes, $CpRu(PPh_3)_2SR$, reacted with HBF_4 to give the corresponding thiol complex salts $[CpRu(PPh_3)_2(HSR)]BF_4$ and with $[MeSSMe_2]BF_4$ to give $[CpRu(PPh_3)_2(SMe_2)]BF_4$ regardless of the starting thiolates. The complexes $CpRu(PPh_3)_2SR$ reacted with the sulfur transfer agent MeSphth (phth= phthalimido) to give $CpRu(PPh_3)_2(phth)$ and the dimers (μ-SMe)(μ-SR)$[CpRu(phth)]_2$ for $R= CMe_3$ or $CHMe_2$, while for R= 4-C_6H_4Me the same reaction gave $CpRu(PPh_3)(phth)(MeSS\text{-}4\text{-}C_6H_4Me)$ and (μ-SMe)(μ-S-4-C_6H_4Me)$[CpRu(S\text{-}4\text{-}C_6H_4Me)]_2$. The complex $CpRu(PPh_3)_2SCH_2CH{=}CH_2$, prepared from the reaction of $CpRu(PPh_3)_2Cl$ and $LiSCH_2CH{=}CH_2$, reacted with CO and CS_2 to give $CpRu(PPh_3)(CO)SCH_2CH{=}CH_2$ and $CpRu(PPh_3)S_2CSCH_2CH{=}CH_2$, respectively. Refluxing a toluene solution of $CpRu(PPh_3)_2SCH_2CH{=}CH_2$ gave $(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH{=}CH_2)[CpRu]_3$ in which the C-S bond has been cleaved.

The complexes $(PPh_3)_2Pt(SR)_2$ ($R= H, CMe_3, CHMe_2$, 4-C_6H_4Me) were treated with SO_2 as models for the Claus process. These reactions produced adducts of formula $(PPh_3)_2Pt(S(SO_2)R)_2$, which have a labile thiolate-bound SO_2 molecule, for $R= CMe_3$, 4-C_6H_4Me and $CHMe_2$. The reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 gave $(PPh_3)_2Pt(S_3O)$ and H_2O, a reaction which mimics Claus chemistry. The complexes *cis*-$(PPh_3)_2Pt(SH)_2$,

$(PPh_3)_2Pt(S_3O)$ and $(PPh_3)_2Pt(SR)_2$ catalyze the Claus reaction ($2H_2S + SO_2 \longrightarrow 3/8S_8 + 2H_2O$).

The complexes $(PPh_3)_2Pt(SR)_2$ reacted with CS_2 to form the mixed thiolato-thioxanthato complexes $(PPh_3)Pt(SR)(S_2CSR)$ wherein CS_2 had inserted into one of the Pt-S bonds. The complex *cis*-$(PPh_3)_2Pt(SH)_2$ reacted with CS_2 to give the known complex, $(PPh_3)_2Pt(S_2CS)$, which contains a trithiocarbonate group.

The structures of $[CpRu(PPh_3)(NO)SCMe_3]BF_4$, $(\mu\text{-}SMe)(\mu\text{-}S\text{-}4\text{-}C_6H_4Me)[CpRu(S\text{-}4\text{-}C_6H_4Me)]_2$, $(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH{=}CH_2)[CpRu]_3$, $(PPh_3)_2Pt(S_3O)$ and $(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$ were determined by x-ray crystallography.

REACTIVITE DE COMPLEXES THIOLATE DU RUTHENIUM ET DU PLATINE. DEVELOPPEMENT DE NOUVEAUX CATALYSEURS HOMOGENES DE LA CHIMIE CLAUS

Ph.D. Mohammad El-Khateeb Chimie

RÉSUMÉ

Les complexes $CpRu(PPh_3)(L)SR$ ($Cp = \eta^5$-cyclopentadienyle; $R = CMe_3$, $CHMe_2$, $4\text{-}C_6H_4Me$) réagissent avec $NOBF_4$ pour donner $[CpRu(PPh_3)(NO)SR]BF_4$ dans le cas où $L = PPh_3$ et des complexes contenant des ligands disulfure dans le cas où $L = CO$. Les complexes bisphosphine $CpRu(PPh_3)_2SR$ réagissent avec HBF_4 pour donner les complexes thiols correspondants $[CpRu(PPh_3)_2(HSR)]BF_4$ et avec $[MeSSMe_2]BF_4$ pour donner $[CpRu(PPh_3)_2(SMe_2)]BF_4$, complexe ne contenant plus les ligands thiolate SR. Les complexes $CpRu(PPh_3)_2SR$ réagissent avec l'agent soufré MeSphth (phth= phthalimido) pour donner $CpRu(PPh_3)_2(phth)$ et les dimères $(\mu\text{-SMe})(\mu\text{-SR})[CpRu(phth)]_2$ pour $R = CMe_3$, $CHMe_2$ tandis que pour $R = 4\text{-}C_6H_4Me$, la même réaction conduit à la formation de $CpRu(PPh_3)(phth)(MeSS\text{-}4\text{-}C_6H_4Me)$ et $(\mu\text{-SMe})(\mu\text{-S-}4\text{-}C_6H_4Me)[CpRu(S\text{-}4\text{-}C_6H_4Me)]_2$. Le complexe $CpRu(PPh_3)_2SCH_2CH{=}CH_2$, préparé à partir de la réaction de $CpRu(PPh_3)_2Cl$ avec $LiSCH_2CH{=}CH_2$, réagit avec CO et CS_2 pour donner $CpRu(PPh_3)(CO)SCH_2CH{=}CH_2$ et $CpRu(PPh_3)S_2CSCH_2CH{=}CH_2$ respectivement. Une solution de $CpRu(PPh_3)_2SCH_2CH{=}CH_2$ portée a reflux donne $(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH{=}CH_2)[CpRu]_3$ dans lequel une liaison C-S est rompue.

Les complexes $(PPh_3)_2Pt(SR)_2$ ($R = H$, CMe_3, $CHMe_2$, $4\text{-}C_6H_4Me$) sont traités avec SO_2 dans le but de modéliser le procédé Claus. Ces réactions produisent des composés du type $(PPh_3)_2Pt(S(SO_2)R)_2$ qui possèdent une liaison thiolate-SO_2 labile, pour $R = CMe_3$, $4\text{-}C_6H_4Me$ et $CHMe_2$. La réaction de *cis*-$(PPh_3)_2Pt(SH)_2$ avec SO_2 donne $(PPh_3)_2Pt(S_3O)$ et H_2O; une réaction qui imite la chimie Claus. Les complexes *cis*-

$(PPh_3)_2Pt(SH)_2$, $(PPh_3)_2Pt(S_3O)$ et $(PPh_3)_2Pt(SR)_2$ catalysent la réaction Claus ($2H_2S + SO_2 \longrightarrow 3/8S_8 + 2H_2O$).

Les complexes $(PPh_3)_2Pt(SR)_2$ réagissent avec CS_2 pour former des complexes mixtes thiolate-thioxanthate $(PPh_3)Pt(SR)(S_2CSR)$ dans lesquels CS_2 s'est inséré dans une des liaisons Pt-S . Le complexe *cis*-$(PPh_3)_2Pt(SH)_2$ réagit avec CS_2 pour donner le composé connu, $(PPh_3)_2Pt(S_2CS)$, qui contient un groupe trithiocarbonate .

Les structures de $[CpRu(PPh_3)(NO)SCMe_3]BF_4$, $(\mu\text{-SMe})(\mu\text{-S-4-}C_6H_4Me)[CpRu(S\text{-4-}C_6H_4Me)]_2$, $(\mu_3\text{-S})_2(\mu\text{-SCH}_2CH{=}CH_2)[CpRu]_3$, $(PPh_3)_2Pt(S_3O)$ et $(PPh_3)Pt(S\text{-4-}C_6H_4Me)(S_2CS\text{-4-}C_6H_4Me)$ ont été determinées par crystallographie aux rayons X.

To Sawsan, Laith
and Osama

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LIST OF ABBREVIATIONS

Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
R	organic alkyl group
Ar	organic aryl group
Me	methyl
Et	ethyl
C_3H_7	*n*-propyl
$CHMe_2$	*i*-propyl
CMe_3	*t*-butyl
n-Bu	*n*-butyl
Ph	phenyl
CH_2Ph	benzyl
$4\text{-}C_6H_4Me$	p-tolyl
phth	phthalimido
Cy	cyclohexyl
X	halogen
en	ethylenediamine
OTs	tosylate
HDS	hydrodesulfurization
M	transition metal
THF	tetrahydrofuran
Å	Ångström (1 Ångström = 10^{-10} m)
NMR	nuclear magnetic resonance
IR	infrared
ORTEP	Oak Ridge Thermal Elipsoid Plot
Anal.	analysis
Calcd.	calculated
FAB	fast atom bombardment
NBA	nitrobenzyl alcohol
TMS	tetramethylsilane

Abbreviations used in NMR

s	singlet
d	doublet
dd	doublet of doublets
t	triplet
m	multiplet
J	coupling constant
Hz	Hertz
ppm	part per million

Abbreviations used in IR

w	weak
m	moderate
s	strong
sh	shoulder
br	broad
ν	frequency, cm^{-1}

CHAPTER 1

INTRODUCTION

GENERAL INTRODUCTION

The thiolato anion (RS^-) is a fundamental ligand. The anionic nature of this ligand enhances its affinity for metal ions. Because of this, and the rich chemistry of sulfur donors, a large variety of transition metal complexes with thiolato ligands are known.[1-14]

The thiolato anion may be classified as a pseudo halide, which is comparable as a ligand with halo ligands (F^-, Cl^-, Br^-, I^-), and RS^- can often be used to replace halide. In fact, Jørgensen[15] placed RS^- in the spectrochemical series between F^- and Cl^-:

$$Br^- < Cl^- < RS^- < F^- < OH^- < H_2O < NH_3 < en < NO_2^- < CN^-$$

The RS^- ligand can be compared to the S^{2-} ligand except that the R group can be modified so that the environment around the metal center can be manipulated. Depending on the nature of the R group, steric or electronic control can be achieved.[10]

The thiolato ligand can act as a terminal or as a bridging ligand. It can bridge between two or three metal atoms through the donation of one or two lone pairs of electrons of the sulfur atom (Figure 1.1).

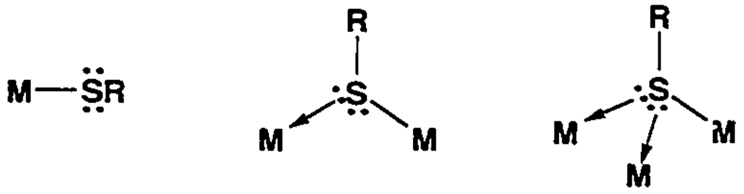


Figure 1.1: Bonding modes of thiolato ligand (RS^-).

The chemistry of thiolato complexes is essential in biological systems.[16-37] A variety of metalloproteins are known to contain sulfur as part of the coordination sphere of the metal ion. Nitrogenase, iron sulfur protein, metallothionines and copper blue proteins are common enzymes containing sulfur ligands.

Nitrogenase,[16-26] a Fe-Mo-S enzyme, is found in blue-green algae and in free-living bacteria. This enzyme is known to catalyze the reduction of dinitrogen to ammonia, a process known as nitrogen fixation. The general idea of this process is that the molybdenum atom (or atoms) bind the dinitrogen and that the iron atoms participate in one or more redox reactions that supply the electrons needed to reduce it. Nitrogenase consists of two distinct oxygen-sensitive proteins, the Mo-Fe protein and the Fe protein. The first has a molecular weight of 200,000-230,000 and appears to contain one or two Mo atoms and nearly equivalent amounts of Fe and S^{2-} (15-30 atoms) and about 20 cysteine residues. The Fe protein (Molecular weight *ca.* 60,000) contains approximately four iron atoms and four sulfide type sulfur atoms, probably in the form of an Fe_4S_4 ferrodoxin-type cluster. A smaller fragment called the FeMo-cofactor has been isolated from the large protein and its structure is shown in Figure 1.2.[27,28] It consists of Fe_4S_4 and Fe_3MoS_3 cubane fragments which are bridged by two S^{2-} groups and one "Y" group, possibly NH or O donor. One of the Fe atoms in the Fe_4S_4 fragment is bound to a sulfur atom of cysteine residue and the Mo atom is bound to a nitrogen atom of a histidine residue and to two oxygen atoms of homocitrate ligand. Recently, the crystallographic structure of the nitrogenase protein isolated from Azotobacter Vineladii was determined.[29]

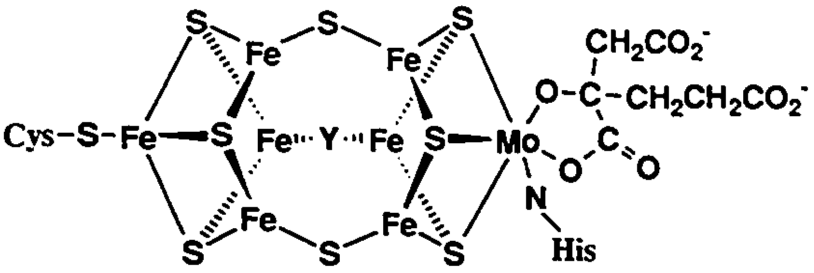
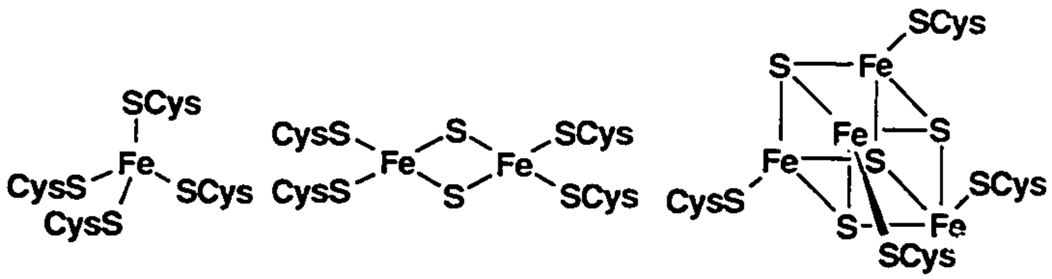


Figure 1.2: Structure of FeMo-cofactor.

Iron sulfur proteins, such as nitrogenase, Rubredoxin and Ferredoxins, play an important role in biological redox reactions such as photosynthesis and nitrogen fixation.[18-20,30-35] The schematic representation of the active sites of Rubredoxin and Ferredoxins are shown in Figure 1.3. Rubredoxin is a one electron transfer agent which consists of one iron atom and 50-60 amino acids having molecular weights of approximately 7000. A crystallographic study of Rubredoxin (reduced form) showed that the iron atom was coordinated tetrahedrally by four thiolate sulfur atoms from cysteine residues. The two- and four-iron atoms containing proteins are called Ferredoxins. These are small proteins (Molecular weight 6000-12000) which contain iron atoms, sulfide bridging ligands and terminal S-bound cysteinyl residues.

Metallothioneins are enzymes found in equine, human renal cortex and liver and in lower vertebrates.[16,36-39] These enzymes contain about 60 amino acids (of which 20 are cysteine bound to the metal atoms through the sulfur atom) and seven metal atoms (a mixture of Cd and Zn). The purpose of these enzymes is not firmly established.



Rubredoxin 2Fe-Ferredoxin 4Fe-Ferredoxin

Figure 1.3: The schematic representation of the active sites of Rubredoxin and Ferredoxins.

Copper blue proteins are found in plants where they seem to act as electron transfer agents.[16,35-37] The crystallographic structure for one of the plastocyanins (examples of copper blue proteins) was determined.[40] It contains one copper atom which is bonded to the nitrogen atoms of two histedine residues, the sulfur atom of a cysteine thiolate residue and the sulfur atom of a methonine group in a very distorted tetrahedral arrangement.

Complexes containing sterically hindered thiolato ligands were studied as organometallic analogs of the above mentioned enzymes.[43-52] The molybdenum complexes, $[Mo(CO)_2(SC_6H_2(CHMe_2)_3)_3]^-$, $[Mo(SC_6H_2(CHMe_2)_3)_4(CH_3CN)]$ and *cis*-$Mo(SCMe_3)_2(NCCMe_3)_4$ have been prepared and structurally characterized as models for nitrogenase.[49,50] However, no interaction with dinitrogen was observed. As models for copper blue proteins and metallothionines, the complexes $[Cu(2\text{-}SC_6H_4(SiMe_3)]_{12}$ and $(Et_4N)_2[Cd(2\text{-}SC_6H_4(SiMe_3))_4]$ were prepared and structurally characterized.[52]

Metal thiolato species are also implicated in industrial processes such as the hydrodesulfurization (HDS) of fossil fuels.[53-65] This process is necessary to prevent catalyst poisoning by organic sulfur compounds, to reduce the amount of SO_2 pollutant formed by combustion of petrolum fuels, and to remove bad smell from oil. Crude oil undergoes hydrodesulfurization *via* treatment with hydrogen gas over metal sulfide catalysts to give saturated hydrocarbons and hydrogen sulfide (Equation 1.1). The toxic H_2S is converted to elemental sulfur *via* the Claus process (Equation 1.2).[66] This reaction is a heterogeneous catalyzed process which is typically done over an alumina-based catalyst. Initially, some H_2S is oxidized to SO_2 and these two gases are then reacted together to form elemental sulfur and water.

$$\mathrm{RSH} + \mathrm{H_2} \xrightarrow{\text{Cat.}} \mathrm{RH} + \mathrm{H_2S} \qquad (1.1)$$

$$\mathrm{SO_2} + 2\,\mathrm{H_2S} \xrightarrow{\text{Cat.}} 2\,\mathrm{H_2O} + 3/x\,\mathrm{S_x} \qquad (1.2)$$

THE SYNTHESIS OF TRANSITION METAL THIOLATE COMPLEXES

A variety of methods used to prepare transition metal thiolate complexes[67-104] are listed below.

1. Metathesis of a transition metal halide with a metal thiolate: many transition metal thiolates are prepared using this method due to the availability of the halide which is usually easily substituted.[67-79] The formation of an insoluble halide salt is often the driving force for this reaction. Lithium, sodium and potassium salts of thiols are commonly used. The tetrakisthiolate $Mo(SCMe_3)_4$ was prepared from $MoCl_4$ and $LiSCMe_3$ (Equation 1.3).[68]

$$\mathrm{MoCl_4} + 4\,\mathrm{LiSCMe_3} \longrightarrow \mathrm{Mo(SCMe_3)_4} + 4\,\mathrm{LiCl} \qquad (1.3)$$

The trimethylsilyl (Me_3Si)[1,74] and trialkyltin (R_3Sn)[80-82] groups can also effectively transfer the thiolato anion to a metal center (Equations 1.4[74] and 1.5[82]).

$$\mathrm{MoCl_4 + 4\,Me_3SiSR \longrightarrow Mo(SR)_4 + 4\,Me_3SiCl} \qquad (1.4)$$

$$\mathrm{R = 2,4,5\text{-}C_6H_2(CHMe_2)_3}$$

$$\mathrm{2\,(PPh_3)Mn(CO)_4Br + 2\,Me_3SnSR \longrightarrow [(PPh_3)Mn(CO)_3SR]_2 + 2\,Me_3SnBr + 2\,CO} \qquad (1.5)$$

$$\mathrm{R = Me,\ 4\text{-}C_6H_4Me}$$

The reaction of thiols with a metal halide in the presence of a base gave thiolato complexes such as *cis*-$(PPh_3)_2Pt(SR)_2$, as shown in Equation 1.6.[83]

$$\mathit{cis}\text{-}\mathrm{(PPh_3)_2PtCl_2 + 2\,RSH \xrightarrow{Et_3N}} \mathit{cis}\text{-}\mathrm{(PPh_3)_2Pt(SR)_2 + 2\,Et_3N.HCl} \qquad (1.6)$$

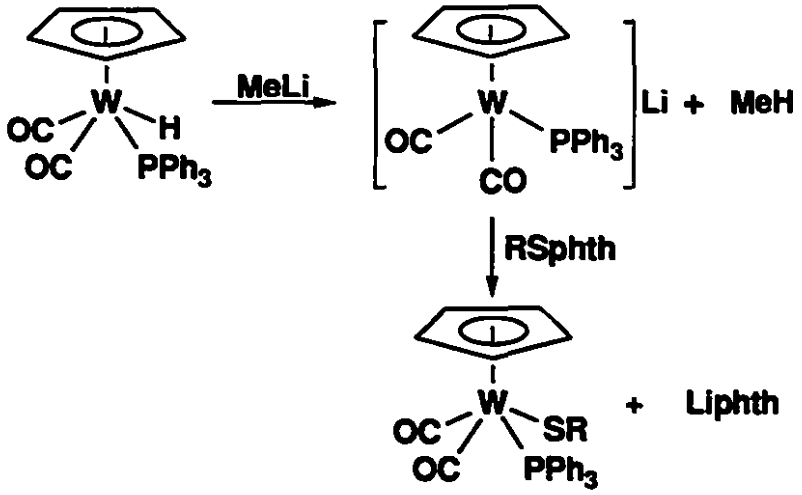
$$\mathrm{R = CH_2Ph,\ CHMe_2,\ CMe_3}$$

2. Oxidative addition of disulfides or thiols to low-valent transition metal complexes: certain metal carbonyl complexes oxidatively add disulfides[78,84,85] or thiols[84-89] to form metal thiolate complexes. The vanadium dimer $[CpV(SMe)_2]_2$ was prepared in this manner (Equations 1.7 and 1.8).[84]

$$2\,CpV(CO)_4 + 2\,MeSSMe \longrightarrow [CpV(SMe)_2]_2 + 8\,CO \qquad (1.7)$$

$$2\,CpV(CO)_4 + 4\,MeSH \longrightarrow [CpV(SMe)_2]_2 + 8\,CO + 2\,H_2 \qquad (1.8)$$

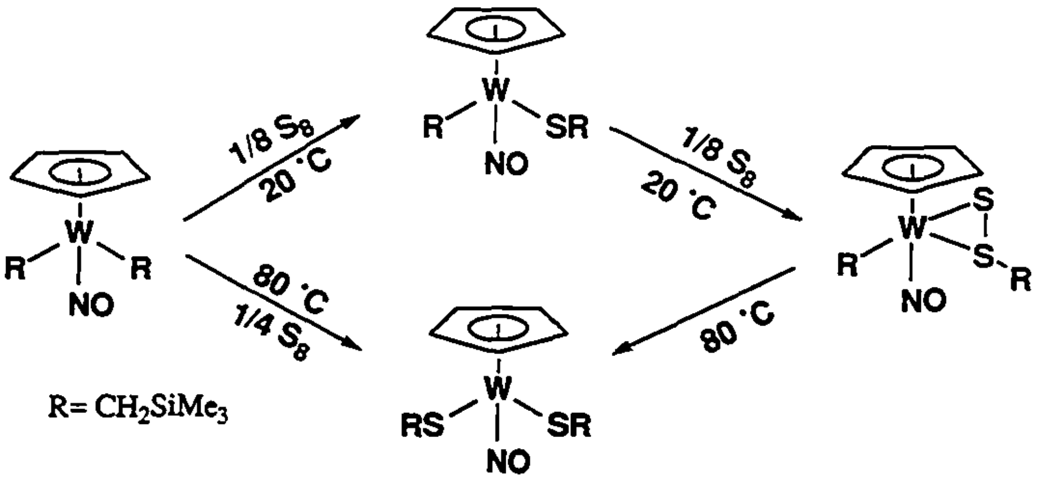
3. Reactions of organometallic anions with sulfur transfer agents: the sulfur transfer agents,[90,91] RSphth (phth= phthalimido) are a stable, readily available source of (RS^+) which have been proven to be very effective in the preparation of thiolato complexes.[92-94] An example is the preparation of $CpW(CO)_2(PPh_3)SR$ from the corresponding hydride (Equation 1.9).[95]



(1.9)

R= $CHMe_2$, CH_2Ph, 4-C_6H_4Me, Ph, phth

4. Insertion of elemental sulfur into a metal alkyl bond: the complexes $CpW(NO)R_2$ inserted sulfur in a sequential manner to give $CpW(NO)(SR)R$ and $CpW(NO)(SR)_2$ (Scheme 1.1).[96-98]



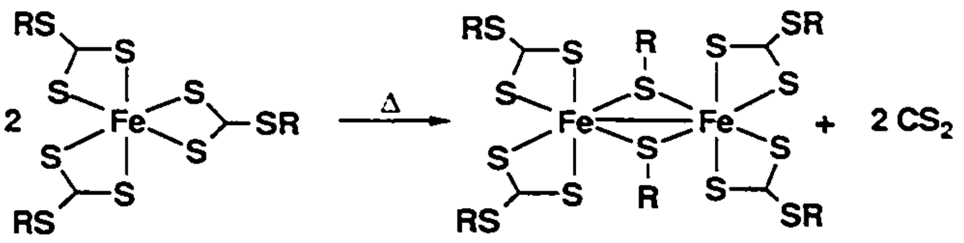
Scheme 1.1

5. Alkylation of a metal sulfide: alkyl halides reacted with the sulfido bridged iron dianion dimer $Na_2[(CO)_3Fe(\mu\text{-}S)]_2$ to give the thiolates shown in Equation 1.10.[99,100]

$$\left[(OC)_3Fe(S\text{-}S)Fe(CO)_3\right]^{2-} + 2\,RI \longrightarrow (OC)_3Fe(SR\text{-}SR)Fe(CO)_3 + 2\,I^- \qquad (1.10)$$

R= Me, Et

6. Degradation of a metal thioxanthate: neutral metal thiolate complexes may be synthesized from the corresponding thioxanthates by CS_2 elimination.[101-104] The complexes $[Fe(\mu\text{-}SR)(S_2CSR)_2]_2$ were prepared using this method (Equation 1.11).[104]



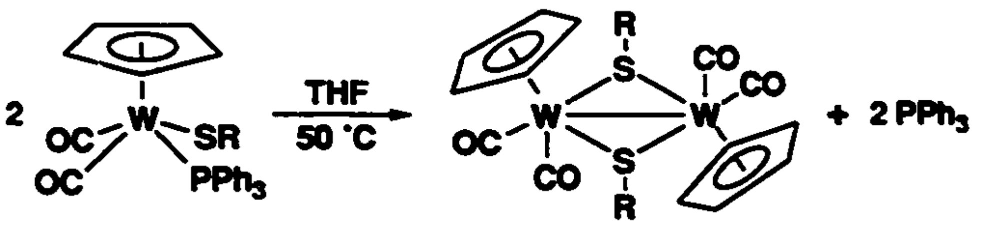
(1.11)

R= Et, C_3H_7, *n*-Bu, CH_2Ph

THE REACTIVITY OF TRANSITION METAL THIOLATE COMPLEXES

Transition metal thiolate complexes are highly reactive compounds. A summary of their reactions is given below.

1. Formation of sulfur bridges: a feature of many thiolato complexes is their tendency to form oligomers.[1,10,12,105-107] Thiolates can bridge between two[108-112] or three[113-117] metal atoms to give dinuclear, linear or three-dimensional cluster compounds or high polymers. The bridges can consist of two,[111,112,118,119] three,[1,120-122] or four[78,84,123,124] thiolato sulfur atoms. When the tungsten thiolates, $CpW(CO)_2(PPh_3)SR$, were mildly heated in solution, the thiolato bridge dimers were obtained as shown in Equation 1.12.[125]

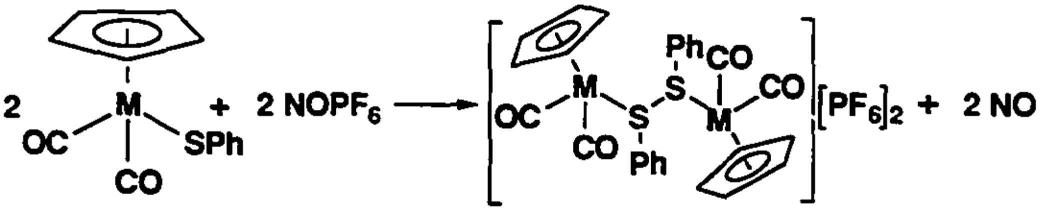


(1.12)

R= $CHMe_2$, CH_2Ph, 4-C_6H_4Me, Ph

2. Redox reactions: the availability of nonbonding electron pairs on the sulfur atom of thiolato ligands can lead to oxidation. Oxidation of thiolato complexes can lead to sulfur-sulfur bond formation,[126-131] or it can lead to oxidation at sulfur which, in turn, can give $MS(O)_xR$ complexes (x= 1, 2),[132-150] depending on the complex.

The nitrosonium salt oxidation of $CpM(CO)_2SPh$ gave disulfide dimers as shown in Equation 1.13.[128,131]



(1.13)

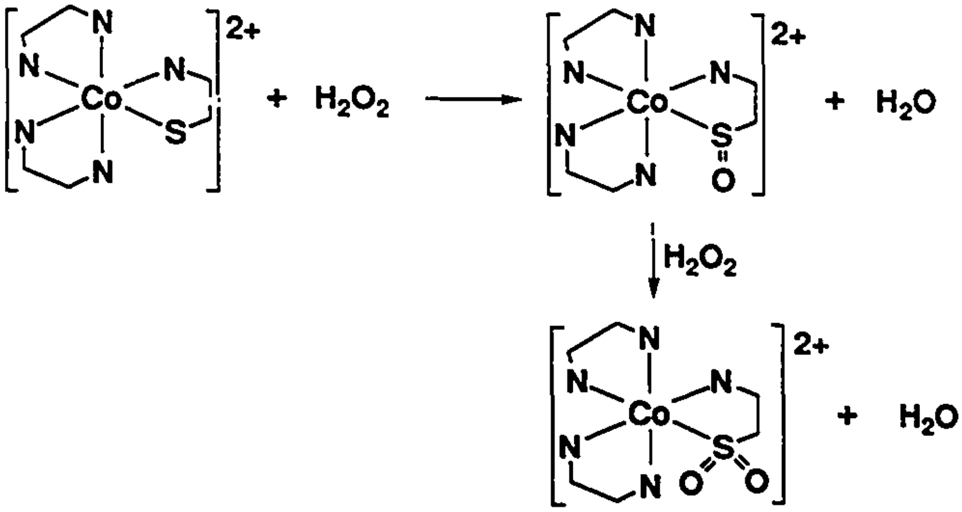
M= Fe, Ru

In some cases the free disulfide ligands were isolated. Equation 1.14 illustrates one such reaction in which the Mo center is reduced to its (+2) oxidation state.[127]

$$\mathrm{Mo(SCMe_3)_4} + 4\,\mathrm{CNCMe_3} \longrightarrow \textit{cis}\text{-}\mathrm{Mo(SCMe_3)_2(CNCMe_3)_4} + \mathrm{Me_3CSSCMe_3} \tag{1.14}$$

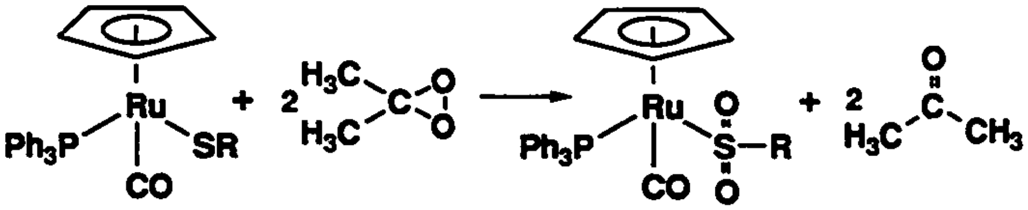
Oxidation of coordinated thiolato ligands can involve oxidation at sulfur to form sulfenato $[RS(O)]^-$ and sulfinato $[RS(O)_2]^-$ ligands.[132-150] Oxidants such as organic peroxy acids, hydrogen peroxide and dimethyldioxirane have been shown to be useful reagents for such transformations. Stoichiometric oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (en= ethylenediamine) with H_2O_2 gave the sulfenato analog.

Subsequent oxidation with H_2O_2 converted the sulfenato complex to the corresponding sulfinato complex (Equation 1.15).[133]



(1.15)

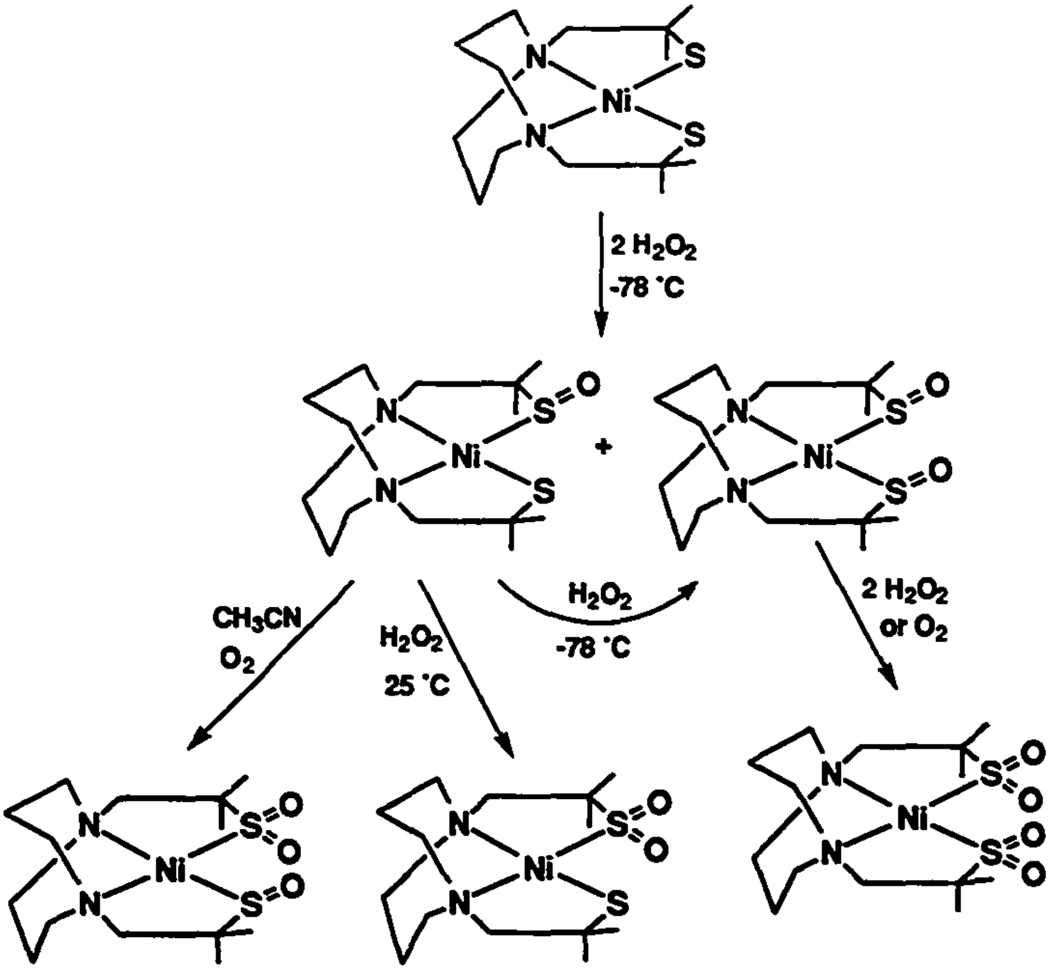
The direct formation of the sulfinato complexes $CpRu(CO)(PPh_3)S(O)_2R$ by the oxidation of $CpRu(CO)(PPh_3)SR$ with dimethyldioxirane is represented in Equation 1.16.[134] When the oxidant is used in stoichiometric quantities, one obtains 1:1 mixture of the sulfinato complexes and the starting Ru-complexes.



(1.16)

R= Me, Ph, 4-C_6H_4Me

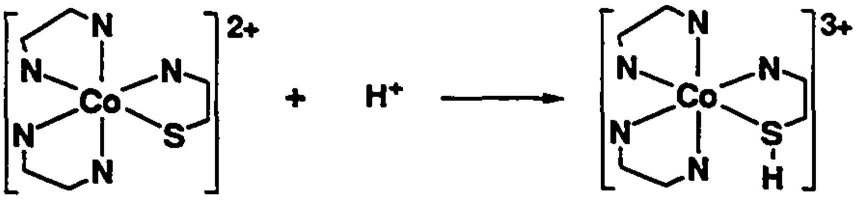
The oxidation of nickel thiolate complexes have been studied as models for oxygen-degraded enzymes.[139-150] The complex [1,5-bis(mercapto-2-methylpropyl)-1,5-diazocyclooctanato]nickel(II) underwent reactions with oxygen or hydrogen peroxide to produce a series of the corresponding sulfenato and sulfinato nickel complexes as shown in Scheme 1.2.[139,147] The complexes shown in Scheme 1.2 were isolated and characterized by spectroscopic techniques as well as x-ray crystallography.[139,147]



Scheme 1.2

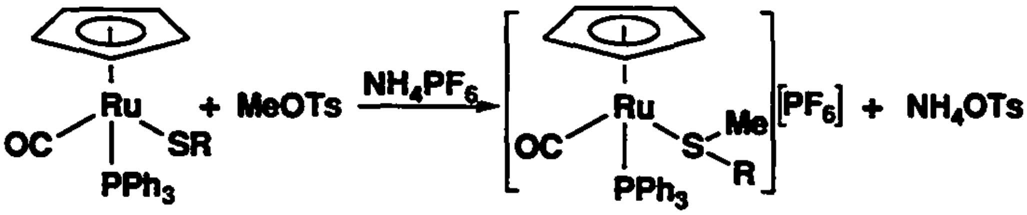
3. Reactions with electrophiles: the sulfur atom of thiolato complexes may retain considerable Lewis basicity, and nucleophilicity.[151-154] This can result in the protonation, alkylation or coordination of a thiolato ligand at sulfur.[151-157] Examples of electrophilic attack at coordinated thiolato group are given below.

An example of protonation at the sulfur atom is the treatment of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with $HClO_4$ to give the corresponding thiol complex (Equation 1.17).[151]



(1.17)

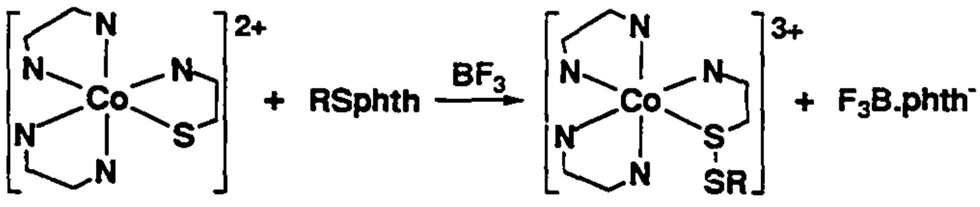
The S-alkylation of coordinated thiolato groups has been observed to occur when certain metal complexes are treated with alkyl halides.[153-158] A typical example of this type of reaction is the methylation of the Ru(II)-thiolates shown below (Equation 1.18).[155]



(1.18)

R= Me, Ph, 4-C_6H_4Me

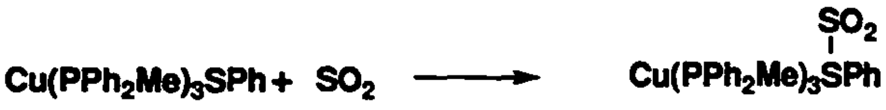
The reaction of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ with alkylthiophthalimide in the presence of BF_3 gave a disulfide complexes $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ (Equation 1.19).[158]



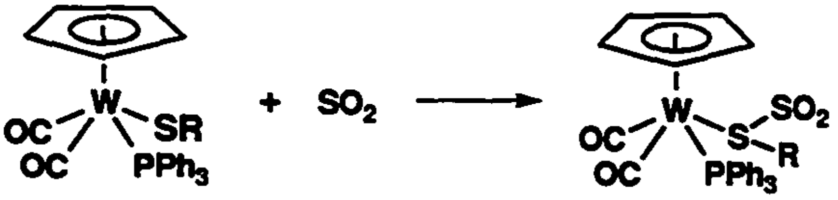
(1.19)

R= Me, Et, $CHMe_2$, CMe_3, Ph

4. Reactions with sulfur dioxide: metal thiolate complexes reacted with SO_2 to give adducts that have an S-bound SO_2 group. Examples are shown in Equations 1.20,[159] 1.21[160] and 1.22.[161]

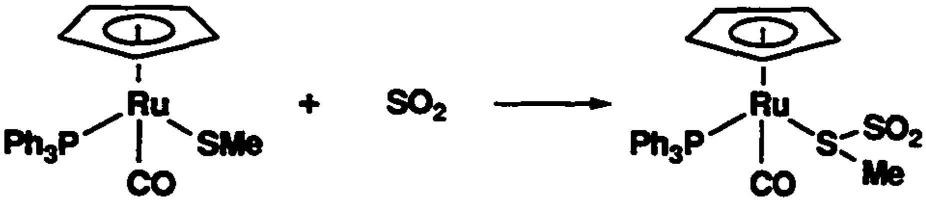


$$Cu(PPh_2Me)_3SPh + SO_2 \longrightarrow Cu(PPh_2Me)_3\overset{SO_2}{S}Ph \qquad (1.20)$$



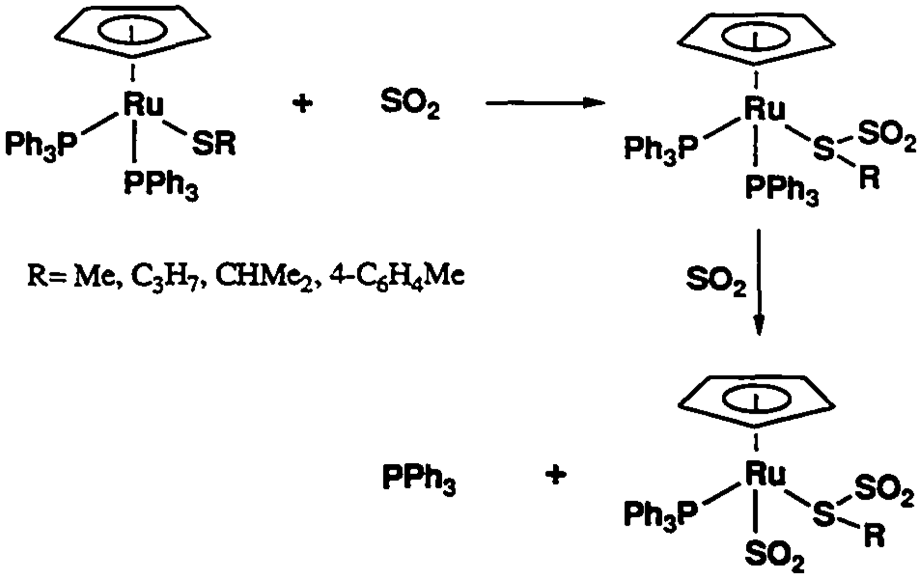
(1.21)

R= $CHMe_2$, CH_2Ph, 4-C_6H_4Me



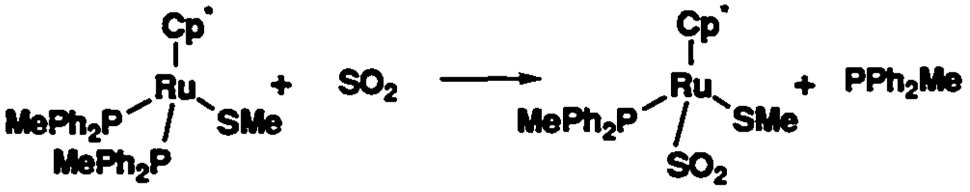
(1.22)

In contrast to the above three reactions, the ruthenium complexes $CpRu(PPh_3)_2SR$ reacted with SO_2 to give $CpRu(PPh_3)_2(S(SO_2)R)$ and $CpRu(PPh_3)(SO_2)(S(SO_2)R)$ (Equation 1.23). The first complex is similar to the above adducts having a labile SO_2 bound to the thiolato ligand. The second complex has two SO_2 ligands, one Ru-bound and the other thiolate bound, neither of them being labile at room temperature.[161,162]



(1.23)

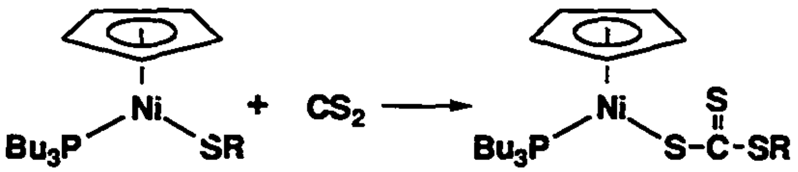
The complex $Cp^*Ru(PPh_2Me)_2SMe$ reacted with SO_2 to give the substituted product $Cp^*Ru(PPh_2Me)(SO_2)SMe$ (Equation 1.24).[161]



(1.24)

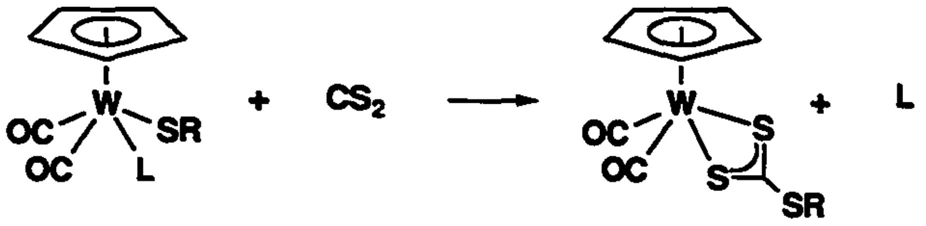
5. Insertion reactions: transition metal thiolate complexes undergo insertion reactions with small molecules such as carbon disulfide,[163-169] alkynes[170-174] or carbenes.[175]

The electrophilic attack by CS_2 on the sulfur atom of a thiolato ligands can lead to insertion into the metal-sulfur bond. Some examples of the products of these insertions include mononuclear systems with an η^1-thioxanthato ligands such as CpNi(*n*-Bu_3P)(SC(S)SR)[165] (Equation 1.25), η^2-thioxanthates such as $CpW(CO)_2(S_2CSR)$[75,95] (Equation 1.26) and $CpRu(PPh_3)(S_2CSR)$[176] (Equation 1.27) and clusters such as $Cu_8(SR)_4(S_2CSR)_4$[168] (Equation 1.28).



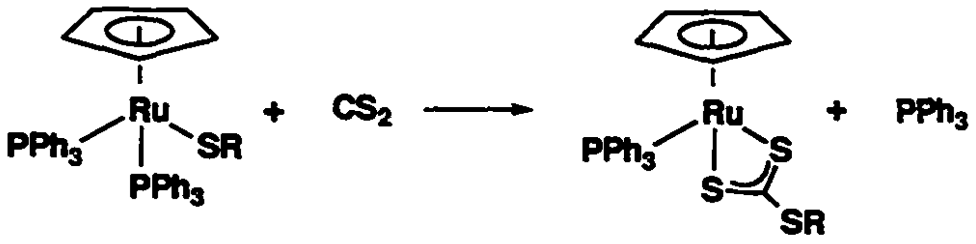
(1.25)

R= Me, Et, Ph



(1.26)

L= PPh_3, CO; R= Me, Ph



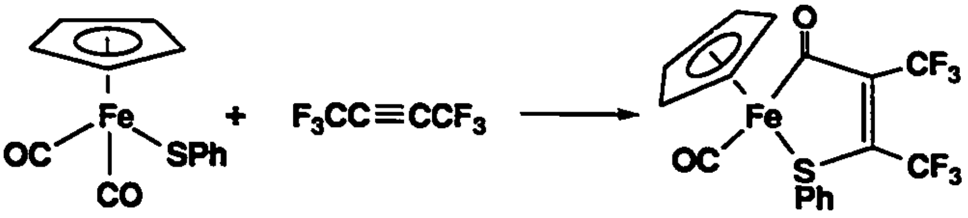
(1.27)

R= C_3H_7, $CHMe_2$, 4-C_6H_4Me.

$$8\,CuSR \quad + \quad 4\,CS_2 \longrightarrow Cu_8(SR)_4(S_2CSR)_4 \qquad (1.28)$$

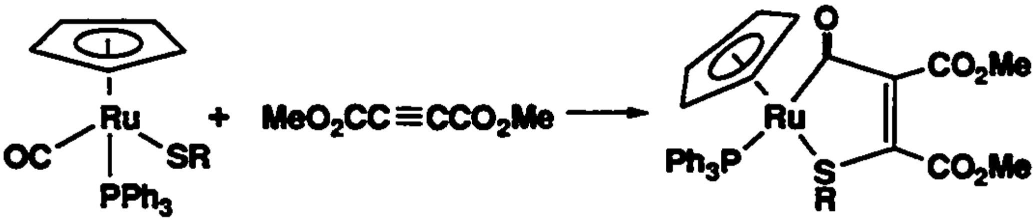
$R = C(Me)_2CH_2CH_3$

Activated alkynes, such as hexafluorobut-2-yne and dimethyl acetylenedicarboxylate, inserted into the metal-sulfur bond of certain metal thiolate complexes to give metallacyclic complexes.[170-173] Accordingly, $CpFe(CO)_2SPh$ reacted with hexafluorobut-2-yne to give an iron-metallacyclic complex (Equation 1.29).[172]



(1.29)

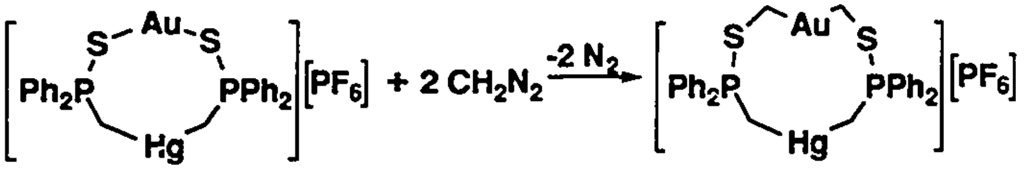
Another example is the reaction of $CpRu(PPh_3)(CO)SR$ with dimethyl acetylenedicarboxylate as shown in Equation 1.30.[155]



(1.30)

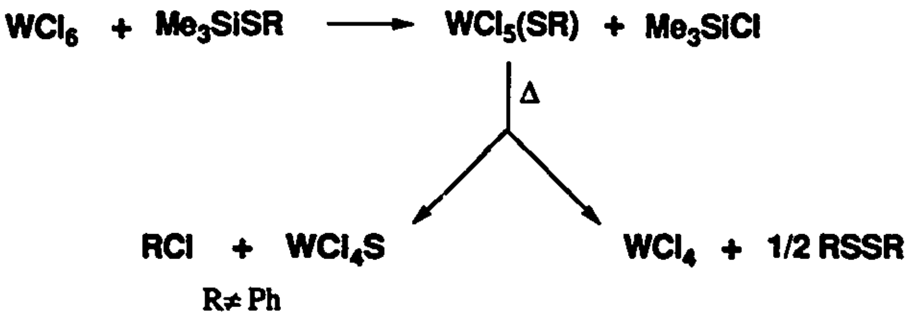
R= Me, CH_2Ph

The CH_2 carbene can insert into the metal-sulfur bond of the bimetallic complex $[HgAu(SPPh_2CH_2)_2]PF_6$ to give the product shown in Equation 1.31.[175]



(1.31)

6. Cleavage of the carbon-sulfur bond: metal thiolate complexes can also undergo cleavage of the carbon sulfur bond.[177-179] For example, WCl_5SR underwent heterolytic cleavage of the C-S bond to generate a carbocation, which can further abstract chloride to give a RCl and a tungsten sulfide complex. The intermolecular elimination of free RSSR was an alternative route for the decomposition of WCl_5SR (Scheme 1.3).[178]



R= Me, Et, $CH(Me)CH_2Me$, CMe_3, CH_2Ph, Ph

Scheme 1.3

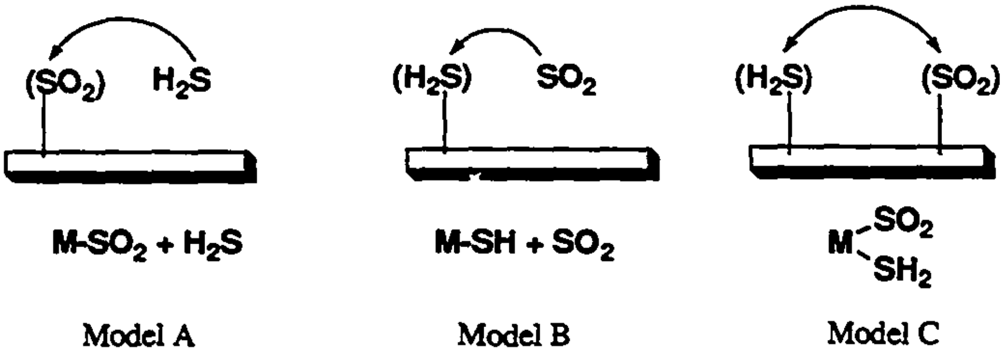
HYDRODESULFURIZATION AND THE CLAUS PROCESS

The presence of sulfur in fossil fuels is a major contributor to air pollution: therefore, the removal of sulfur from fossil fuels is very important in the energy industry. Industrially sulfur is removed from petroleum by catalytic hydrodesulfurization (HDS) (Equation 1.1) as H_2S and converted from H_2S to elemental sulfur *via* the Claus process (Equation 1.2). Hydrodesulfurization is carried out with hydrogen gas at high temperature over a metal sulfide catalyst.[54] This process is efficient although side reactions, such as hydrogenolysis of C-C and C-N bonds and hydrogenation of unsaturated compounds, lead to a significant waste of hydrogen and the generation of undesired byproducts. The mechanisms of the various steps involved in the HDS reaction have been studied both on surfaces[55-57] and on organometallic models[57-58] and the results of such studies have been reviewed.[56,59,60]

Several groups have reported studies of adsorption of thiophene (a major contaminant of petroleum) on metal surfaces such as Ni(100), Pt(111), Mo(100) and W(211).[55-57] These studies have led to the development of systems with homogeneous metal complexes.[55-60] The bonding and reactivity of thiophene complexes of Ru, Os, Ir and Rh have been examined and the results used to formulate mechanisms for the observed reactivity of thiophenes on HDS catalysts.[53,57-60]

In the Claus reaction, one third of the H_2S produced from HDS is burned in air to give SO_2. The latter is reacted with the remaining H_2S, over a catalyst at 400 °C, to give elemental sulfur and water. Many materials were reported to catalyze the Claus reaction; these include, alumina, iron oxide, manganese oxide, glass, activated carbon as well as sulfides of silver, cobalt and molybdenum.[66]

Even though the catalytic Claus process can remove over 99% of sulfur from the H_2S, the mechanism of this reaction is still poorly understood. Conceptually, possible mechanisms of this reaction can be described by three models as shown in Scheme 1.4. Model A depicts the reaction of H_2S with preadsorbed SO_2, model B involves the reaction of SO_2 with preadsorbed H_2S and model C involved the reaction of adsorbed SO_2 with adsorbed H_2S.



Scheme 1.4

Several attempts have been made by different groups to understand the mechanism of the Claus reaction. The adsorption of H_2S, SO_2 and a mixture of them on alumina or zeolites has been studied by IR and EPR spectroscopy.[180-188] The results of these studies showed that: 1) SO_2 is bonded (chemisorbed) to a metal atom of the surface in a unidentate fashion through the sulfur atom in either the pyramidal or the planar form.[189-193] 2) the chemisorbed SO_2 was reactive toward H_2S. 3) H_2S is adsorbed on alumina in two different forms, physical adsorption and dissociative adsorption. Both of these forms involve adsorption on an aluminum ion site. More details about the Claus chemistry will be presented in Chapter 5.

SCOPE OF THESIS

This work describes some reactions of ruthenium and platinum thiolate complexes. In the first part of the thesis, the reactivity of the electron rich bisphosphine ruthenium thiolate complexes $CpRu(PPh_3)_2SR$ and their carbonyl analogs, $CpRu(PPh_3)(CO)SR$, with various electrophilies is investigated. In addition the preparation and the reactions of $CpRu(PPh_3)_2SCH_2CH{=}CH_2$ are discussed.

In the second part, the reactions of $(PPh_3)_2Pt(SR)_2$ (R= H, CMe_3, 4-C_6H_4Me, $CHMe_2$) with SO_2 are studied as homogenous models for the Claus Process (Model B). The compound *cis*-$(PPh_3)_2Pt(SH)_2$ proved to be a good catalyst for the Claus reaction. An intermediate in this reaction, namely $(PPh_3)_2PtS_3O$, was isolated and shown to contain a four membered PtS_3 ring with an oxygen atom attached to the middle sulfur atom. These results generate new insight into fundamental Claus type chemistry. The insertion of CS_2 into the Pt-S bonds of the platinum thiolate complexes is also presented.

CHAPTER 2

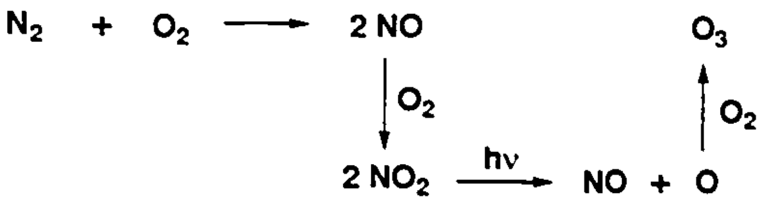
REACTIONS OF $CpRu(PPh_3)(L)SR$ WITH $NOBF_4$ ($L= PPh_3$, CO; $R= CMe_3$, $CHMe_2$, $4\text{-}C_6H_4Me$)

INTRODUCTION

Transition metal complexes containing nitrogen monoxide as a ligand have been known[194-199] for a long time and have been reviewed.[200-210] The study of nitrosyl complexes is related to the concern over the role of NO as a major air pollutant. Millions of tons of nitrogen oxides, mainly as NO, are produced in the fossil fuel combustion processes, chiefly those occurring in internal combustion engine, according to equation 2.1.[211]

$$1/2\ O_2 + 1/2\ N_2 \longrightarrow NO \qquad \Delta H_f^{\circ} = 21.6\ \text{kcal/mol} \qquad (2.1)$$

One of the most serious problems caused by nitrogen oxides is the formation of photochemical smog.[212] The products, which appear as a white yellow haze, are respiratory, eye and nose irritants with long term health effects and cause severe distress. Among the pollutants in photochemical smog are NO, NO_2, O_3, hydrocarbons and aldehydes. The inorganic photochemistry of smog is simplified in Scheme 2.1.[212]

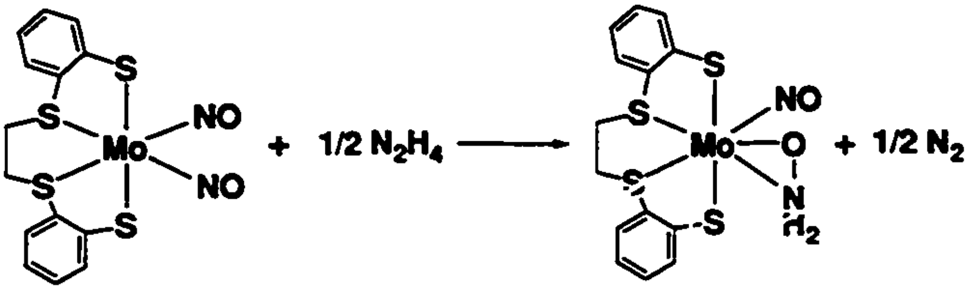


Scheme 2.1

The reactions shown in Scheme 2.1 can be further complicated by the formation of free radicals that interact with unburned hydrocarbons and lead to formation of aldehydes and other organic molecules.

The formation of nitrogen oxides can be minimized by modifying the combustion conditions and by developing catalysts which can convert NO into less harmful chemical entities, namely nitrogen and oxygen.[213-218] Thus the reactions of nitrogen monoxide with organometallic complexes continue to be of interest, since these latter transformations can be studied in detail.

Since NO^+ is isoelectronic with N_2, the study of nitrosyl complexes may offer significant insight into the reduction of dinitrogen to ammonia in biological systems.[17,219-221] An example of the reduction of NO ligand into hydroxylamine ligand is represented in Equation 2.2.[221]



(2.2)

Nitrogen monoxide, which is a gas at standard temperature and pressure, coordinates to transition metals through the nitrogen atom. The NO ligand can act as either a formal one electron or a three-electron donor. The modes of coordination of this ligand are represented in Figure 2.1; these include linear, bent, doubly- and triply-bridged.

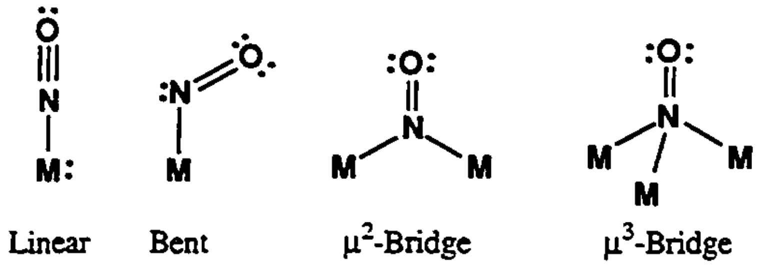


Figure 2.1: Coordination modes of nitrogen monoxide.

The linear coordination mode, as in CpNi(NO),[222] is similar to that of a terminal CO ligand, in which considerable M-NO synergistic bonding is present (Figure 2.2). The NO stretching frequency is usually in the range 1800-1900 cm^{-1}, but it can be as low as 1650 cm^{-1} depending on the charge and type of ancillary ligands on the metal atom. The bent coordination mode, e.g. in $Ir(PPh_3)_2(CO)(Cl)(NO)$,[223] on the other hand, was proposed by Sidgwick[224] as being analogous to that of a halide ion and structurally similar to organic nitroso compounds. The M-N-O bond angle is close to 120° and the $\nu_{(NO)}$ stretching frequency is in the range of 1620-1680 cm^{-1}.

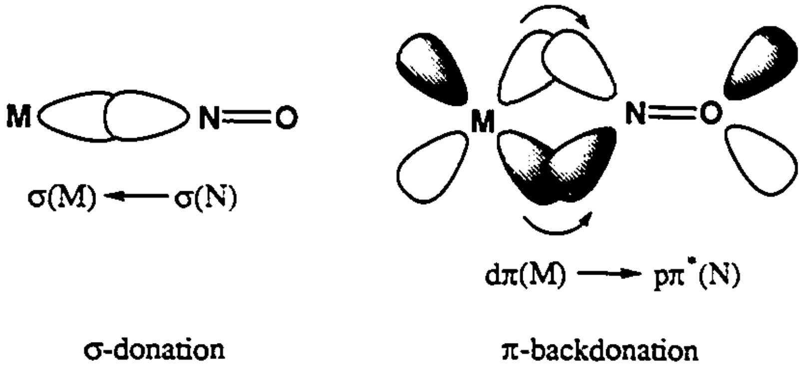
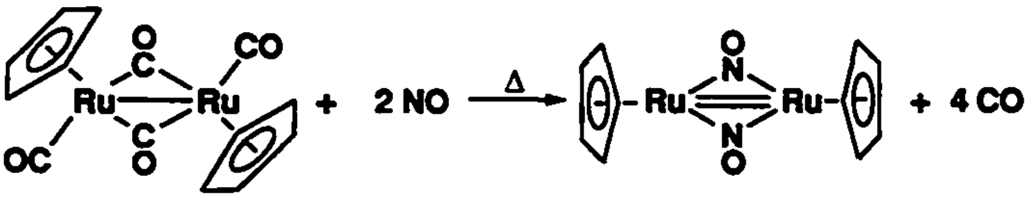


Figure 2.2: Synergistic interactions between a transition metal and a linear nitrosyl ligand.

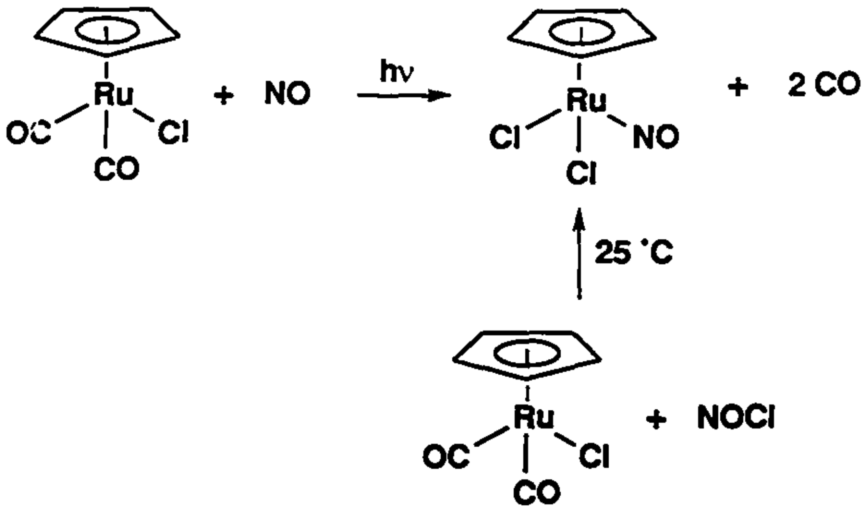
The doubly bridging NO ligand, which is found in the dimer $[CpCr(NO)_2]_2$,[225] donates two electrons to one metal and one electron to the other, like a μ_2-halide ligand. For μ_2-NO ligands, $\nu_{(NO)}$ is usually in the range 1550-1400 cm^{-1}. The triply bridging coordination mode, found in $Cp_3Mn_3(NO)_4$,[226] is quite rare. In this mode, the NO ligand donates one electron to each metal atom and the $\nu_{(NO)}$ bands are observed around 1320 cm^{-1}.

Organometallic nitrosyl complexes can be prepared by the use of NO gas, nitrosonium salts, nitrosyl halide, nitrite and nitronium salts as a source of NO.[184-200] For example, the nitrosyl dimer, $[CpRu(NO)]_2$, resulted from the treatment of the dicarbonyl dimer precursor with NO gas at high temperature (Equation 2.3).[227]



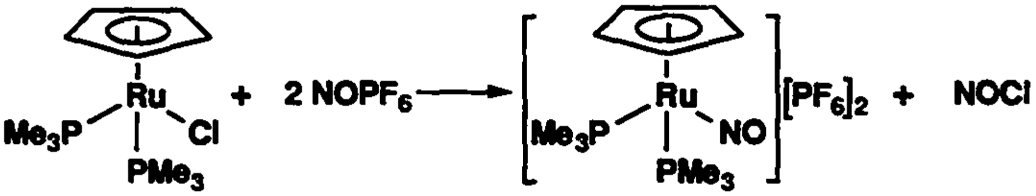
(2.3)

The complex $CpRu(NO)Cl_2$ was prepared by the reaction of $CpRu(CO)_2Cl$ with NO gas under UV irradiation[228] or with NOCl at room temperature (Scheme 2.2).[229]

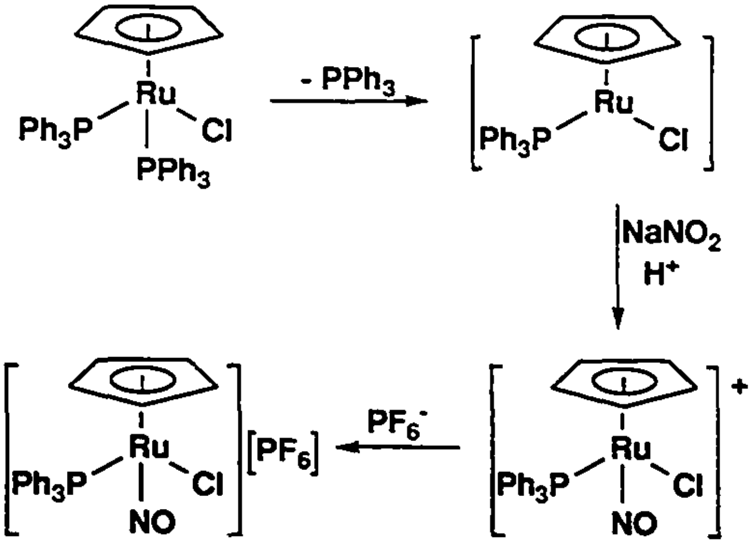


Scheme 2.2

The complex $CpRu(PMe_3)_2Cl$ reacted with $NOPF_6$ to give the nitrosyl salt $[CpRu(PMe_3)_2NO][PF_6]_2$ (Equation 2.4).[230]

 (2.4)

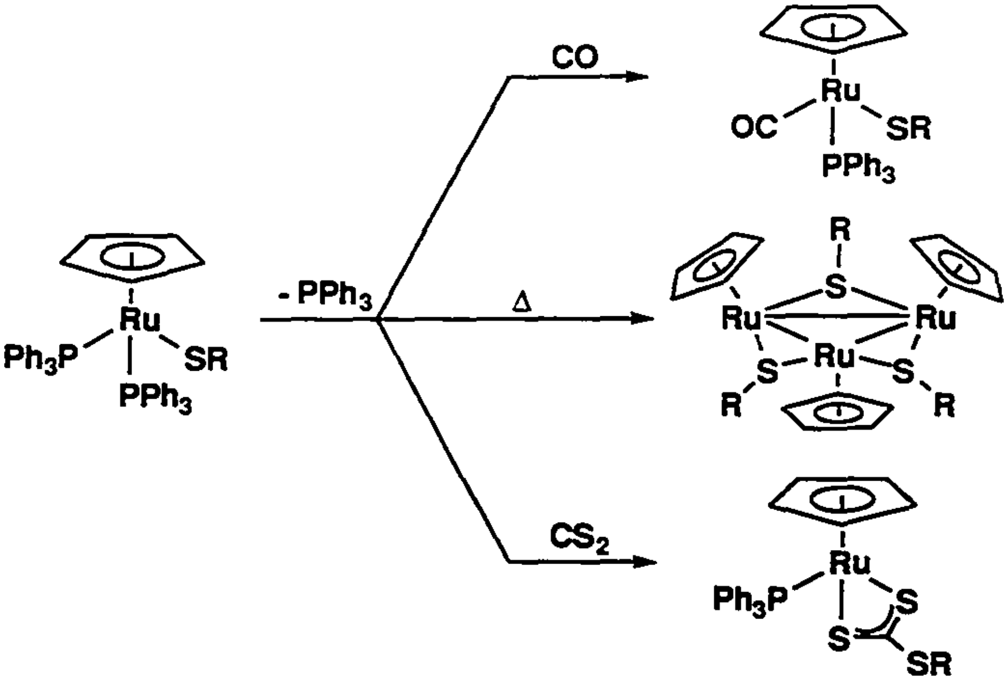
Treatment of $CpRu(PPh_3)_2Cl$ with sodium nitrite in hot acidified ethanol followed by anion exchange gave a red crystalline solid $[CpRu(PPh_3)(NO)Cl]PF_6$ (Scheme 2.3).[231]



Scheme 2.3

The similarity between the complex $CpRu(PPh_3)_2Cl$ and $CpRu(PPh_3)_2SR$ raised the possibility that the thiolato complexes might be good precursors for the synthesis of nitrosyl complexes.

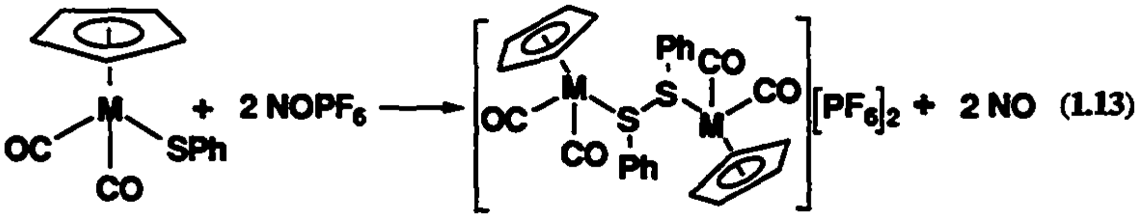
The complexes $CpRu(PPh_3)_2SR$, prepared in our lab,[176] were found to be reactive owing to pπ-dπ donation from the thiolato ligand to the Ru-center. However, the compounds were prone to loss of PPh_3 leading to: (i) ligand substitution in the presence of CO to give $CpRu(PPh_3)(CO)SR$; (ii) insertion of CS_2 into Ru-SR bond to give $CpRu(PPh_3)S_2CSR$; and (iii) aggregation in the absence of added ligands to give trimers $[CpRu(SR)]_3$ (Scheme 2.4).[232]



R= C_3H_7, $CHMe_2$, 4-C_6H_4Me

Scheme 2.4

The dicarbonylthiolato complexes, $CpM(CO)_2SPh$ (M= Fe, Ru), reacted with $NOPF_6$ to give dimers of the type $[(CpM(CO)_2)_2S_2Ph_2][PF_6]_2$ wherein the thiolato ligand had been oxidatively coupled (Equation 1.13).[128,131] In these reactions, the site of NO attack was the sulfur atom of the thiolato ligand.

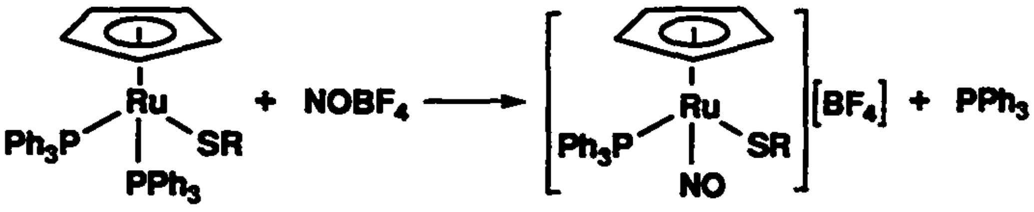


M= Fe, Ru

In this chapter, the reactions of the ruthenium thiolate complexes $CpRu(PPh_3)_2SR$ and their carbonyl analogs, $CpRu(PPh_3)(CO)SR$, with $NOBF_4$ were investigated. Treatment of the carbonyl complexes, $CpRu(PPh_3)(CO)SR$, with $NOBF_4$ gave disulfide bridged dimeric dications analogous to those observed for the dicarbonyl complexes. However, treatment of $CpRu(PPh_3)_2SR$ with $NOBF_4$ resulted in attack at the ruthenium atom to give ruthenium nitrosyl salts of the type $[CpRu(PPh_3)(NO)SR]BF_4$, where the R group is CMe_3, $CHMe_2$ and $4\text{-}C_6H_4Me$.

RESULTS

Treatment of $CpRu(PPh_3)_2SR$ with $NOBF_4$ in THF at room temperature gave $[CpRu(PPh_3)(NO)SR]BF_4$, where R= CMe_3; **1a**, $CHMe_2$; **1b**, $4\text{-}C_6H_4Me$; **1c** in isolated yields ranging from 58% to 90% (Equation 2.5). These salts are air sensitive in solution and in the solid state. They are soluble in acetone and in chlorinated solvents. They were characterized by IR, ^1H NMR spectroscopy and elemental analyses. The structure of $[CpRu(PPh_3)(NO)SCMe_3]BF_4$ was determined by x-ray crystallography and is depicted in Figure 2.3.[233] The crystal data, atom coordinates, thermal parameters and bond lengths and bond angles are given in Appendix 1, Tables A1.1-A1.4 respectively.



(2.5)

R= CMe_3; **1a**, $4\text{-}C_6H_4Me$; **1b**, $CHMe_2$; **1c**.

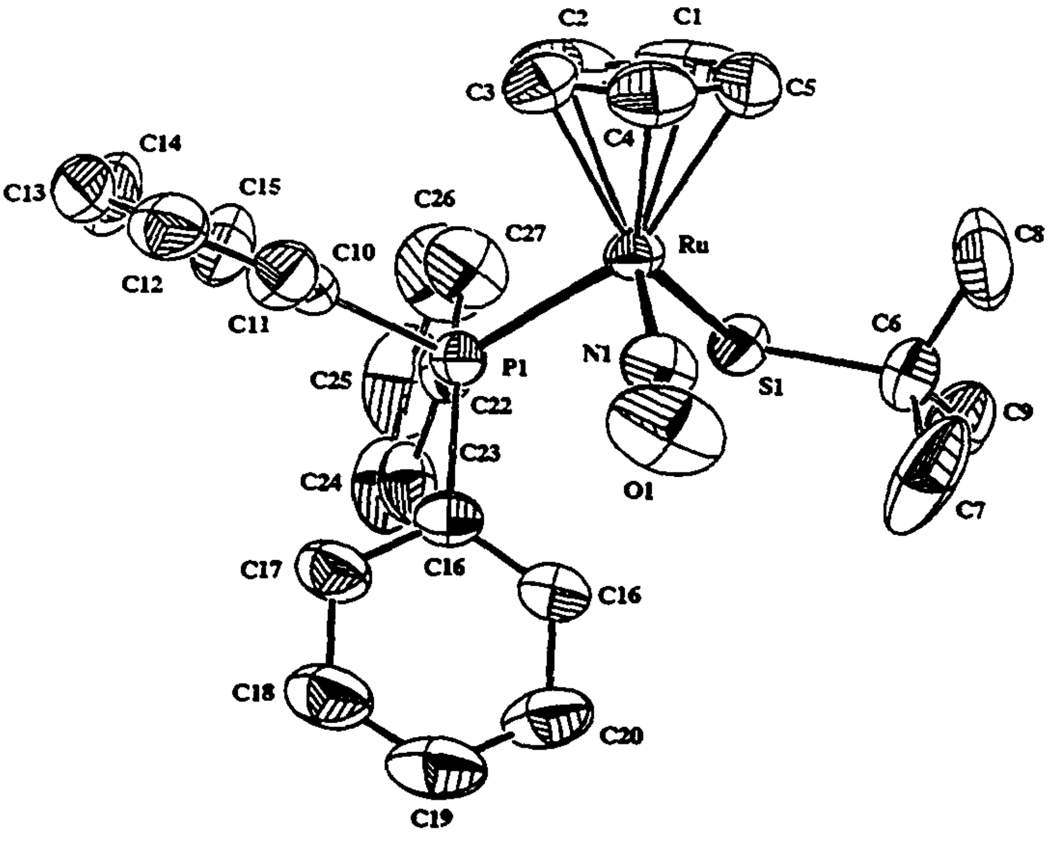


Figure 2.3: ORTEP drawing of [CpRu(PPh$_3$)(NO)SCMe$_3$]BF$_4$, 1a.

The RuNO moiety in $[CpRu(PPh_3)(NO)SCMe_3]BF_4$ is reasonably linear (Ru-N-O =170.7(7)°) and the Ru-N bond distance (1.753(6) Å) is in the range observed for such systems (average= 1.743(27) Å).[234] The S-Ru-N angle (102.6(2)°) is comparable to the Cl-Ru-N angle (102.0(2)°) observed in $[CpRu(PPh_3)(NO)Cl]PF_6$.[234] The Ru-S bond distance (2.386(2) Å) is similar to that observed in complexes of the type $CpRu(PPh_3)(CO)E$ where E= $SSCHMe_2$ (2.393(3) Å),[235] $SSSC_3H_7$ (2.370(2) Å),[235] $SS(O)CHMe_2$ (2.379(2) Å),[236] $SS(O)CH_2Ph$ (2.377(3) Å)[237] and $SS(O)_2$-4-C_6H_4Me (2.383(2) Å).[236]

The infrared spectrum of each of the complexes displayed a strong band in the range 1817-1822 cm^{-1} characteristic of the linear nitrosyl group (Table 2.1).[201]

Table 2.1: $\nu_{(NO)}$ in cm^{-1} for $[CpRu(PPh_3)(NO)SR]BF_4$, **1a-c**, in CH_2Cl_2 solution.

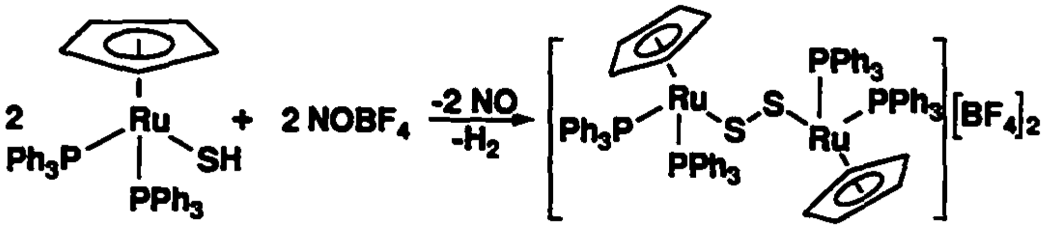
R	CMe_3	4-C_6H_4Me	$CHMe_2$
$\nu_{(NO)}$ (cm^{-1})	1822	1817	1821

In the ^1H NMR spectrum (acetone-d_6) the peak due to the Cp ligand of each complex appeared in the range 6.10-6.31 ppm which was shifted from the range (4.06-4.26 ppm) in the starting compounds (Table 2.2). The shift to a lower field is consistent with the reduction of electron density at ruthenium. In the ^1H NMR spectrum of $[CpRu(PPh_3)(NO)SCHMe_2]BF_4$ an overlapping doublet of doublets was observed for the diastereotopic methyl groups, indicating that the chiral ruthenium center is configurationally stable on the NMR time scale at room temperature.

Table 2.2: Cp-chemical shifts (ppm) of $CpRu(PPh_3)_2SR$ and $[CpRu(PPh_3)(NO)SR]^+$ in acetone-d_6.

R	$CpRu(PPh_3)_2SR$	$[CpRu(PPh_3)(NO)SR]^+$
CMe_3	4.26	6.30
$4\text{-}C_6H_4Me$	4.06	6.10
$CHMe_2$	4.25	6.31

The thiolo complex $CpRu(PPh_3)_2SH$ gave the known[238] S_2-bridged dication $[(CpRu(PPh_3)_2)_2S_2]^{2+}$ upon treatment with $NOBF_4$ (Equation 2.6). The complex was isolated as the BF_4 salt and identified by its ^1H NMR spectrum.



(2.6)

Treatment of $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$ with $NOBF_4$ in THF at room temperature gave the disulfide bridged dicationic dimer $[(CpRu(PPh_3)(CO))_2S_2(4\text{-}C_6H_4Me)_2][BF_4]_2$, **2**, in good yield (Equation 2.7). The infrared spectrum, the ^1H NMR spectrum and the elemental analysis were consistent with the absence of NO ligand and the presence of PPh_3, CO and $S\text{-}4\text{-}C_6H_4Me$. In addition the ^1H NMR spectrum (Figure 2.4) revealed two Cp-peaks in the ratio 4:1 each accompanied by methyl peaks in the same ratio. There were also two CO stretching bands in roughly a 4:1 ratio in the infrared spectrum. These observations are consistent with the proposed formulation since the presence of the

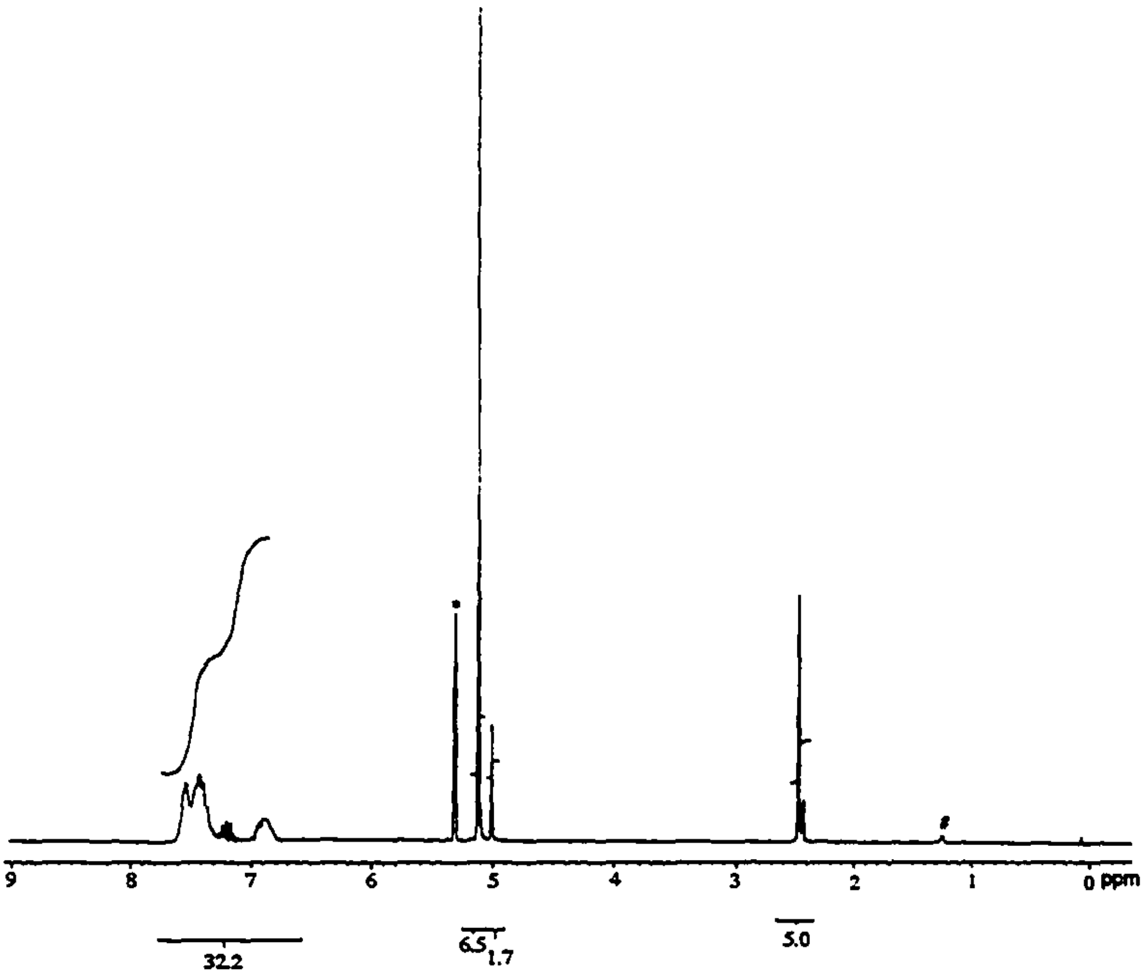
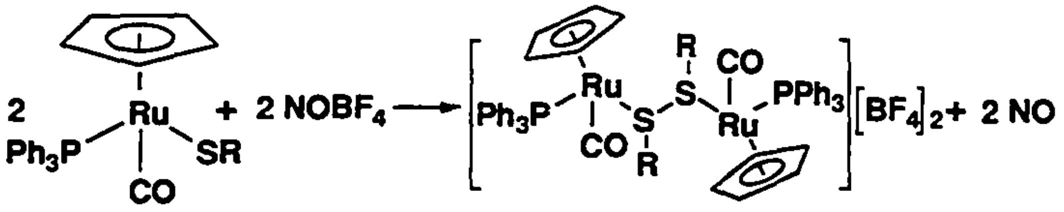


Figure 2.4: ^{1}H NMR spectrum of $[(CpRu(PPh_3)(CO))_2S_2(4\text{-}C_6H_4Me)_2][BF_4]_2$, **2**, in CD_2Cl_2; (*= solvent peak, #= water peak).

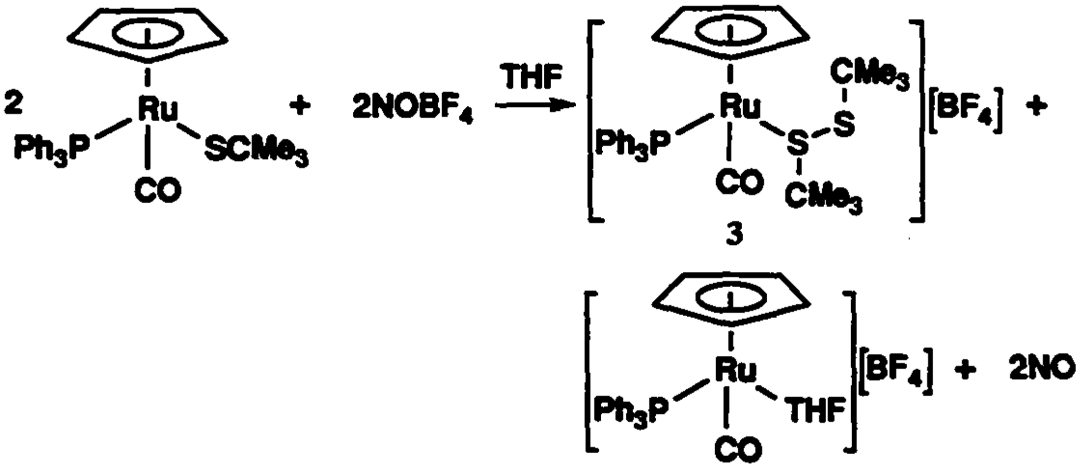
two chiral ruthenium centers would be expected to generate diastereomerism and lead to the multiplicity of peaks and bands observed.



(2.7)

R = 4-C_6H_4Me, 2.

When $CpRu(PPh_3)(CO)SCMe_3$ was treated with $NOBF_4$ in THF the disulfide complex $[CpRu(PPh_3)(CO)S_2(CMe_3)_2]BF_4$, 3, precipitated (Equation 2.8). Samples of the solution were taken at early stages of the reaction, stripped to dryness and redissolved in acetone-d_6. The ^1H NMR spectra of these samples revealed the presence of peaks due to the acetone ligated cation[239] $[CpRu(PPh_3)(CO)(acetone)]^+$ in addition to those due to the disulfide complex which precipitated. Thus the monomeric disulfide product probably arises *via* cleavage of the corresponding dimeric dication $[(CpRu(PPh_3)(CO))_2S_2(CMe_3)_2]^{2+}$, as observed for reactions of $CpFe(CO)_2SR$.[240]



(2.8)

DISCUSSION

Complexes of the type $CpRu(CO)_2SR$ were reported to react with NO^+ to give the disulfide bridged dications $[(CpRu(CO)_2)_2S_2R_2]^{2+}$. Replacement of one of the CO groups in the starting material with PPh_3 gave similar complexes containing disulfide ligands. However if both CO groups are replaced by PPh_3 ligands the site of attack by NO^+ shifts from the sulfur atom to the ruthenium atom to give cations of the type $[CpRu(PPh_3)(NO)SR]^+$. These reactions illustrate nicely the effects of the electronic and steric environment of the Cp-ruthenium thiolate moiety on its chemical reactivity.

The reactivity of $CpRu(PPh_3)(CO)SR$ towards NO^+ is not entirely surprising. In this case, oxidation occurred at the sulfur center and the resultant radical dimerizes to give the observed product. This behavior is similar to that of $CpM(CO)_2SPh$ (M= Ru, Fe).[128,240] The oxidation of $CpRu(PPh_3)_2SH$ was reported to yield $[(\mu\text{-}HSSH)(CpRu(PPh_3)_2)_2]^{2+}$ *via* the proposed intermediate $[(\mu\text{-}S_2)(CpRu(PPh_3)_2)_2]^{2+}$.[238]

As mentioned earlier, the complexes $CpRu(PPh_3)_2SR$ have a tendency to lose triphenylphosphine, which is due to (i) steric acceleration caused by the presence of two bulky triphenylphosphine ligands on the ruthenium center (Tolman's cone angle of PPh_3= 145°. The cone angle derived from x-ray data for Ru is 123-125°),[241] and to (ii) the electronic effects that are described below.

Molecular orbital calculations on $CpFe(CO)_2SH$ suggest[242] that the HOMO is an antibonding orbital involving the sulfur p and metal d orbitals whereas calculations on CpFe(CO)SH indicate[242] that the sulfur lone pair can stabilize the 16 electron species through $p\pi\text{-}d\pi$ bonding. The filled sulfur p orbital has the proper symmetry to overlap with an empty metal d-orbital (Figure 2.5).

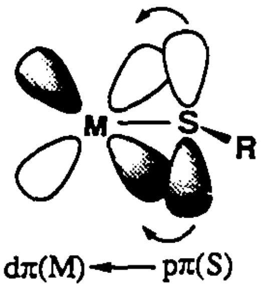
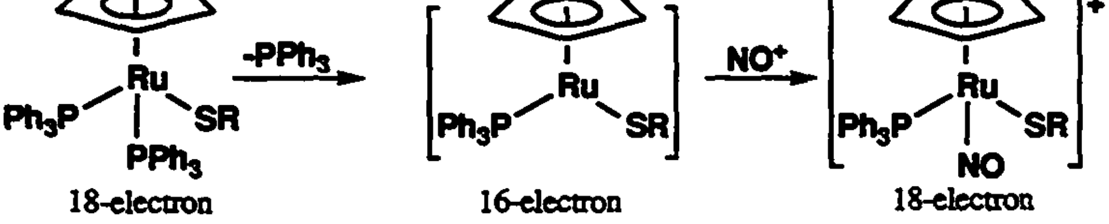


Figure 2.5: The pπ-dπ interaction between the metal and the thiolato ligand.

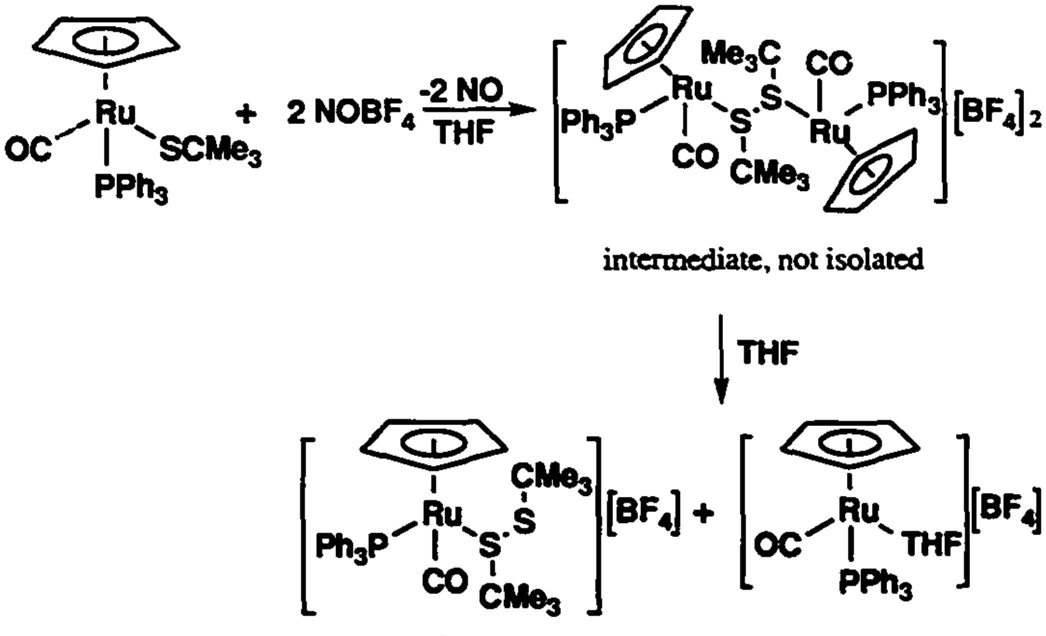
The stability of the electron deficient complexes $CpMo(NO)(SPh)_2$[243,244] and $Ru(SC_{10}H_{13})_4(NCCMe_3)$[245,246] was justified by this pπ-dπ back bonding. Therefore, one might expect that the 18-electron complexes $CpRu(PPh_3)_2SR$ have an electron rich ruthenium center which is easily attacked by NO^+.

A ^1H NMR study of the reaction of $CpRu(PPh_3)_2S$-4-C_6H_4Me and $NOBF_4$ revealed that the addition of an excess of PPh_3 slowed down the formation of $CpRu(PPh_3)(NO)S$-4-C_6H_4Me, **1b**. This result, together with the ease of PPh_3 loss from $CpRu(PPh_3)_2SR$ complexes,[176] suggests that this reaction may proceed *via* a dissociative mechanism. The complex $CpRu(PPh_3)_2SR$ initially loses a PPh_3 group to form a coordinatively unsaturated intermediate, $[CpRu(PPh_3)SR]$. This species is stabilized by the pπ-dπ donation from the thiolato ligand to the metal. Then, electrophilic attack of NO^+ on the Ru-center takes place to give the expected product (Scheme 2.5).



Scheme 2.5

Oxidation of $CpRu(PPh_3)(CO)SCMe_3$ by $NOBF_4$ produced a yellow monomer, $[CpRu(PPh_3)(CO)S_2(CMe_3)_2]BF_4$, 3. The formation of 3 may be explained by comparison with analogous iron system. When $[(CpFe(CO)_2)_2S_2Ph_2][PF_6]_2$ was dissolved in polar solvents, $[CpFe(CO)_2S_2Ph_2]PF_6$ and $[CpFe(CO)_2(Solvent)]^+$ were produced.[128,240] Similarly, the formation of 3 probably arises from the cleavage of the corresponding dimer, $[(CpRu(PPh_3)(CO))_2S_2(CMe_3)_2][BF_4]_2$. This dimer would be unstable due to the presence of two bulky *t*-butyl groups (Scheme 2.6), and would probably dissociate to give 3 and the THF adduct.



3

Scheme 2.6

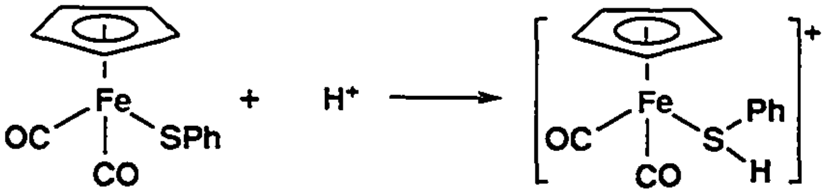
CHAPTER 3

REACTIONS OF $CpRu(PPh_3)_2SR$ WITH ELECTROPHILES ($R= CMe_3$, $CHMe_2$, $4\text{-}C_6H_4Me$)

INTRODUCTION

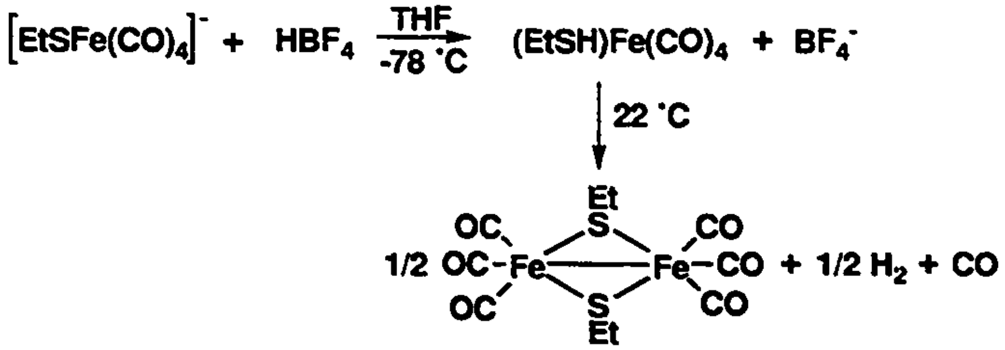
Organometallic thiolate complexes, M-SR, possess two sites which can react with electrophiles, namely the sulfur atom of the thiolato ligand and the metal center. The reactivity of the thiolato ligand towards electrophiles is due to the availability of lone pairs of electrons on the sulfur atom. Electrophiles such as H^+, R^+ or RS^+ usually attack the sulfur atom of a thiolato ligand to give complexes containing thiol,[151,247-251] thioether[153,155,248,250,252] or disulfide[158] ligands. Electrophilic attack at the metal center is observed only when the metal center is electron rich,[249,253,254] this latter case will not be discussed further in this chapter.

Protonation of thiolato complexes can give complexes containing thiol as a ligand, but in most cases the product thiol complexes were not isolated.[247-251] However, simple protonation at sulfur in the parent compound gave the thiol complex $[(en)_2Co(HSCH_2CH_2NH_2)]^{3+}$ (Equation 1.17).[151] In most other cases the thiol complexes could only be detected at low temperature or they could not be isolated in pure form. Protonation of $CpFe(CO)_2SPh$ with either HBr or HBF_4 gave the corresponding thiol complex $[CpFe(CO)_2(HSPh)]^+$ which could not be isolated (Equation 3.1).[247] However, this complex was prepared directly by the reaction of $[CpFe(CO)_2(THF)]BF_4$ and PhSH.[247]



(3.1)

The reaction of the thiolato anion $[EtSFe(CO)_4]^-$ with acids (HBF_4 in ether or gaseous HCl) was reported to give $[EtSFe(CO)_3]_2$ and H_2 gas. The intermediate thiol, $(HSEt)Fe(CO)_4$, was observed at -78 °C but at room temperature it converted to the dimer, $[(\mu\text{-}SEt)Fe(CO)_3]_2$ (Equation 3.2).[248,249]

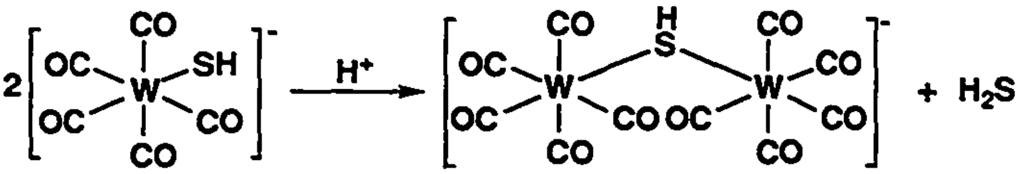


(3.2)

When the analogous phenylthiolato anion, $[PhSFe(CO)_4]^-$ was protonated, no intermediate thiol was detected even at -78 °C; the only observed product at any temperature was $[(\mu\text{-}SPh)Fe(CO)_3]_2$. When one of the CO ligands was substituted as in $[PhSFe(CO)_3(P(OEt)_3)]^-$, the reaction with HBF_4 gave $[PhSFe(H)(CO)_3(P(OEt)_3)]$ in which the proton had attacked the iron center rather than the sulfur atom of the thiolato ligand (Equation 3.3).[249,254] In this case, the phosphite ligand has enhanced the electron density at the metal, making it more susceptible to electrophilic attack.

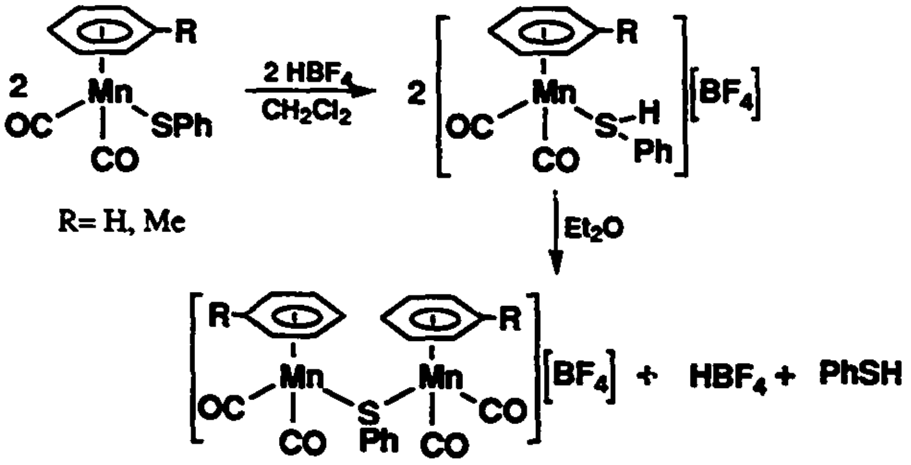
$$\left[PhSFe(CO)_3(P(OEt)_3)\right]^- + HBF_4 \longrightarrow PhSFe(H)(CO)_3(P(OEt)_3) + BF_4^- \qquad (3.3)$$

The protonation of $[W(SH)(CO)_5]^-$ gave a thiolo-bridged complex $(\mu\text{-}SH)[W(CO)_5]_2^-$ instead of the expected compound $W(CO)_5(SH_2)$ (Equation 3.4).[251]



(3.4)

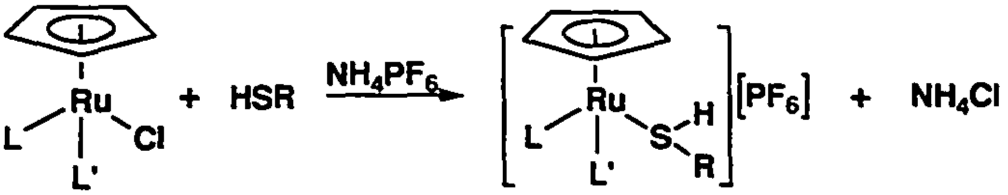
Protonation of $(\eta^6\text{-}C_6H_5R)Mn(CO)_2SPh$ with HBF_4 afforded the cationic thiophenol complexes $[(\eta^6\text{-}C_6H_5R)Mn(CO)_2(HSPh)]BF_4$ which were characterized spectroscopically (Equation 3.5).[250] The high acidity of these thiol complexes made their manipulation difficult. In acetone or ether they were easily deprotonated, and consequently, binuclear complexes such as $(\mu\text{-}SPh)[(\eta^6\text{-}C_6H_5R)Mn(CO)_2]_2$ were formed.



(3.5)

It was concluded from the above discussion that protonation of thiolato complexes is not a good method to prepare complexes containing thiol as a ligand.

Organometallic thiol complexes are known in the literature.[10] They have been prepared by substitution of a chloride ion in organometallic chlorides by thiol. An example of this synthetic route is shown in Equation 3.6.[255]

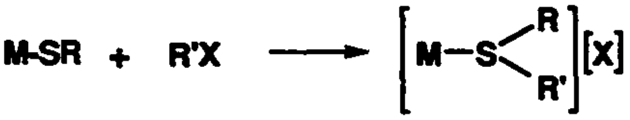


(3.6)

$L= L'= PPh(OMe)_2, PPh_2(OMe), P(OMe)_3; L= PPh_3, L'= CO, P(OMe)_3.$

The complexes $[CpRu(PPh_3)(L)(HSR)]BF_4$, where L= PPh_3 and R= Me, C_3H_7,[256] CH_2Ph, CH_2CH_2Ph,[257] L= $CNCMe_3$ and R= CMe_3[258] were prepared similarly. The air-sensitive complexes $[Cp'M(CO)_3(HS\text{-}4\text{-}C_6H_4Me)]BF_4$ (Cp'= $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_9H_7$; M= Mo, W) were also prepared and found to be strong acids.[259]

Alkyl halides are other electrophilic reagents that have been used with metal thiolato complexes. The reactions between thiolato complexes and alkyl halides usually give complexes containing thioether ligands (Equation 3.7).[252]

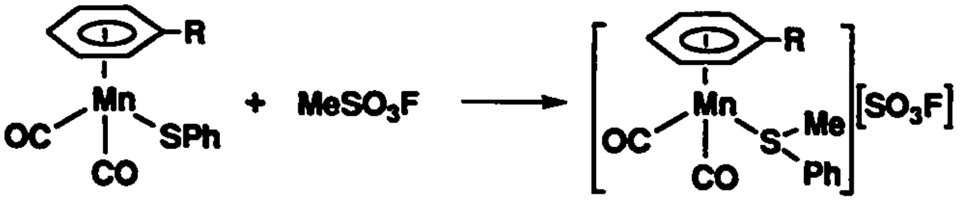


(3.7)

Several organometallic thioether complexes were prepared using this method. The complexes $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$ were prepared by alkylation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$.[153] Methylation of $CpRu(PPh_3)(CO)SR$ or $CpRu(dppe)SR$ with methyl tosylate in the presence of NH_4PF_6 gave the salts $[CpRu(PPh_3)(CO)(MeSR)]PF_6$ and $[CpRu(dppe)(MeSR)]PF_6$ (dppe= $Ph_2PCH_2CH_2PPh_2$; R= Me, Ph, CH_2Ph), respectively.[155] The complex $[PhSFe(CO)_4]^-$ reacted with methyl iodide to give a product having a methylphenyl thioether ligand (Equation 3.8).[249,253]

$$[PhSFe(CO)_4]^- + MeI \longrightarrow (PhSMe)Fe(CO)_4 + I^- \qquad (3.8)$$

Methylation of the arene complexes $(\eta^6\text{-}C_6H_5R)Mn(CO)_2SPh$ by $MeSO_3F$ gave the thioether complexes $[(\eta^6\text{-}C_6H_5R)Mn(CO)_2(MeSPh)](SO_3F)$ (Equation 3.9).[250]

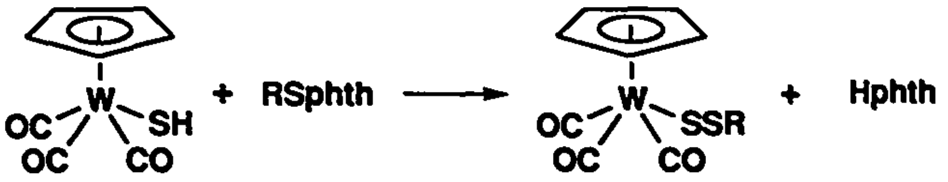


(3.9)

R= H, Me.

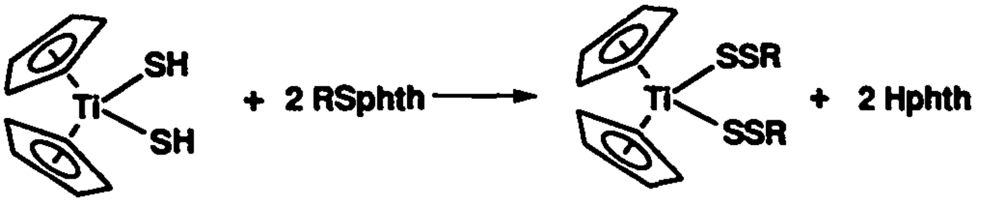
The same thioether complexes were obtained by the reaction of $[(\eta^6\text{-}C_6H_5R)Mn(CO)_3]PF_6$ with MeSPh in the presence of Me_3NO.[250]

The sulfur transfer reagents, RSphth, are well known in organic chemistry as a source of an electrophilic "RS⁺" group.[260] The applications of such reagents in organometallic chemistry have been demonstrated in this laboratory. By analogy with organic thiols,[260,261] transition metal thiolo complexes (M-SH) react with the sulfur transfer reagents to give disulfido complexes (MSSR) (Equations 3.10-3.12). For example, the complexes $CpW(CO)_3SSR$,[93] $Cp_2Ti(SSR)_2$[262] and CpRu(L)(CO)SSR (L= CO[263], PPh_3[235]) have been prepared in this way in good yields. The reactivity and stability of these complexes vary depending on the metal and the R groups of the disulfido ligand.



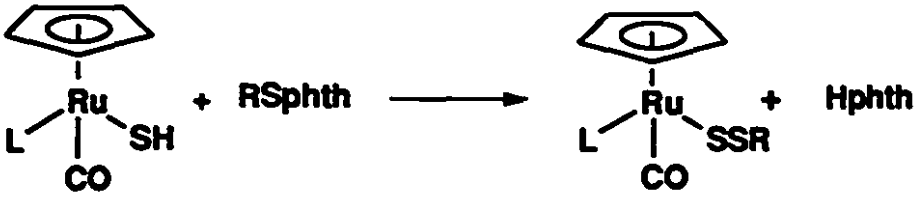
(3.10)

R= alkyl or aryl



(3.11)

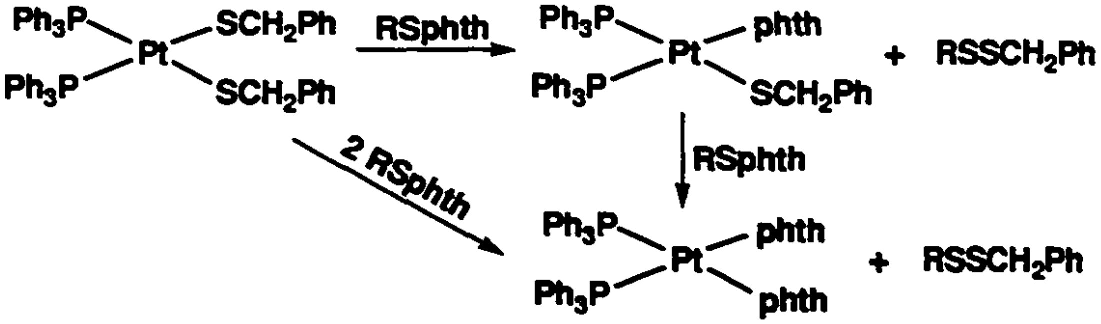
R= alkyl



(3.12)

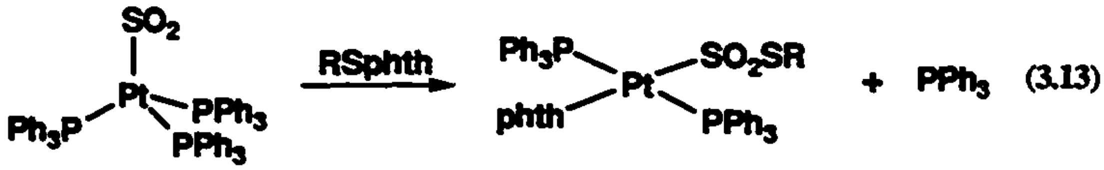
L= CO; R= CH_2Ph, Ph, L= PPh_3; R= C_3H_7, $CHMe_2$, 4-C_6H_4Me, These sulfur transfer reagents can also react with organometallic anions to form thiolato complexes. The compounds $CpW(CO)_2(L)SR$ ($L= CO^{264}$, PPh_3^{95}) were prepared by this method, which could not be extended to other carbonyl anions such as $[CpMo(CO)_3]^-$.[264]

When the sulfur transfer reagents were used with thiolato complexes such as $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ disulfide complexes $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ were obtained.[158] The reaction between *cis*-$(PPh_3)_2Pt(SCH_2Ph)_2$ and RSphth gave *cis*-$(PPh_3)_2Pt(phth)_2$ and the disulfides $RSSCH_2Ph$ (Scheme 3.1).[265]



Scheme 3.1

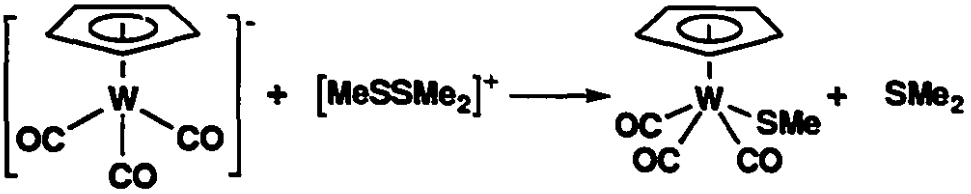
Recently, these sulfur transfer reagents were reacted with the tetrahedral complex $(PPh_3)_3PtSO_2$ to give *trans*-$(PPh_3)_2Pt(phth)(SO_2SR)$ as shown in Equation 3.13.[266]



R= Me, $CHMe_2$, Et, CH_2Ph, 4-C_6H_4Me.

Dimethylthiomethylsulfonium tetrafluoroborate, $[MeSSMe_2]BF_4$, is useful in synthetic chemistry as a donor of an electrophilic "MeS^+" group.[240,267] Examples of the use of this reagent in organometallic synthesis were demonstrated by Treichel and are discussed below.

The reagent $[MeSSMe_2]BF_4$ reacted with nucleophilic metal carbonyl anions to give methylthiolato metal carbonyl complexes. Equation 3.14 shows an example of such a reaction.[267]



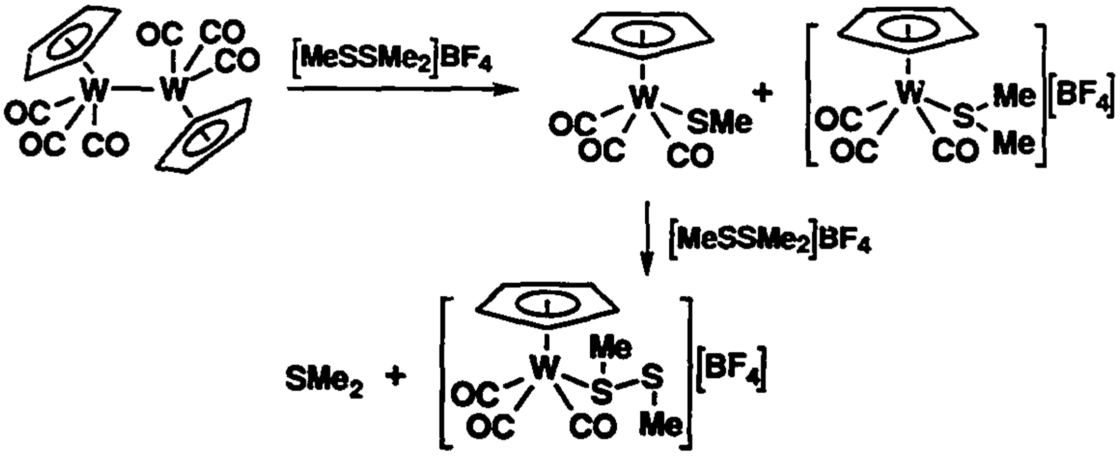
(3.14)

The complexes $[M(CO)_3(L)_2SMe]BF_4$ (M= Fe; L= PPh_2Me, $PPhMe_2$, $P(OMe)_3$, M= Ru; L= PPh_3) were prepared by the reaction of $[MeSSMe_2]BF_4$ with the appropriate neutral $M(CO)_3(L)_2$ precursors (Equation 3.15).[268]

$$M(CO)_3(L)_2 + [MeSSMe_2]BF_4 \longrightarrow [M(CO)_3(L)_2SMe]BF_4 + SMe_2 \quad (3.15)$$

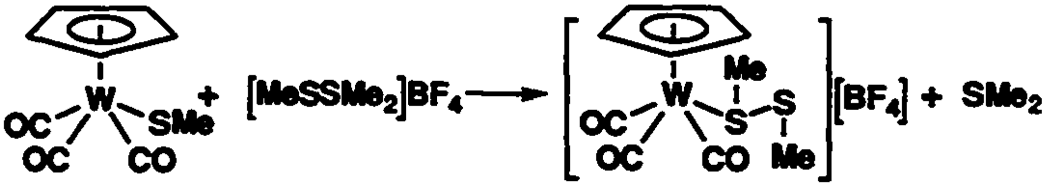
M= Fe; L= PPh_2Me, $PPhMe_2$, $P(OMe)_3$, M= Ru; L= PPh_3

Organometallic complexes having a metal-metal bond are also reactive toward $[MeSSMe_2]BF_4$. The metal-metal bond is cleaved and two products are formed, one containing a methyl thioether ligand and the other having a methylthiolato ligand. The methylthiolato complex, in some cases, can react with excess [MeSSMe$_2$]BF$_4$ to give a methyl disulfide complex. This type of reaction was observed for Mn$_2$(CO)$_{10}$, M$_2$(CO)$_8$(PPh$_3$)$_2$ (M= Mn, Re) and [CpMn(CO)$_3$]$_2$.[269] Scheme 3.2 illustrates one example.[269]



Scheme 3.2

The reaction of [MeSSMe$_2$]BF$_4$ with metal thiolate complexes led to complexes having monodentate organic disulfide ligands.[240] The complex [CpW(CO)$_3$S$_2$Me$_2$]BF$_4$ was prepared using this method (Equation 3.16).[240]

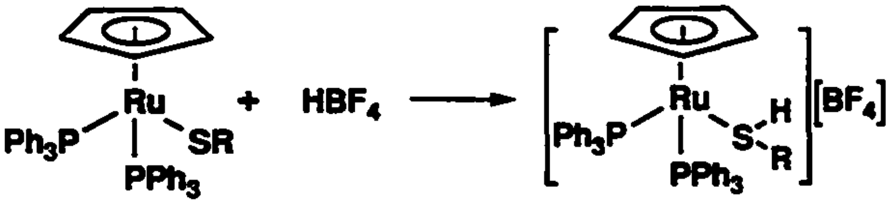


(3.16)

In this chapter the reactions of the complexes $CpRu(PPh_3)_2SR$, where R= CMe_3, 4-C_6H_4Me and $CHMe_2$, with the electrophilic reagents HBF_4, $[MeSSMe_2]BF_4$ and MeSphth are discussed. Reactions of these complexes with HBF_4 gave the corresponding thiol complexes, $[CpRu(PPh_3)_2(HSR)]BF_4$ in very good yields. Treatment of the thiolato complexes with $[MeSSMe_2]BF_4$ gave the methyl thioether complex, $[CpRu(PPh_3)_2SMe_2]BF_4$. Reactions of $CpRu(PPh_3)_2SR$, where R= CMe_3 and $CHMe_2$ with MeSphth gave $CpRu(PPh_3)_2(phth)$ and the dimers $(\mu\text{-SMe})(\mu\text{-SR})[CpRu(phth)]_2$ in which the Ru center has been oxidized. For R= 4-C_6H_4Me the same reaction gave $CpRu(PPh_3)(phth)(MeSS\text{-}4\text{-}C_6H_4Me)$, in which the S atom of the thiolato ligand was attacked, and also, the dimer $(\mu\text{-SMe})(\mu\text{-S-4-}C_6H_4Me)[CpRu(S\text{-}4\text{-}C_6H_4Me)]_2$ where the metal center has been oxidized.

RESULTS

Protonation of $CpRu(PPh_3)_2SR$ by HBF_4 (85% in ether) gave the corresponding thiol complexes, $[CpRu(PPh_3)_2(HSR)]BF_4$, where R= CMe_3; **4a**, 4-C_6H_4Me; **4b**, $CHMe_2$; **4c**, in very good yields (80-88%) (Equation 3.17). These yellow complexes are air stable in the solid state and unstable in solution. They are soluble in THF, acetone and chlorinated solvents but are insoluble in hexanes. They were characterized by IR, ^1H NMR spectroscopy and elemental analysis.



(3.17)

R= CMe_3; **4a**, 4-C_6H_4Me; **4b**, $CHMe_2$; **4c**

The IR spectra of **4a-c** showed a decrease in the SH stretching frequency compared to that in the free thiols (Table 3.1).

Table 3.1: $\nu_{(SH)}$ in cm^{-1} for $[CpRu(PPh_3)_2(HSR)]BF_4$ (KBr disks), **4a-c**, and RSH (neat).[a]

R	$CpRu(PPh_3)_2(HSR)^+$	HSR
CMe_3	2505	2588
$4-C_6H_4Me$	2514	2590[b]
$CHMe_2$	2512	2580

a) Data were obtained from Aldrich library of FT-IR spectra. b) Vapor at 250 °C.

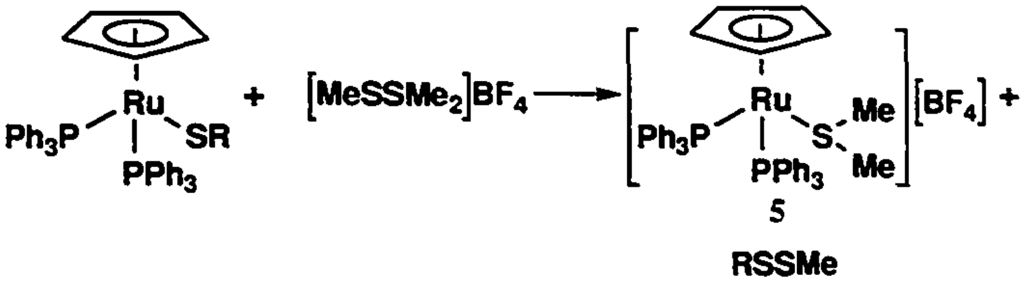
In the ^1H NMR spectra of these complexes, the chemical shift of the S<u>H</u> proton is shifted downfied relative to that of the free thiol (Table 3.2). The peak for this proton appeared as a triplet in **4a** and **4b** due to coupling with two equivalent phosphorus atoms. In **4c**, this peak appeared as a multiplet due to coupling with the methine proton of the isopropyl group in addition to the two equivalent phosphorus atoms.

Table 3.2: S<u>H</u>-chemical shifts (ppm) of $[CpRu(PPh_3)_2(HSR)]^+$ and of the free thiol in $CDCl_3$.[a]

R	$[CpRu(PPh_3)_2(HSR)]^+$	HSR
CMe_3	2.60	1.80
$4-C_6H_4Me$	4.93	3.35
$CHMe_2$	2.93	1.65

a) Data were obtained from Aldrich library of NMR spectra.

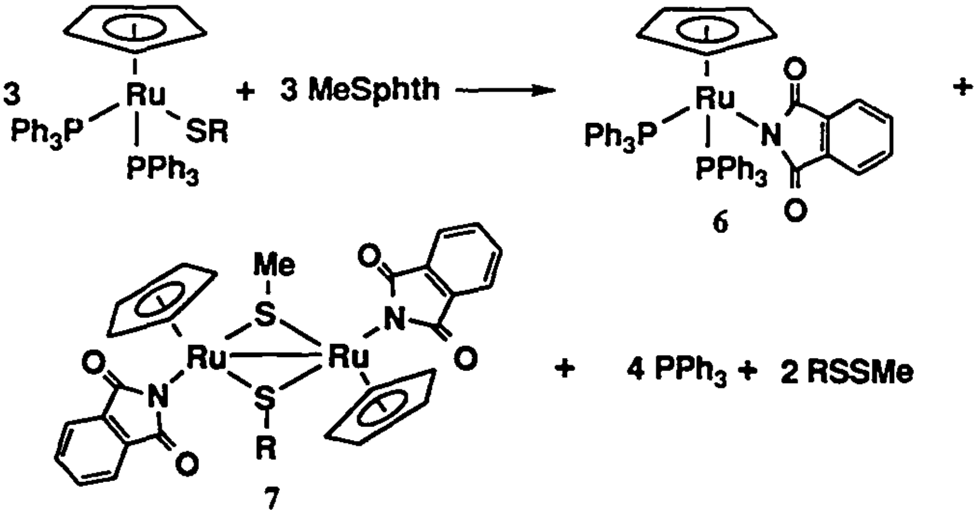
Treatment of the thiolato complexes $CpRu(PPh_3)_2SR$ where R= CMe_3, 4-C_6H_4Me or $CHMe_2$ with $[MeSSMe_2]BF_4$ in THF at room temperature gave the air stable thioether complex, $[CpRu(PPh_3)_2(SMe_2)]BF_4$, 5, in good yields (70-85%) (Equation 3.18). The complex was characterized by ^1H NMR and elemental analysis. The free alkylmethyl disulfide was detected in the ^1H NMR spectra of the reaction mixture. Thus 5 probably arises by ligand substitution of the disulfide salt, $[CpRu(PPh_3)_2(MeSSR)]BF_4$.



(3.18)

R= CMe_3, 4-C_6H_4Me, $CHMe_2$

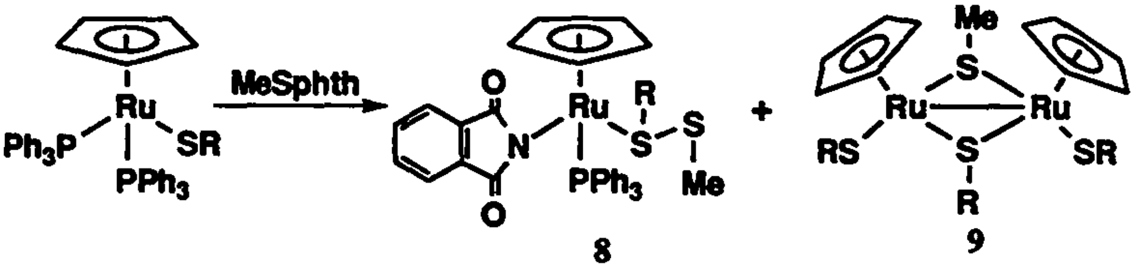
The reaction of $CpRu(PPh_3)_2SR$ with MeSphth gave the substitution product, $CpRu(PPh_3)_2(phth)$, **6**, (78%: R= CMe_3, 84%: R= $CHMe_2$) and the dimers (μ-SMe)(μ-SR)$[CpRu(phth)]_2$, R= CMe_3; **7a** (43%), $CHMe_2$; **7b** (31%) according to Equation 3.19. The air stable compound **6** and the dimers **7a,b** were characterized by IR, ^1H NMR spectroscopy and elemental analysis. The IR spectra of **7a,b** had a carbonyl band in the range 1658-1663 cm^{-1} indicative of the presence of a coordinated phthalimido ligand.[270] Their ^1H NMR spectra showed a multiplet in the aromatic region integrating for 8 protons due to two phthalimido ligands. It also showed a singlet Cp-peak integrating for 10 protons, while the aliphatic protons appeared in the expected region in the appropriate intensity.



(3.19)

R= CMe_3; 7a, $CHMe_2$; 7b

The reaction of $CpRu(PPh_3)_2S$-4-C_6H_4Me with MeSphth gave the disulfide complex **8** in 15% yield and the dimer **9** in 30% yield together with other unidentified compounds (Scheme 3.3). Compounds **8** and **9** were characterized by IR, ^1H NMR and mass spectroscopy. The IR spectrum of **8** showed a carbonyl band at 1652 cm^{-1} while that of **9** showed no such band. Figure 3.1 shows the ^1H NMR spectrum of **8** which confirmed the presence of the disulfide and phthalimido ligands.



R= 4-C_6H_4Me

Scheme 3.3

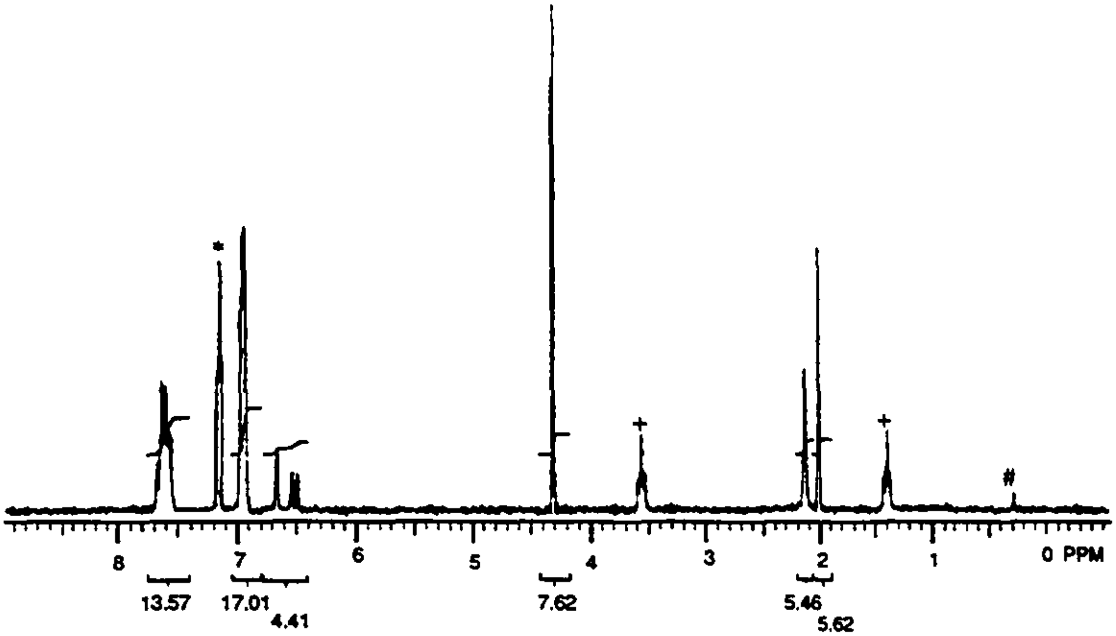


Figure 3.1: ^{1}H NMR spectrum of CpRu(PPh$_3$)(phth)(MeSS-4-C$_6$H$_4$Me), **8**, in C$_6$D$_6$; (*= solvent peak, #= water peak, += THF impurity).

The structure of 9 was determined and is depicted in Figure 3.2.[233] The crystal data, atom coordinates, thermal parameters and bond lengths and angles are given in Appendix 2, Tables A2.1-A2.4, respectively. Molecule 9 is very symmetric but its mirror plane is not crystallographically required. The compound has a Ru-Ru bond of (2.780(1) Å) which is longer than the corresponding bond (average= 2.714 Å) observed in the Ru(II) trimer[232] $[CpRuS(C_3H_7)]_3$ and than that observed in $[Cp^*Ru(SPh)_3RuCp^*]Cl$ (2.630(1) Å) ($Cp^*= C_5Me_5$).[271] The Ru-S_b (bridge) bond lengths (average 2.326 Å) are longer than the Ru-S_b bond in the Ru(II)-trimer (average 2.306 Å). The terminal Ru-S bond lengths (2.398(3), 2.391(3) Å) are similar to those observed in complexes of the type $CpRu(PPh_3)(CO)E$, where E= $SSCHMe_2$ (2.393(3) Å),[235] $SSSC_3H_7$ (2.370(2) Å),[235] $SS(O)CHMe_2$ (2.379(2) Å),[236] $SS(O)CH_2Ph$ (2.377(3) Å)[237] and $SS(O)_2$-4-C_6H_4Me (2.383(2) Å).[236]

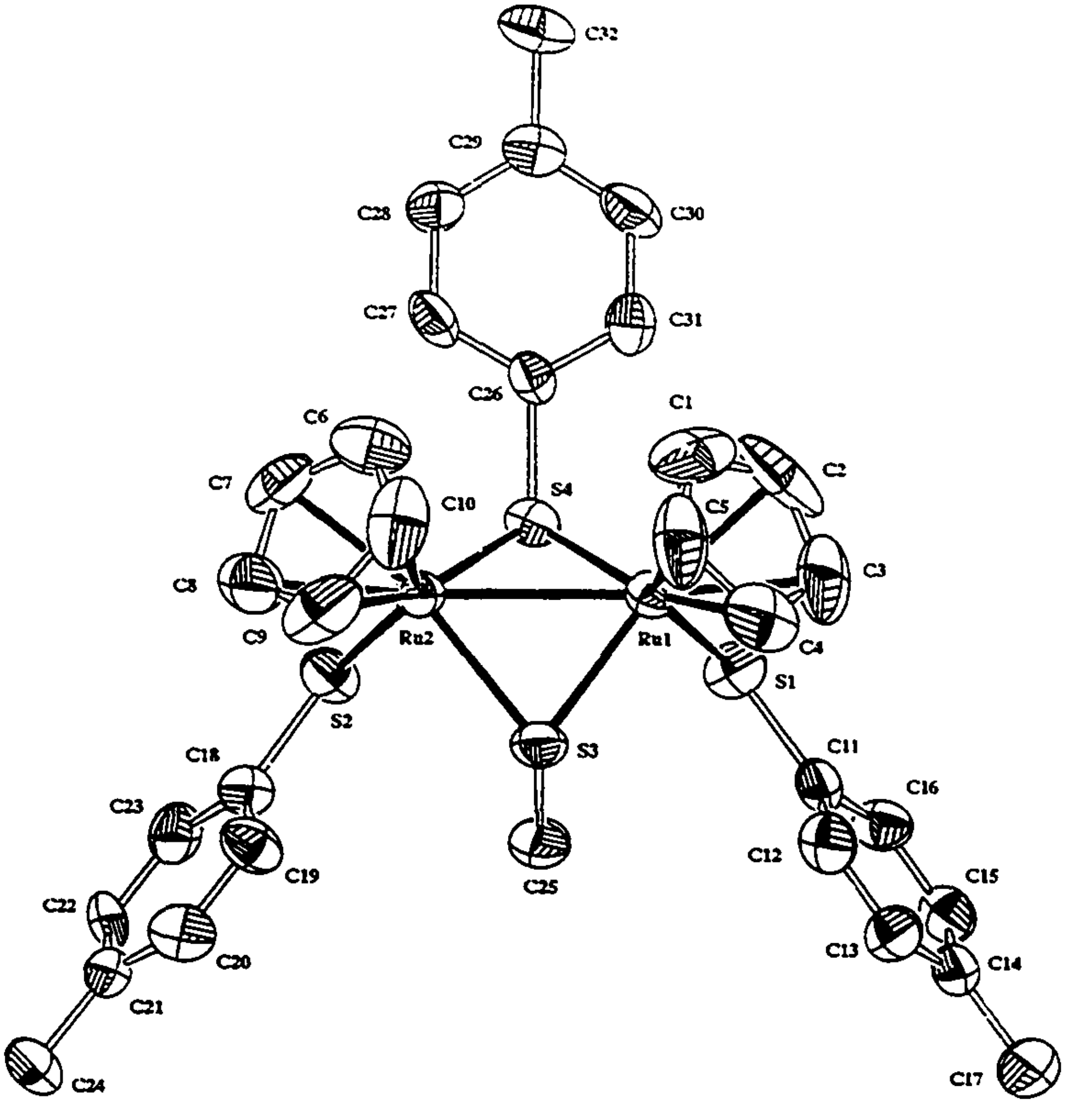


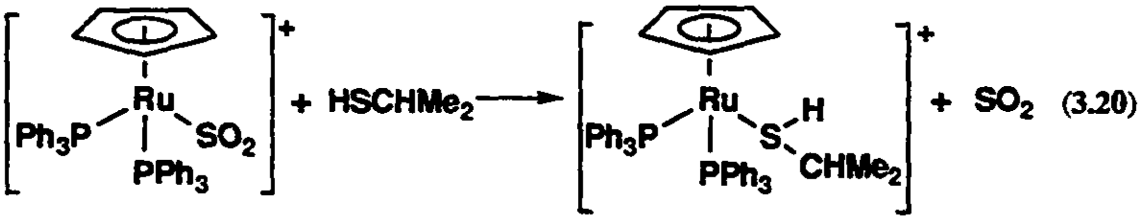
Figure 3.2: ORTEP drawing of (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)]$_2$, **9**.

DISCUSSION

As discussed in Chapter two, the electrophilic NO^+ group attacked the Ru-center of $CpRu(PPh_3)_2SR$ to give the salts $[CpRu(PPh_3)(NO)SR]^+$. In contrast, treatment of $CpRu(PPh_3)_2SR$ with HBF_4 gave thiol salts of the formula, $[CpRu(PPh_3)_2(HSR)]BF_4$, **4a-c**, in which the electrophile attacked the sulfur atom of the thiolato ligands. This result is a good example of a simple protonation at sulfur of organometallic thiolate complexes.

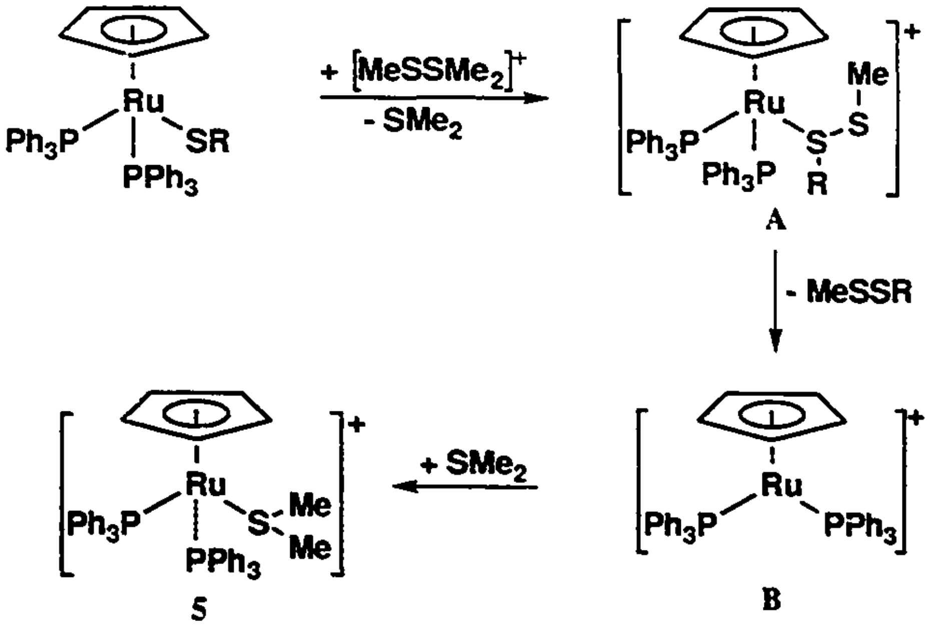
Each of the IR spectra of **4a-c** contains a weak band in the range 2514-2505 cm^{-1} due to the SH stretching frequency. These values are lower than those observed for the free thiols and indicated that the S-H bond is weakened upon coordination to the Ru-moiety. This shift to lower values was also observed for other systems.[256-259]

Complex **4c** has also been prepared by the reaction of $[CpRu(PPh_3)_2SO_2]^+$ with excess $HSCHMe_2$ (Equation 3.20), and was isolated as the PF_6 salt and structurally characterized.[266]



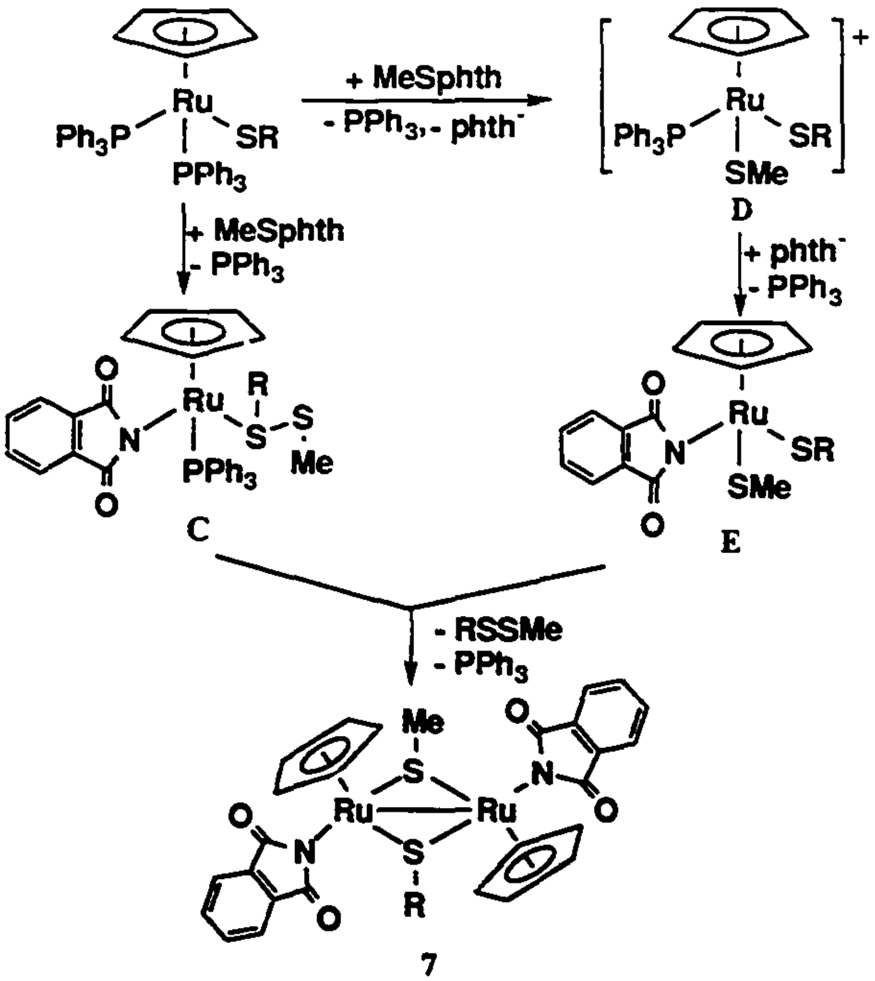
4c

The analogy between the electrophiles H^+ and RS^+ led to test the reactivity of the thiolato complexes with "RS^+" donors. The reaction of $CpRu(PPh_3)_2SR$ with $[MeSSMe_2]BF_4$ gave a methyl thioether complex, $[CpRu(PPh_3)_2SMe_2]BF_4$, **5**, regardless of the starting thiolato complex. A proposed route to **5** is shown in Scheme 3.4. The complexes $CpRu(PPh_3)_2SR$ undergo nucleophilic attack of the thiolato ligand at the S-atom of the sulfur transfer agent to give the intermediate **A** which loses a disulfide to give **B**. The latter reacts with Me_2S to give 5.



Scheme 3.4

The easily prepared N-thiophthalimides are good precursors of "RS^+". The reaction of $CpRu(PPh_3)_2SR$ (R= CMe_3, $CHMe_2$) with MeSphth gave the phthalimido compound, $CpRu(PPh_3)_2(phth)$, **6**, and the dimers (μ-SR)(μ-SMe)[CpRu(phth)]$_2$, **7a,b**. The formation of **6** is analogous to the formation of **5**, with the reaction of the phthalimide anion with intermediate **B** to give **6** being the only difference. A possible pathway to **7** is shown in Scheme 3.5. The disulfide complex, **C**, may form by nucleophilic attack of the thiolato ligand at the S-atom of the sulfur transfer agent. This is followed by the substitution of the PPh_3 ligand by the anionic phthalimido ligand. Intermediate **E**, which may be formed by the oxidative addition of MeSphth to the starting thiolato complex, reacts with **C** to form the dimer **7**.

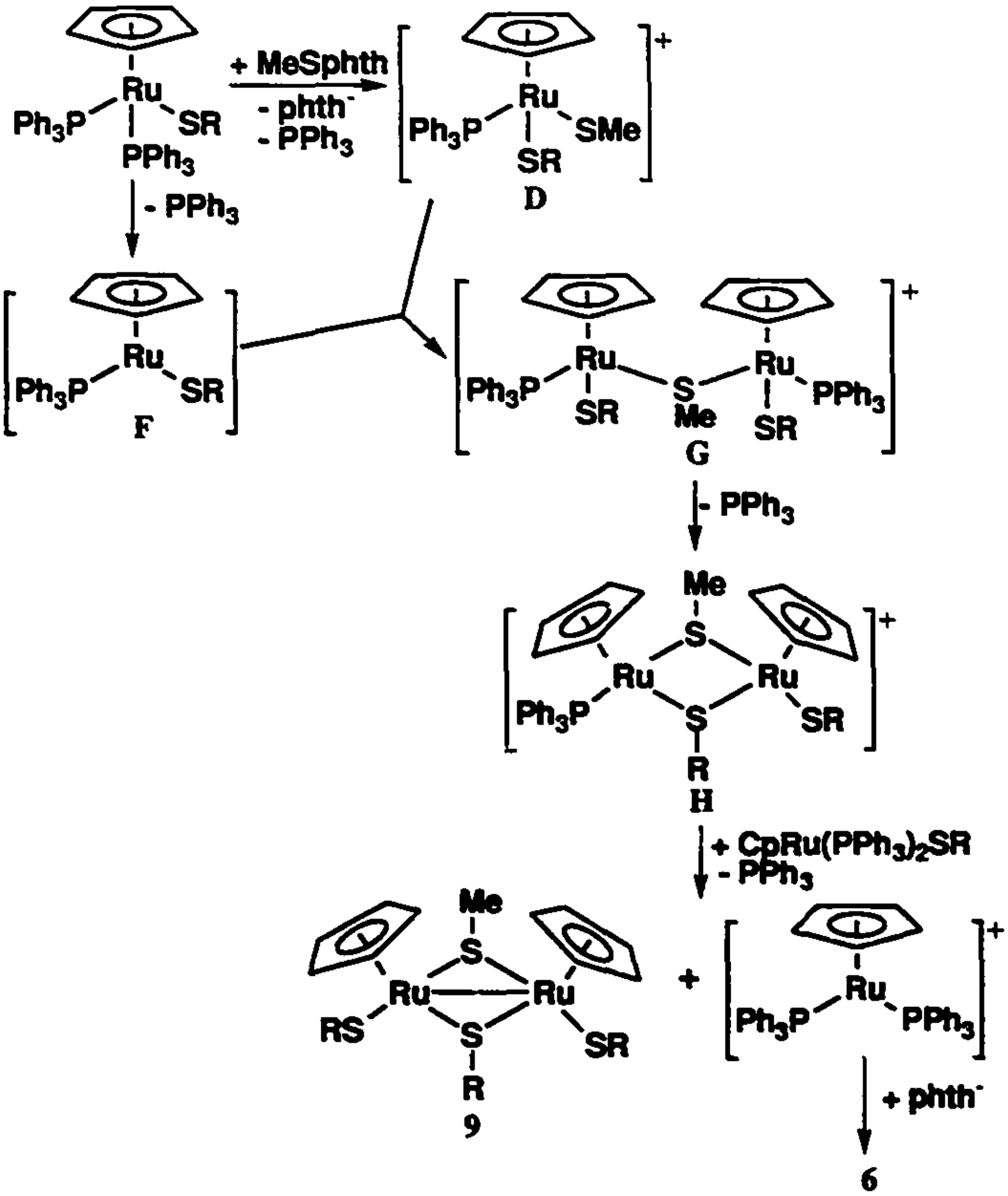


7

Scheme 3.5

The reaction of $CpRu(PPh_3)_2S\text{-}4\text{-}C_6H_4Me$ with MeSphth gave the expected disulfide complex, $CpRu(PPh_3)(phth)(MeSS\text{-}4\text{-}C_6H_4Me)$, **8**, the dimer $(\mu\text{-}SMe)(\mu\text{-}S\text{-}4\text{-}C_6H_4Me)[CpRu(S\text{-}4\text{-}C_6H_4Me)]_2$, **9**, and other unidentified compounds. Mechanistically, **8** is an isolated example of intermediate **C** in Scheme 3.5. A possible pathway to **9** is shown in Scheme 3.6 in which $CpRu(PPh_3)_2S\text{-}4\text{-}C_6H_4Me$ loses PPh_3 to give the unsaturated intermediate **F** which reacts with intermediate **D** to give the dimer **G**. The latter loses PPh_3 to give **H**, which in turn, reacts with another molecule of $CpRu(PPh_3)_2S$-

4-C_6H_4Me to give **9** and the unsaturated intermediate [CpRu(PPh_3)$_2$]. The latter intermediate reacts with the phthalimido anion to give **6**, which was detected in the NMR spectrum of the reaction mixture. Speculations such as these serve to provide a framework for consideration of the possible chemistry of the system and are not intended to be description of the events.



Scheme 3.6

CHAPTER 4

CHEMISTRY OF $CpRu(PPh_3)_2SCH_2CH=CH_2$

INTRODUCTION

The cleavage of the carbon-sulfur bond is very important in both biological systems[272] and industrial applications.[273] Particularly relevant to industry is the removal of sulfur from organosulfur compounds in crude oil. This is achieved by treatment of petroleum-based feedstocks with hydrogen at high temperature over metal catalysts.[274-292] This process, known as hydrodesulfurization (Equation 1.1), is the largest industrial application of transition metal catalysis presently practiced.[58]

The industrially-used catalyst for HDS is a $Co\text{-}Mo/Al_2O_3$ system which is prepared by the coimpregnation of Mo and Co salts on an alumina support followed by sulfidation with H_2S. The active sites are believed to be MoS_2 crystals with Co atoms coordinated to the sulfur at the edges of the basal planes.[274] Although the Mo based catalyst is the commercially used catalyst due to its low cost, higher activity catalysts exist based on Rh, Ir, Ru, Os, Pt and Pd.[275-278]

The sulfur content in petroleum varies over a wide range from 0.05 to 14%, depending upon the geological history of petroleum.[293] Sulfur is an expected constituent of petroleum because of the sulfur contained in the biological precursors of petroleum.[294] The common sulfur containing compounds present in petroleum are thiols, disulfides and thiophenes.[293,294] Thiophenes are the most difficult compounds to desulfurize, thus the majority of the studies done to understand the HDS process have been performed on thiophene and its derivatives.

Due to the commercial importance of HDS, the mechanism of the steps involved in it have been studied using surface science[53-55] and organometallic models.[56-60,295-349] These models have focused on the reactions of metal complexes with thiophenes. The mechanism of the HDS of thiophene involves three general steps, namely the coordination of thiophene to a metal center, carbon-sulfur bond cleavage and finally the hydrogenation of the organic part to give C_4 organic compounds.

Two mechanisms for the first step have been proposed. One involves initial coordination of thiophene to the metal *via* either π-donation (η^2, η^4, η^5)[295-312] or σ-donation (S-bonded thiophene)[313-329] as shown in Figure 4.1, and the other involves insertion of the metal atom into the carbon-sulfur bond to form a metallathiabenzene complex (Figure 4.2).[330-340]

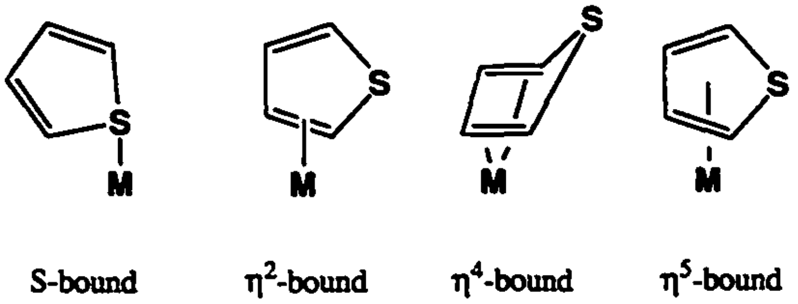


Figure 4.1: Coordination modes of thiophene.

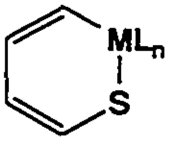
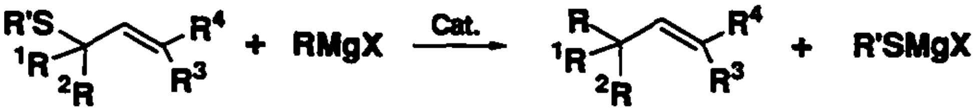


Figure 4.2: Metallathiabenzene formed by insertion of M into the C-S bond of thiophene.

Models have also been proposed for the subsequent steps in HDS which involves the carbon-sulfur bond cleavage, leading to desulfurization and hydrogenation. These models have demonstrated that the hydrogenation step can occur prior to[341-345] or after[346-349] the carbon sulfur bond cleavage.

Allylic carbon-sulfur bond cleavage reactions,[350-357] like those of allylic-oxygen and allylic halogen,[358-374] are used in synthetic organic chemistry. An important example is the synthesis of alkenes by the reaction of allylic sulfides with Grignard reagents (Equation 4.1).[350-355,375-385]

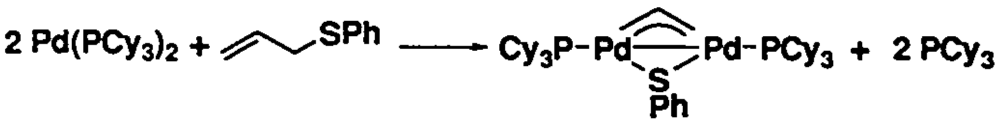


(4.1)

R= alkyl or aryl

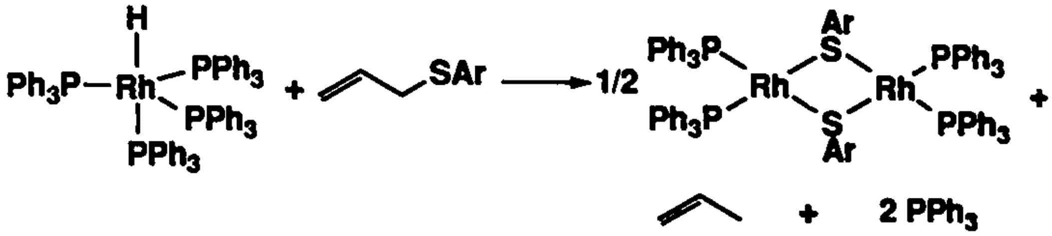
These reactions are catalyzed by Ni or Pd complexes as well as Cu(I) salts.[375-385] Alkenes with or without double bond migration are produced from these reactions. The ratio of the products can be influenced by changing the solvent, the catalyst and the leaving group. A proposed mechanism for these reactions involves formation of a π-allyl intermediate by C-S bond cleavage and subsequent external attack of the nucleophile on the π-allyl ligand.

The π-allyl intermediate, $(\mu\text{-SPh})(\mu\text{-C}_3\text{H}_7)[(\text{PCy}_3)_2\text{Pd}]_2$, as an example, has been isolated from the reaction of $\text{Pd(PCy}_3)_2$ with allylphenyl sulfide (Equation 4.2).[355]



(4.2)

The cleavage of the allylic C-S bonds in allyl aryl sulfides was also catalyzed by rhodium hydride complexes. The reactions of allyl aryl sulfides with rhodium hydride complexes were reported to give propene and the dimers $[(\text{PPh}_3)_2\text{Rh(SAr)}]_2$ (Equation 4.3).[386]



(4.3)

Ar= C_6H_5, 4-C_6H_4Me, 2-C_6H_4Me, 4-C_6H_5F, 4-C_6H_4OMe

The aryl C-S bond was not cleaved in these reactions, as no aromatic compounds were formed. The proposed mechanism for these reactions involved insertion of the carbon-carbon double bonds into the Rh-H bond followed by the reductive elimination of the Rh moiety and the thiolato ligand.

The cleavage of the allyl-sulfur bond can be achieved without a catalyst at high temperature. One example is the preparation of pure propene by the pyrolysis of methylallyl sulfide (Equation 4.4).[357]

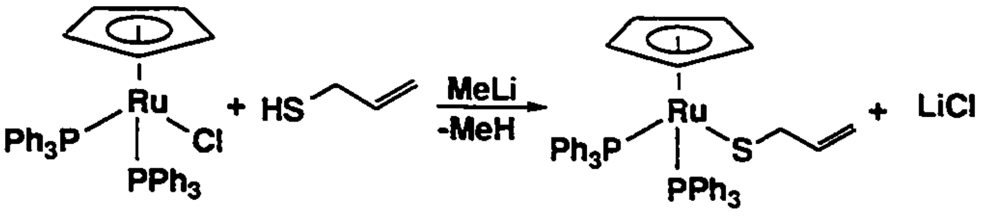
(4.4)

The reactivity of the electron rich ruthenium thiolates, $CpRu(PPh_3)_2SR$, reported here and elsewhere[176,232] prompted the preparation of the complex $CpRu(PPh_3)_2SCH_2CH=CH_2$ to see if carbon-sulfur bond cleavage could be achieved. When this complex was heated in toluene, the result was desulfurization of the allylthiolato ligand to give $(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH=CH_2)[CpRu]_3$. The reactions of the allylthiolato complex with CO and CS_2 are also presented. Protonation and methylation of the carbonyl analog $CpRu(PPh_3)(CO)SCH_2CH=CH_2$ gave $[CpRu(PPh_3)(CO)(HSCH_2CH=CH_2)]^+$, $[CpRu(PPh_3)(CO)(MeSCH_2CH=CH_2)]^+$, respectively.

RESULTS

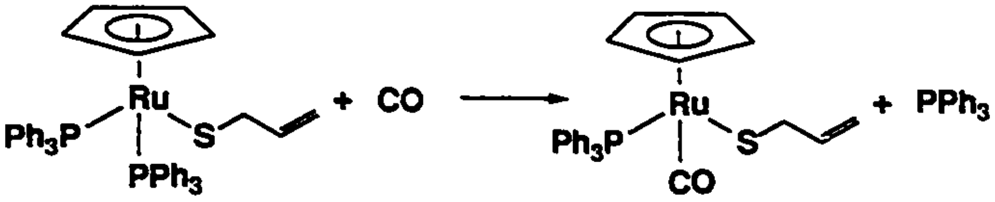
When $CpRu(PPh_3)_2Cl$ was briefly refluxed with excess $LiSCH_2CH=CH_2$ in THF the complex $CpRu(PPh_3)_2SCH_2CH=CH_2$, **10**, was obtained in 81% yield (Equation 4.5). If CO gas was bubbled through a THF solution of **10**, the complex $CpRu(PPh_3)(CO)SCH_2CH=CH_2$, **11**, was produced in which a CO group has replaced a PPh_3 ligand (Equation 4.6). Compound **10** reacted easily with CS_2 to give the thioxanthate complex $CpRu(PPh_3)S_2CSCH_2CH=CH_2$, **12**, in which a CS_2 molecule was inserted into the Ru-S bond (Equation 4.7). These reactions are analogous to the reactions of the simple Ru-thiolate complexes, $CpRu(PPh_3)_2SR$.[176] These complexes (**10**, **11** and

12) are moderately air stable both in solution and in the solid state. They were characterized by IR, ^{1}H NMR spectroscopy and elemental analysis.



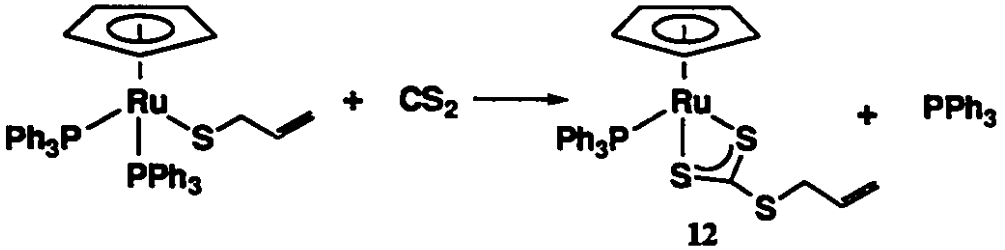
10

(4.5)



11

(4.6)

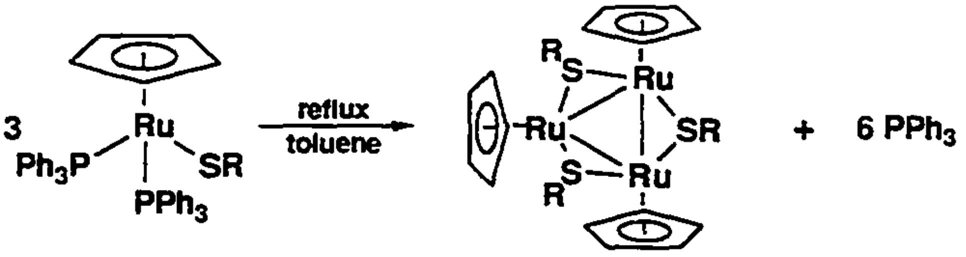


12

(4.7)

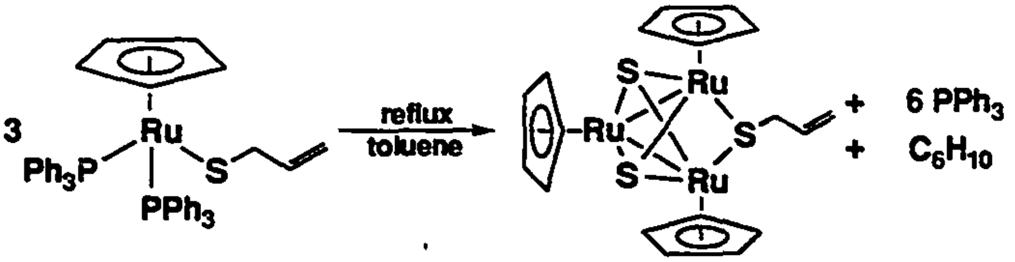
Simple Ru-thiolate complexes, CpRu(PPh$_3$)$_2$SR lose both PPh$_3$ groups in refluxing toluene to give the trimers [CpRu(SR)]$_3$^{232} (Equation 4.8). Compound **10** underwent C-S bond cleavage in addition to the loss of both PPh$_3$ ligands to give the trimer (μ_3-S)$_2$(μ-SCH$_2$CH=CH$_2$)[CpRu]$_3$, **13**, in 42 % yield (Equation 4.9). The air stable complex **13** is soluble in THF, benzene and ether. Its ^{1}H NMR spectrum showed two peaks in the Cp-region in a 2:1 ratio. The crystal structure of **13** is presented in Figure

4.3.[233] The crystal data, thermal parameter, atom coordinates and bond lengths and bond angles are given in Appendix 3, Tables A3.1-A3.4 respectively.



(4.8)

R= C_3H_7, $CHMe_2$, 4-C_6H_4Me



(4.9)

13

Four independent but very similar molecules of **13** were found in the unit cell, of which, only one is depicted in Figure 4.3. The molecule consists of a triangle of ruthenium atoms with one Cp ligand on each metal atom. The two sulfur atoms triply bridge the ruthenium atoms and the one thiolato group bridges two of the ruthenium atoms. The Ru-Ru bond lengths of 2.800(1) and 2.780(2) Å are longer than the corresponding average length in the trimer[232] $[CpRuS(C_3H_7)]_3$ (average 2.715 Å) and similar to those observed in $(\mu_3\text{-Cl})(\mu_3\text{-S})[CpRu]_3$ (average 2.770 Å).[387] The Ru-S(allyl) (doubly bridged) bond lengths of 2.403(4) and 2.388(3) Å are longer than those in $[CpRuS(C_3H_7)]_3$ (average 2.296 Å). The Ru-S (triply bridged) bond lengths (average 2.353 Å) are longer than the corresponding lengths in $(\mu_3\text{-Cl})(\mu_3\text{-S})[CpRu]_3$ (average 2.292 Å).[387]

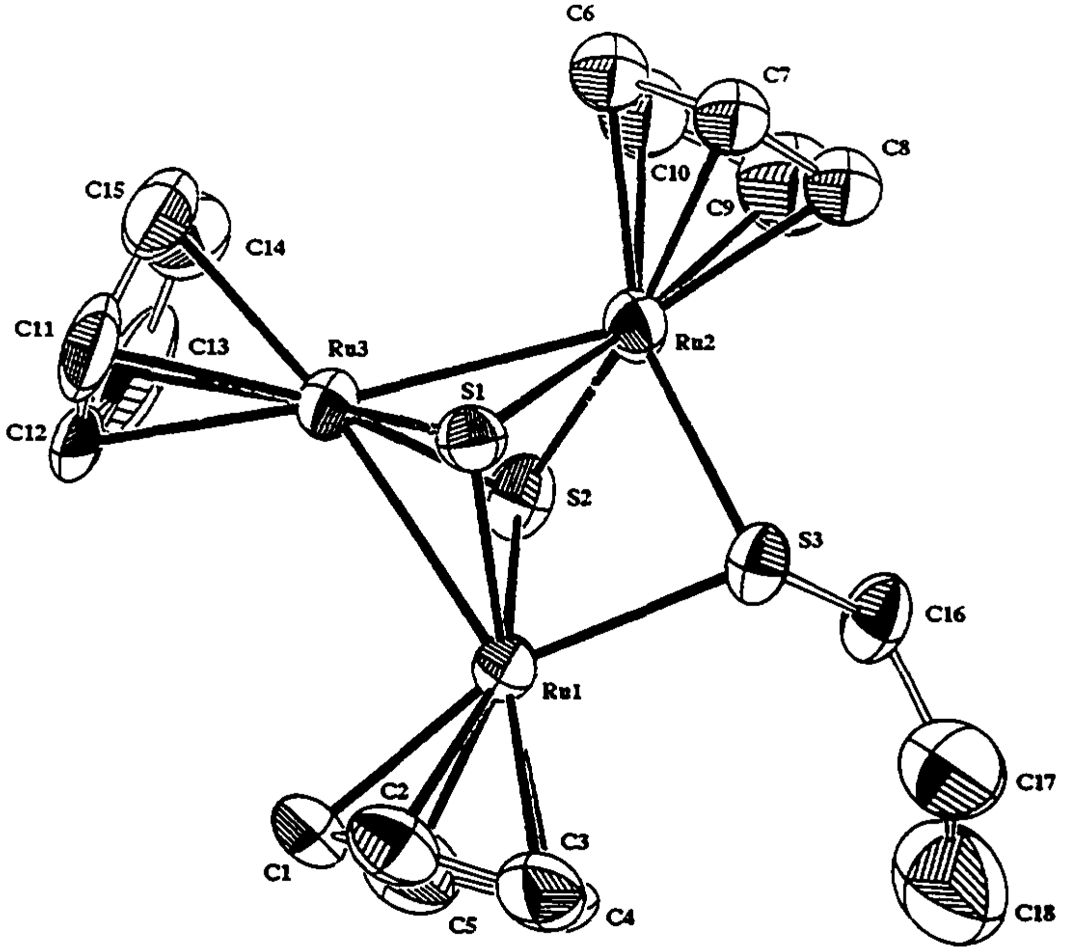
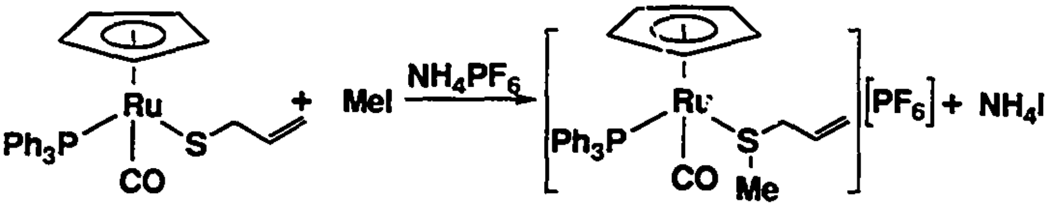


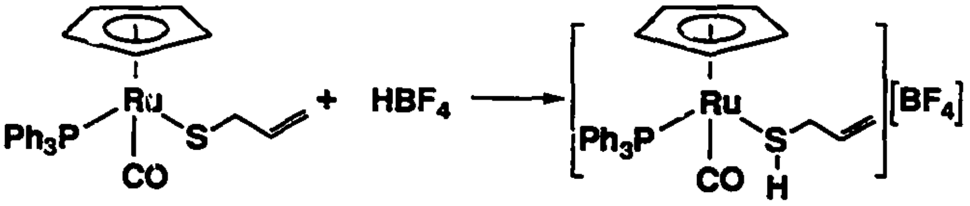
Figure 4.3: ORTEP drawing of $(\mu_3\text{-S})_2(\mu\text{-CH}_2\text{CH=CH}_2)[\text{CpRu}]_3$, **13**.

The complex $CpRu(PPh_3)(CO)SCH_2CH{=}CH_2$, **11**, reacted with MeI in the presence of NH_4PF_6 to give the salt $[CpRu(PPh_3)(CO)(MeSCH_2CH{=}CH_2)]PF_6$, **14**, in very good yield (81%) (Equation 4.10). Compound **11** also reacted with HBF_4 in THF at room temperature to give the thiol complex, $[CpRu(PPh_3)(CO)(HSCH_2CH{=}CH_2)]BF_4$, **15** (Equation 4.11). These salts were characterized by IR, ^1H NMR spectroscopy and elemental analysis. This chemistry of **11** is similar to that of the simple thiolato complexes, $CpRu(PPh_3)(CO)SR$.[155]



14

(4.10)



15

(4.11)

The ^1H NMR spectra of **10-15** contain peaks pertaining to the Cp, the PPh_3 (except **13**) and the S-bonded allyl groups (Table 4.1). The allyl group has three different types of protons (Figure 4.4): H_a, which is coupled to one H_b proton, appears as a doublet in the range 2.79-3.80 ppm; H_b, a multiplet due to coupling to H_a and H_c protons, appears in the range 5.61-5.93 ppm; and H_c and $H_{c'}$, a four doublets due to the coupling to each other and to coupling to H_b, appear in the range 4.86-5.36 ppm. Compound **14** showed a singlet for the methyl group of the thioether ligand. Compound **15** showed a multiplet at 3.40 ppm for the S<u>H</u> proton of the thiol ligand. The presence of two chiral centers in **14** and **15** is expected to generate two diastereomers. The NMR spectrum of **15** showed only one set of peaks consistent with rapid equilibrium of the two isomers at room temperature, while that of **14** showed that the peaks are broad consistent with slow equilibrium on the NMR time scale.

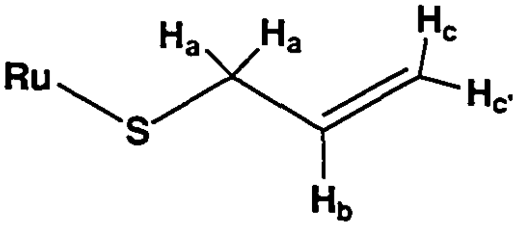


Figure 4.4: The S-bonded allyl group showing the types of the protons.

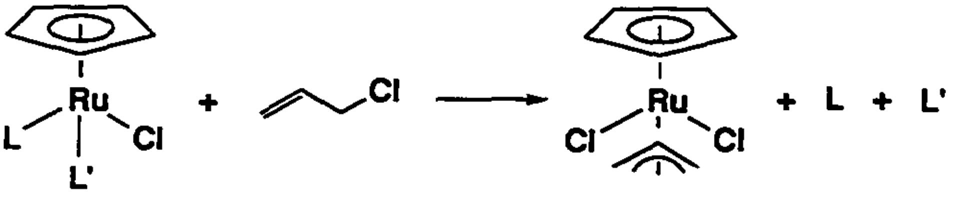
Table 4.1: ^{1}H NMR data for compounds **10-15**.[a]

Compound	Cp	H_a	H_b	H_c
10[b]	4.38	3.06	6.80	5.02, 5.28
11[b]	4.70	3.24	6.21	5.00, 5.21
12[b]	4.25	3.43	5.61	4.86, 4.94
13[b,c]	4.46, 4.78	2.79	5.93	4.95, 5.15
14[d,e]	5.56	3.50	5.70	5.29, 5.36
15[d,f]	5.50	3.40	5.80	5.25, 5.35

a) Phenyl resonances of PPh_3 appeared as two multiplets in the range 7.03-7.44 ppm and 7.45-7.60 ppm in the ratio 3:2. b) In C_6D_6 solution. c) No PPh_3 ligand. d) In acetone-d_6 solution. e) The Me group of the thioether ligand appeared as a broad singlet at 3.80 ppm. f) The SH of the thiol ligand appeared as multiplet at 3.40 ppm.

DISCUSSION

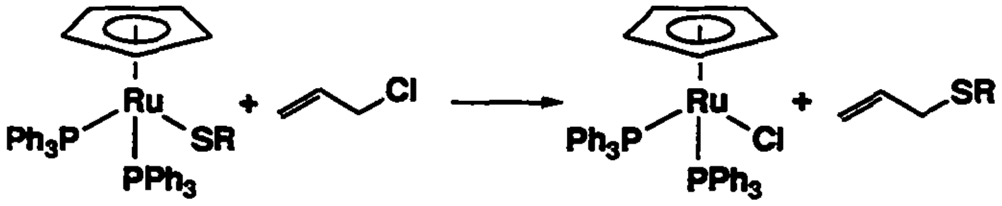
The reactivity of the complexes CpRu(PPh$_3$)$_2$Cl and CpRu(PPh$_3$)$_2$SR toward nitrosyl salts was discussed in Chapter two. When the ruthenium complexes, CpRu(L)(L')Cl, were treated with allyl chloride, oxidative addition occurred to give the η^3-allyl complexes as shown in Equation 4.12.[388-390]



(4.12)

L= L'= CO, PPh$_3$; L= CO, L'= PPh$_3$

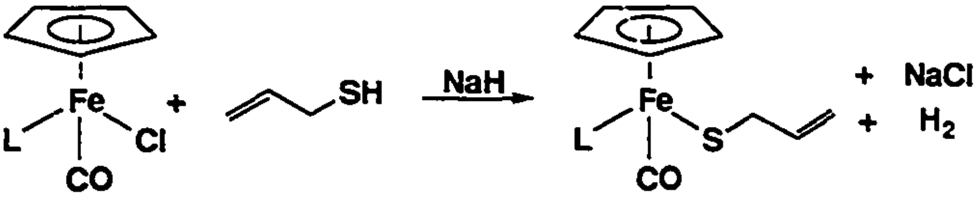
However, reaction of CpRu(PPh$_3$)$_2$SR with allyl chloride in THF at room temperature gave the chloro complex CpRu(PPh$_3$)$_2$Cl (Equation 4.13) in which the chloride ion was substituted for the thiolato ligand. This is not a surprising result, since the ruthenium thiolate complexes, CpRu(PPh$_3$)$_2$SR, are known to react with chlorinated solvents to give the chloro complex.[176]



(4.13)

R= CMe$_3$, 4-C$_6$H$_4$Me, CHMe$_2$

The preparation of $CpRu(PPh_3)_2SCH_2CH=CH_2$, **10**, was achieved by the reaction of $CpRu(PPh_3)_2Cl$ and lithium allylthiolate. That complex **10** has an S-bonded allythiolate ligand was deduced from its IR and ^1H NMR spectra. Similar iron complexes containing an S-bonded allylthiolato ligand have been prepared by the same method (Equation 4.14).[391]



(4.14)

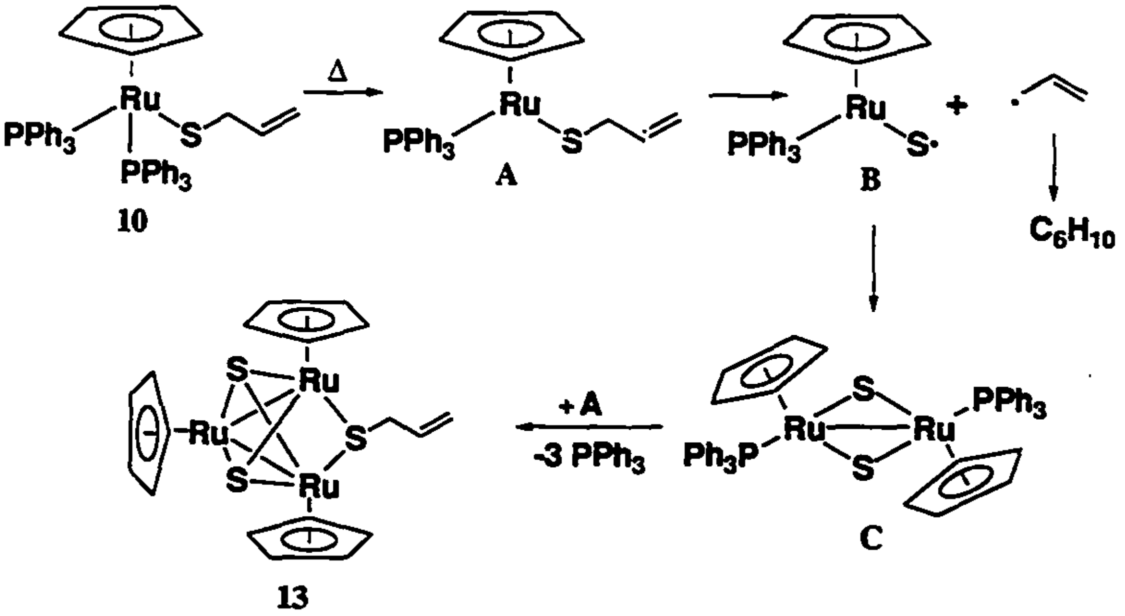
L= CO, PPh_3

Complex **10** reacted with CO gas to give the substituted product $CpRu(PPh_3)(CO)SCH_2CH=CH_2$, **11**, and with CS_2 to give the thioxanthate analog $CpRu(PPh_3)S_2CSCH_2CH=CH_2$, **12**. These reactions did not result in the cleavage of the C-S bond but were similar to those of the simple thiolato complexes, $CpRu(PPh_3)_2SR$ (R= C_3H_7, $CHMe_2$, 4-C_6H_4Me).[176]

The cleavage of the S-C bond was achieved when **10** was heated in toluene resulting in the formation of $(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH=CH_2)[CpRu]_3$, **13**. The sulfur atom fragment of the allyl thiolato ligand remained coordinated to the Ru_3-moiety, while the C_3 organic fragment was no longer coordinated. The analogous reactions of $CpRu(PPh_3)_2SR$ (R= C_3H_7, $CHMe_2$, 4-C_6H_4Me) gave the trimers $[CpRu(SR)]_3$ in which no S-C bond cleavage was observed

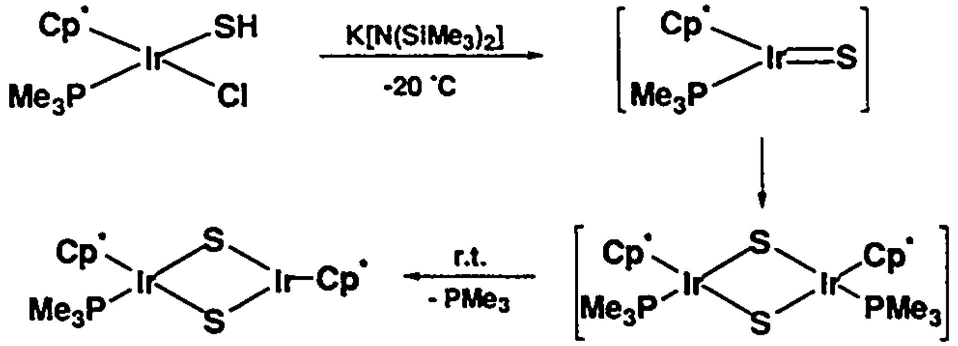
The fate of the C_3 fragment is not known. The product may be a hexadiene (C_6H_{10}). All the isomers of this formula (i.e. 1,3-hexadiene, 1,5-hexadiene) have low boiling points and may have been lost during the reflux or, at a latter stage, during the removal of the solvent. An NMR tube reaction in toluene-d_8 showed multiple peaks in the ranges 2.5-3.0, 4.1-5.2 and 5.5-6.1 ppm that are consistent with the presence of isomers of hexadiene.

One possible reaction sequence for **13** is shown in Scheme 4.1. Compound **10** loses a PPh_3 ligand when heated to form the unsaturated intermediate **A**, which undergoes homolytic C-S bond cleavage to give **B** and an allyl radical. Both radicals dimerize to give **C** and hexadiene, respectively. The dimer **C** reacts with another molecule of **A** to give a trimer that loses three PPh_3 ligand to give **13**.



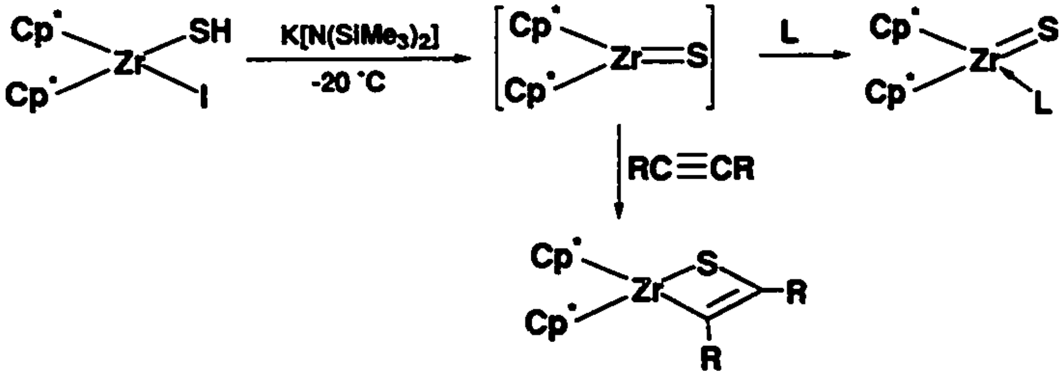
Scheme 4.1

Species such as **B** above are postulated as intermediates in some reactions.[392-396] The complex $Cp^*Ir(PMe_3)(SH)(Cl)$ underwent dehydrohalogenation when it was treated with base to give the intermediate Cp*Ir(PMe$_3$)(=S). The latter rearranged at room temperature to give the dimer Cp$^*{}_2$Ir$_2$S$_2$(PMe$_3$) as shown in Scheme 4.2.[392]



Scheme 4.2

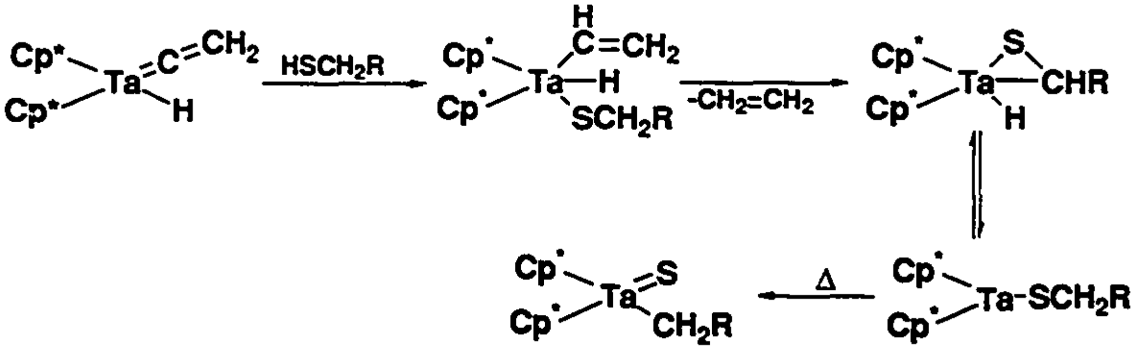
Similarly the thiolo complex Cp$^*{}_2$Zr(SH)(I) underwent dehydrohalogation to give the intermediate Cp$^*{}_2$Zr(=S) which reacted with ligands (L), such as pyridine, to give Cp$^*{}_2$Zr(=S)(L) or reacted with acetylenes to give metallacyclic complexes as shown in Scheme 4.3.[394,395]



L= pyridine, 4-*t*-butylpyridine; R= Et, Ph, 4-C$_6$H$_4$Me

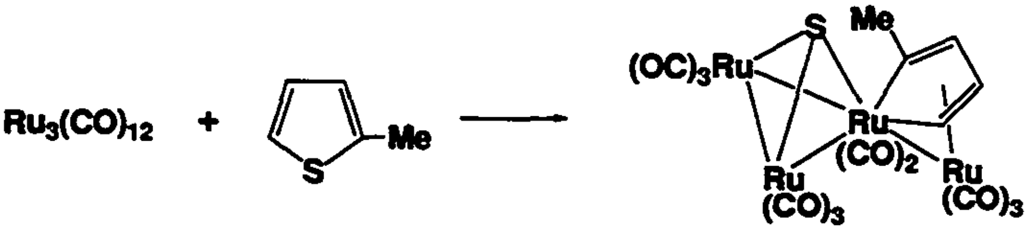
Scheme 4.3

The complexes $Cp^*_2Ta(\eta^2\text{-}S\text{-}CHR)(H)$, which were prepared by the oxidative addition of RSH to $Cp^*_2Ta(=C=CH_2)$, and then followed by the reductive elimination of ethylene, were in rapid equilibrium with the 16-electron thiolato complexes $Cp^*_2Ta(SCH_2R)$. These thiolato complexes gave complexes containing a sulfido ligand when heated as shown in Scheme 4.4.[396]



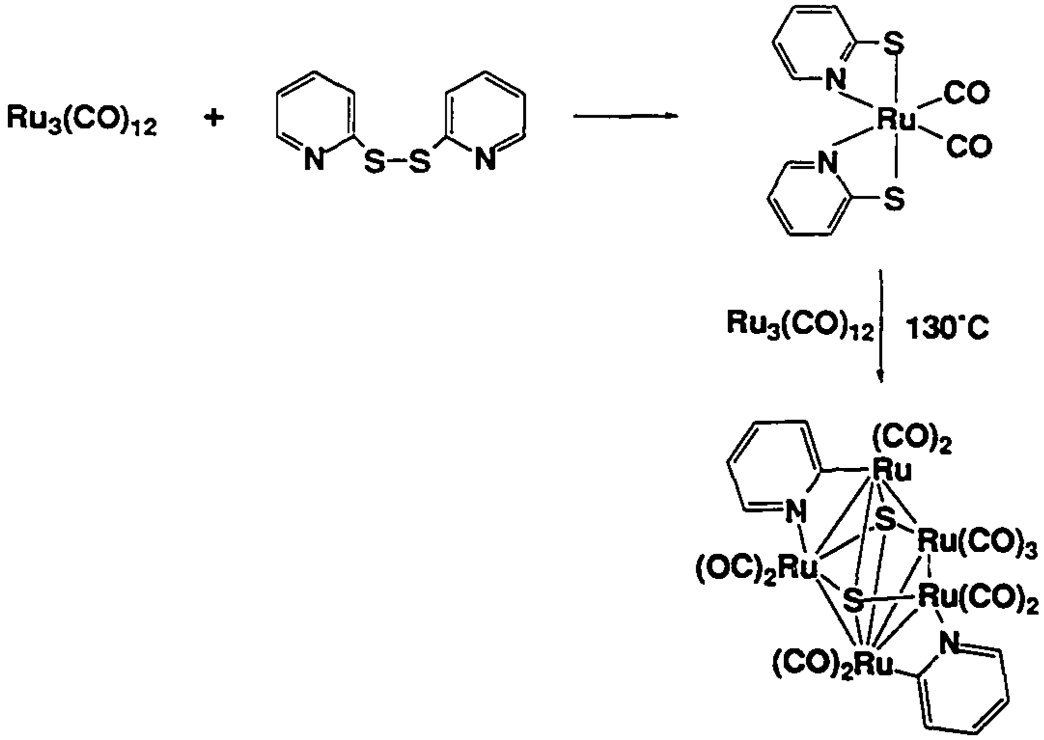
Scheme 4.4

The desulfurization of 2-methylthiophene[311] (Scheme 4.5) and 2,2′-dipyridyldisulfide[397] (Scheme 4.6) by $Ru_3(CO)_{12}$ has been reported. In these cases both fragments, (the sulfur atom and the organic fragment (C_4H_3Me or C_5H_5N)), were found in the coordination sphere of the organometallic products.



+ Other isolated products

Scheme 4.5



Scheme 4.6

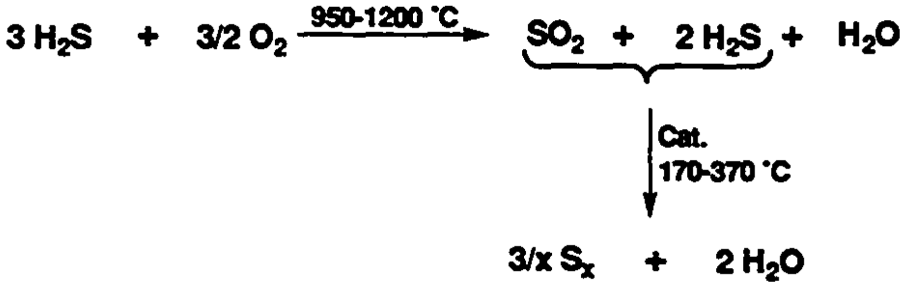
In terms of the hydrodesulfurization process, the desulfurization of allyl thiol has been achieved by heating $CpRu(PPh_3)_2SCH_2CH=CH_2$, which was prepared by the reaction of $CpRu(PPh_3)_2Cl$ with $HSCH_2CH=CH_2$ in the presence of MeLi. In this case the sulfur atoms remained coordinated to the metal atoms while the organic fragments were not retained.

CHAPTER 5

REACTIONS OF $(PPh_3)_2Pt(SR)_2$ WITH SO_2 ($R= H, CMe_3, CHMe_2, 4\text{-}C_6H_4Me$)

INTRODUCTION

Hydrodesulfurisation (HDS) converts organosulfur compounds to hydrocarbons and hydrogen sulfide.[53-60] The noxious H_2S gas is then converted to elemental sulfur and water *via* the Claus Process.[180-188] The Claus process is carried out in two stages (Scheme 5.1); in the first stage, one third of H_2S is converted to SO_2 in the presence of air and in the second stage, this SO_2 is reacted with the remainding H_2S to give sulfur and water.



Scheme 5.1

Although Scheme 5.1 shows the idealized reaction of the Claus process, the number of chemical reactions that describe what occurs in the actual process is very large.[398] Figure 5.1 shows the reactants and products of an actual Claus process as well as the observed contaminants of the Claus reaction. In addition to the expected sulfur products (S_x, H_2S, SO_2), combustion products (H_2O, CO_2) and inert gases (Ar, N_2), other species such as H_2, CO, COS and CS_2 are often found in the product stream. COS and CS_2 contain sulfur atoms and thus decrease sulfur recovery by as much as 10 percent.[398]

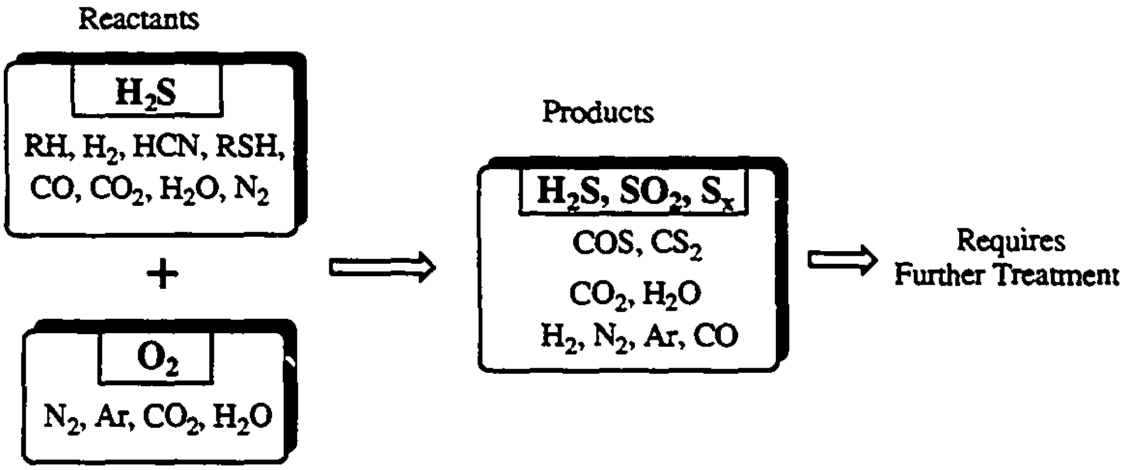


Figure 5.1: Actual reactants and products of the Claus process.

The production of CS_2 is usually attributed to the presence of hydrocarbons in the H_2S feed stream, since CS_2 is commercially produced by the reaction of elemental sulfur with saturated hydrocarbons.[399] One possible reaction for CS_2 formation is the oxidation of methane by sulfur (Equations 5.1 and 5.2).[399,400]

$$CH_4 + S_2 \xrightarrow{\text{high temp.}} CS_2 + 2\,H_2 \qquad (5.1)$$

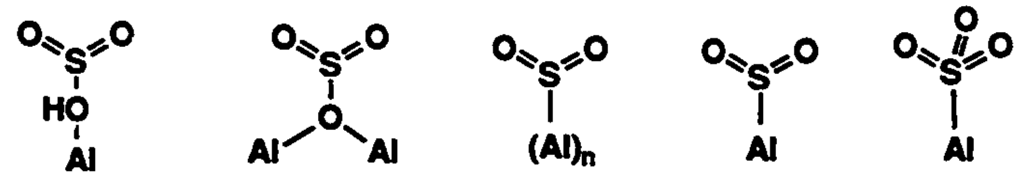
$$CH_4 + 2\,S_2 \xrightarrow{\text{high temp.}} CS_2 + 2\,H_2S \qquad (5.2)$$

On the other hand, the formation of COS appears to be a function of CO concentration. This observation supports the hypothesis that the oxidation of CO by elemental sulfur is the source of COS formation (Equation 5.3).[398-400]

$$\mathrm{CO} + 1/2\,\mathrm{S_2} \xrightarrow{\text{high temp.}} \mathrm{COS} \qquad (5.3)$$

Several attempts have been made to elucidate the mechanism of the Claus reaction through infrared spectroscopic studies[180-188] and the use of organometallic models.[159-162]

Model A (Scheme 1.4) has been investigated by studying the adsorption of SO_2 on an activated alumina[180-185,401-403] or on zeolites[66] followed by its reaction with H_2S, as monitored by IR spectroscopy. Five different types of SO_2-adsorbed species were identified as shown in Figure 5.2. SO_2 can be adsorbed to either acidic (Al atoms or ions) or to basic sites (O atoms or ions). The adsorption on acidic sites gives types III and IV species which contain a planar or pyramidal SO_2 bonded to an Al cluster or atoms. The adsorption on basic sites gives rise to type II species in which the SO_2 is bonded to an oxygen atom or ion. Transfer of an oxygen atom from the surface produces a sulfite-like species that attacks an Al atom in a unidentate fashion to give type V species. At higher SO_2 concentration, the adsorption occurs on the OH groups to give type I, where SO_2 is a weakly held physically adsorbed species.

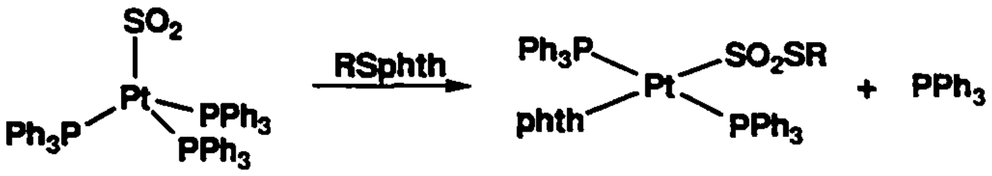


I	II	III	IV	V
1334, 1148	1332, 1140	1255	1189	1135, 1065

Figure 5.2: Possible adsorption modes of SO_2 on alumina with the corresponding $\nu_{(S=O)}$ (cm^{-1}) values.

The addition of H_2S to an alumina sample, on which SO_2 has been preadsorbed, resulted in a decrease in the intensities of the bands that are due to types I-IV, but not V. The physically adsorbed species (type I) were the first to react and followed by the SO_2 species that were adsorbed on acidic sites (types III and IV). Finally, type II species were consumed. The sulfite adsorbed species (type V) did not react with H_2S easily; it required heating to 200 °C for reaction to take place.[178]

Recently, an organometallic model corresponding to model A was demonstrated in our laboratory.[266] The reaction of the complex $(PPh_3)_3Pt(SO_2)$ with sulfur transfer reagents of the type RSphth gave complexes that contain the $(S(O)_2SR)$ group, namely *trans*-$(PPh_3)_2Pt(S(O)_2SR)(phth)$ (Equation 3.13). This is an example of a sulfur-sulfur bond formation which is one step of the Claus reaction.



(3.13)

R= Me, $CHMe_2$, Et, CH_2Ph, 4-C_6H_4Me.

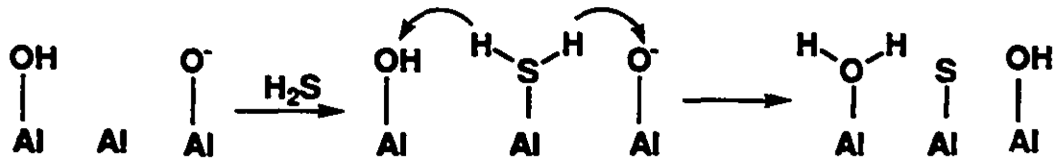
The adsorption of H_2S on activated alumina (model B) has been studied by IR spectroscopy.[182-187,404,405] It appeared from these studies that H_2S is adsorbed on alumina in two different forms, both involving adsorption on Al atoms (Figure 5.3).

VI VII

$\nu_{(SH)}$= 1334, 2578 cm^{-1}

Figure 5.3: Possible adsorption modes of H_2S on alumina.

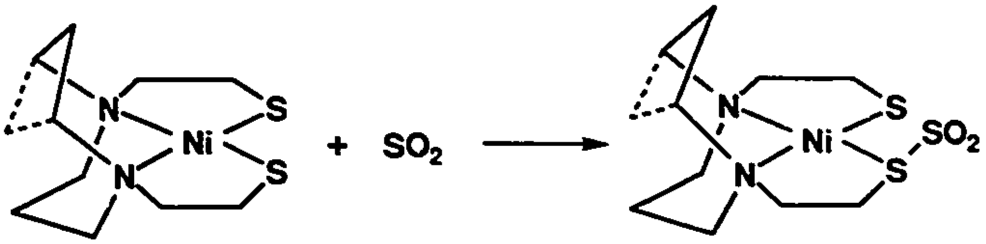
Type VI is non-dissociative in which the H_2S is weakly adsorbed on an isolated Al ion or Al cluster. The second type involves dissociative chemisorption of H_2S which leads to formation of an aluminum sulfide species (type VII). A possible route to the second type is represented in Scheme 5.2.[185] The formation of an Al-S species is the most likely product of chemisorption, since a band at 1720 cm^{-1} (bending vibration of water) appeared and increased in intensity with increased addition of H_2S.[185] The observed formation of metal sulfides by the dissociative adsorption of H_2S on many metal surfaces supports the contention that the species formed is Al-S.[406]



Scheme 5.2

Addition of SO_2 to an alumina sample pretreated with H_2S results in a decrease of the intensity of SH bands.[188] If enough SO_2 is added, the band at 1720 cm^{-1} increases gradually due to the formation of adsorbed water, indicating that Claus chemistry has occurred.

Organometallic analogs to model B are the reactions of SO_2 with thiolato complexes.[159-162] Examples of these reactions were presented in Chapter one (Equations 1.20-1.24). Another example is the formation of the nickel-SO_2 complex, (N,N'-bis(mercaptoethyl-1,5-diazacyclooctane)Ni(SO_2), which has been structurally characterized (Equation 5.4).[407] Several analogous Ni(SO_2) adducts were reported and their stabilities vary dramatically depending on the electronic and steric properties of the ancillary ligands.[407]



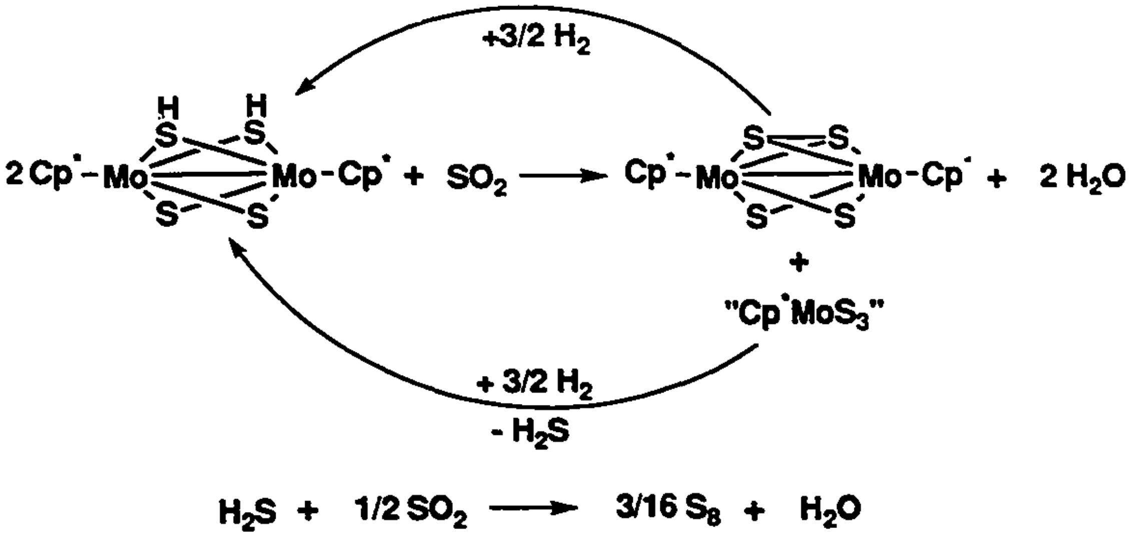
(5.4)

Such adducts (MS(SO_2)R) represent a possible first step in the Claus process (Model B), in which an S-S bond is formed. However no subsequent reactivity such as oxygen transfer has yet been observed.

Transition metal induced reduction[408-414] and oxygen transfer chemistry[415-419] of SO_2 have been reported. The homogeneous catalytic hydrogenation of SO_2 has been demonstrated using the complex $[Cp^*Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (Equation 5.5).[413]

$$3/2\ SO_2 + 3\ H_2 \xrightarrow[75\ ^\circ C]{\text{Mo-Cat.}} 3/16\ S_8 + 3\ H_2O \qquad (5.5)$$

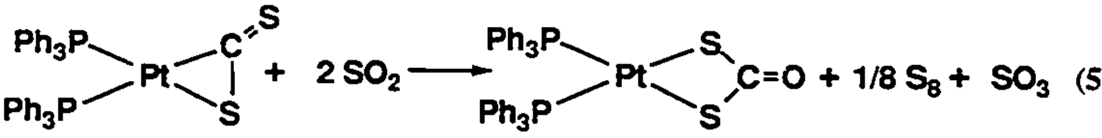
A possible mechanism for this reaction was proposed[413] and is shown in Scheme 5.3. The stoichiometric reaction of $[Cp^*Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ with SO_2 (no H_2) produced $Cp^*{}_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$, $(Cp^*MoS_3)_x$, and H_2O. Both Mo-containing products readily reacted with H_2 to regenerate $[Cp^*Mo(\mu\text{-}S)(\mu\text{-}SH)]_2$ and H_2S. The H_2S produced reacted with excess SO_2 to give sulfur and water (*via* the Claus reaction).



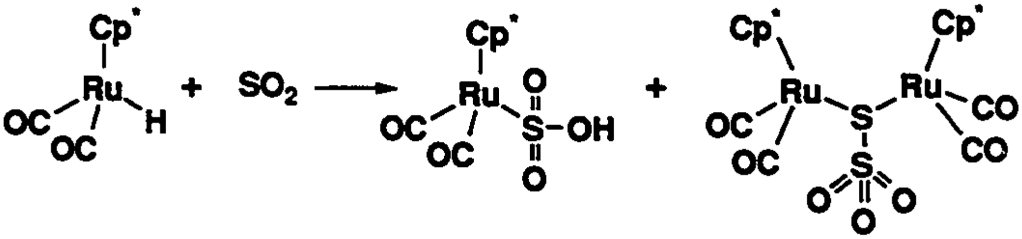
Scheme 5.3

In this catalytic cycle, sulfur is the final product if the catalysis is terminated before all the SO_2 is consumed. On the other hand, H_2S is the final product if excess H_2 is used.[413] The catalytic activity of this system decreases with time. The presence of a weak basic solvent (alcohol) or a catalytic amount of a Bronsted base (amines) promoted the reaction.[413,420]

Oxygen transfer reactions of SO_2 have been demonstrated in the literature.[415-419] The reaction of $(PPh_3)_2Pt(\eta^2\text{-}CS_2)$ and SO_2 demonstrates the function of SO_2 as an oxygen donor and receptor in the same reaction (Equation 5.6).[415,416]

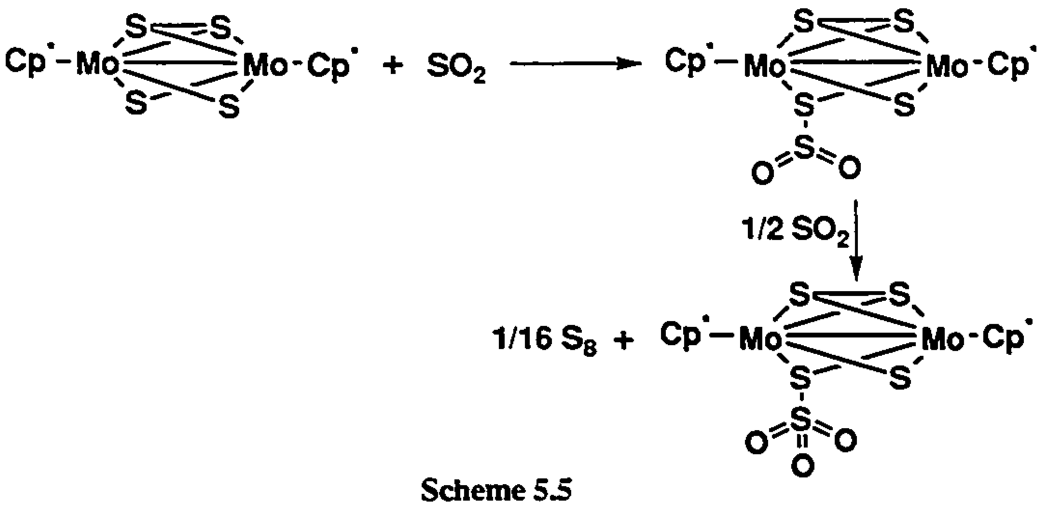

(5.6)

The reaction of the complex $Cp^*Ru(CO)_2H$ with SO_2 resulted in the formation of two soluble and crystallographically characterized complexes, namely, $Cp^*Ru(CO)_2(SO_3H)$ and $(\mu\text{-}S_2O_3)[Cp^*Ru(CO)_2]_2$ as shown below (Scheme 5.4).[417,418] Labeling studies using $S^{18}O_2$ had demonstrated that the ligands, SO_3H and S_2O_3 were formed *via* oxygen transfer from the SO_2 molecule.[418]



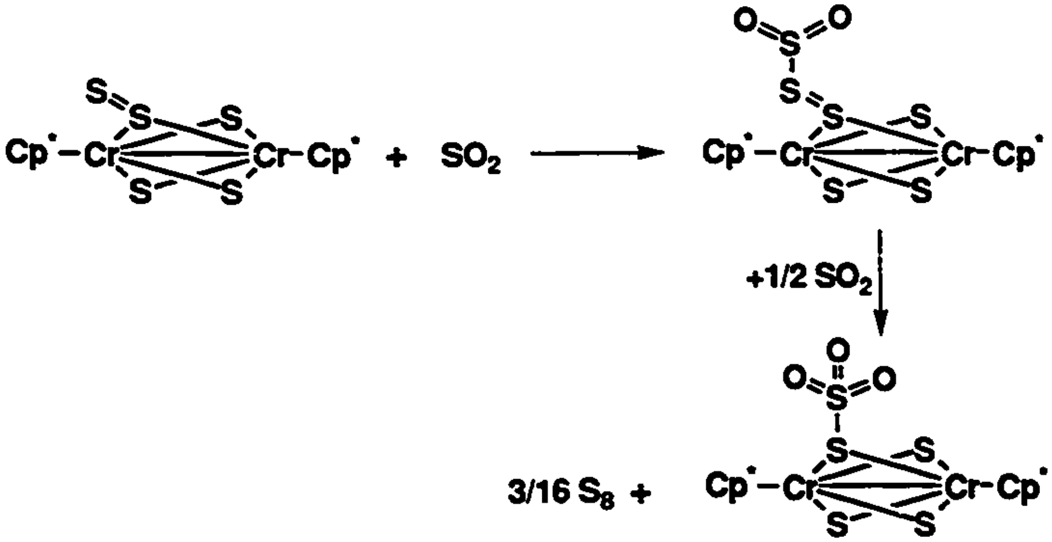
Scheme 5.4

Oxygen transfer has also been observed in the reaction of $Cp^*_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ with SO_2 (Scheme 5.5).[419]



Scheme 5.5

A very similar oxygen transfer has been demonstrated in solution upon treatment of the chromium dimer with SO_2 as shown in Scheme 5.6.[421] Crystallographic and ^{34}S-labeling studies suggested that the mechanism of this reaction involves a base-assisted oxygen transfer from the disulfide-SO_2 bound molecule to a free SO_2 molecule producing SO_3. The SO_3 displaces S_2O (which decomposed to S_8 and SO_2) to give the observed thiosulfate product.



Scheme 5.6

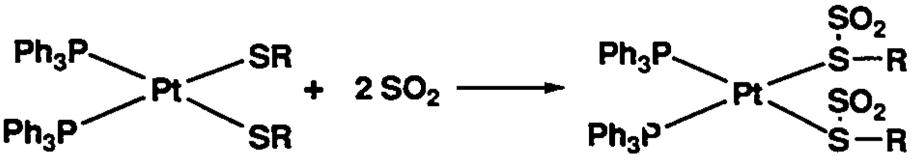
In this chapter, Model B is investigated by reacting the complexes $(PPh_3)_2Pt(SR)_2$ (*cis* for R= H, CMe_3, $CHMe_2$; *trans* for R= H, 4-C_6H_4Me) with SO_2. These reactions produced adducts of formula $(PPh_3)_2Pt(S(SO_2)R)_2$ for R= CMe_3, 4-C_6H_4Me and $CHMe_2$. The reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 gave $(PPh_3)_2Pt(S_3O)$ but no reaction was observed for the *trans*-isomer. The reaction of $(PPh_3)_2Pt(S_3O)$ with H_2S gave the starting thiolo complex, *cis*-$(PPh_3)_2Pt(SH)_2$ thus formally completing a stepwise Claus process. The catalytic activity or these complexes toward the Claus reaction is presented.

RESULTS

Reactions of $(PPh_3)_2Pt(SR)_2$ with SO_2

Methylene chloride solutions of $(PPh_3)_2Pt(SR)_2$ treated with SO_2 changed color from yellow to deep red. Addition of hexanes (saturated with SO_2) gave red-orange solids, $(PPh_3)_2Pt(S(SO_2)R)_2$, *cis* for R= CMe_3; **16a** and R= $CHMe_2$; **16c**, *trans* for R= 4-C_6H_4Me; **16b**, which easily lose SO_2 if not kept under an atmosphere of SO_2 (Equation 5.7). Upon dissolution in organic solvents, loss of SO_2 occurred to give the starting thiolato complexes. Consequently, the NMR spectra of these adducts were recorded in $CDCl_3$ saturated with SO_2. The ^1H NMR data, presented in Table 5.1, showed that the peaks for the thiolato ligands were shifted to higher field compared to those of the starting thiolato complexes. The IR spectra were recorded using KBr disks with quick sample preparation. In the IR spectra of **16a-c**, the SO stretching frequency appeared in the ranges 1280-1285 and 1091-1095 cm^{-1}, which is consistent with previous reports for adducts having a ligand bound SO_2 molecule.[159-162,190,191] The *t*-butyl adduct, $(PPh_3)_2Pt(S(SO_2)CMe_3)_2$, **16a**, was never isolated in pure form. Its IR, ^1H NMR and ^{31}P NMR spectra showed the presence of both the adduct, **16a** and the starting thiolato complexes.

The facile loss of SO_2 exhibited by **16a-c** is reflected by their elemental analysis results which were carried out under nitrogen atmosphere. These results showed that the compounds have higher carbon and hydrogen contents and less sulfur content than the calculated values (based on the presence of two coordinated SO_2 molecule). This is consistent with the easily loss of SO_2 from these adducts.



(5.7)

cis: R= CMe_3; **16a**, $CHMe_2$; **16c**
trans: R= 4-C_6H_4Me, **16b**

Table 5.1: Spectral data of $(PPh_3)_2Pt(S(SO_2)R)_2$, **16a-c**.

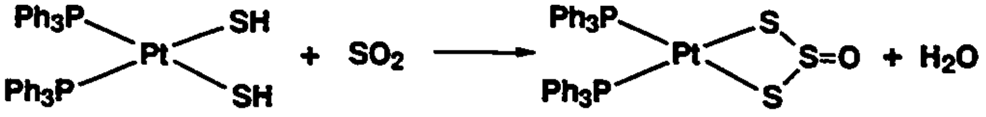
R		CMe_3	C_6H_4Me	$CHMe_2$
isomer		*cis*	*trans*	*cis*
^{1}H NMR[a,b] (ppm)	Me	1.11	2.19	1.22[c]
	$C\underline{H}Me_2$			3.68[d]
	$C_6\underline{H}_4Me$		6.74[c], 7.26[c]	
^{31}P NMR[a] (ppm) ($J_{P\text{-}Pt}$ (Hz))		20.5 (2930)	21.2 (2980)	20.3 (2926)
IR(KBr) $\nu_{(SO)}$ (cm^{-1})		1280, 1095	1282, 1091	1285, 1093

a) In $CDCl_3$ saturated with SO_2. b) PPh_3 resonances appear as a broad singlet in the range 7.26-7.40 ppm. c) Doublet. d) Septet.

The reactions of $Cp_2Ti(SR)_2$ (R= H, CMe_3, $CHMe_2$, 4-C_6H_4Me) with SO_2 in methylene chloride at room temperature were also examined. These reactions resulted in the formation of an orange solid that precipitated from the reaction mixture. This solid was insoluble in common organic solvents. It was characterized by elemental analysis and mass spectroscopy. Both results indicated that the most probable product is a polymer of the formula $(Cp_2TiS)_x$. These materials were not studied further due to their intractability.

Reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2

Treatment of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 in CH_2Cl_2 at room temperature gave $(PPh_3)_2Pt(S_3O)$, **17** in 82% isolated yield (Equation 5.8).



17

(5.8)

The ^1H NMR spectrum of **17** displayed a multiplet in the aromatic region and its ^{31}P NMR spectrum showed a singlet at 18.5 ppm with satellites ($J_{Pt\text{-}P}$= 3200 Hz) arising from coupling to ^{195}Pt (33% abundance, S= 1/2). This value is shifted to a higher field compared to that of *cis*-$(PPh_3)_2Pt(SH)_2$ (21.4 ppm, $J_{Pt\text{-}P}$= 2980 Hz). The IR (Nujol) spectrum displayed a band at 1065 cm^{-1} for the S=O stretching frequency.[190,191] The mass spectrum (FAB in NBA) of **17** showed the following peaks: 832 ($M^{+\bullet}$), 748 ($(PPh_3)_2PtS_2$), 752 ($(PPh_3)_2PtS$) and 720 ($(PPh_3)_2Pt$) together with other fragments. The elemental analysis of the complex agreed with the proposed molecular formula.

From the logic of the synthesis, the reaction shown in Equation 5.8 should give water in addition to **17**. One molecule of water was produced from this reaction as shown from the ^1H NMR spectra shown in Figure 5.4. Figure 5.4A shows the ^1H NMR spectrum of deuterated acetone saturated with dry SO_2 (dried by bubbling through concentrated H_2SO_4 solution and then passed through a column of phosphorus pentoxide). Figure 5.4B shows the ^1H NMR spectrum of the reaction mixture, and one can conclude from the integration of the peaks that water was produced in the appropriate amount relative to **17**.

Attempts to deuterate the complex *cis*-$(PPh_3)_2Pt(SH)_2$ using methanol-d_4 failed for the ^1H NMR spectrum of this reaction mixture showed the disappearance of the SH peak, while no deuterium signal for the intended product, *cis*-$(PPh_3)_2Pt(SD)_2$, was observed in the ^2H NMR spectrum.

The crystal structure of **17** was determined and is shown in Figure 5.5.[233] The crystal data, atom coordinates, bond lengths and bond angles and least square planes are given in Appendix 4, Tables A4.1-A4.5 respectively. The oxidized sulfur atom is disordered over two orientations of relative occupancy 0.77 and 0.23. The Pt-S distances (2.341(3) & 2.318(2) Å) are within the range observed for complexes containing a (PtSCS) rings (Table 5.2) but longer than the Pt-S distance in *trans*-$(PPh_3)_2Pt(phth)S(O)_2SCH_2Ph$.[266] The S-S and S=O distances are similar to those observed for complexes containing $S(O)_2SR$, SS(O)R and $SS(O)_2R$ groups.[235,236,266] The S-Pt-S angle is larger than that in complexes containing the (PtSCS) rings. The sulfur atom S2 is out of plane formed by P1P2PtS1S3; the dihedral angle between the plane containing P1P2PtS1S3 and the plane containing S1S2S3 is 22.34°.

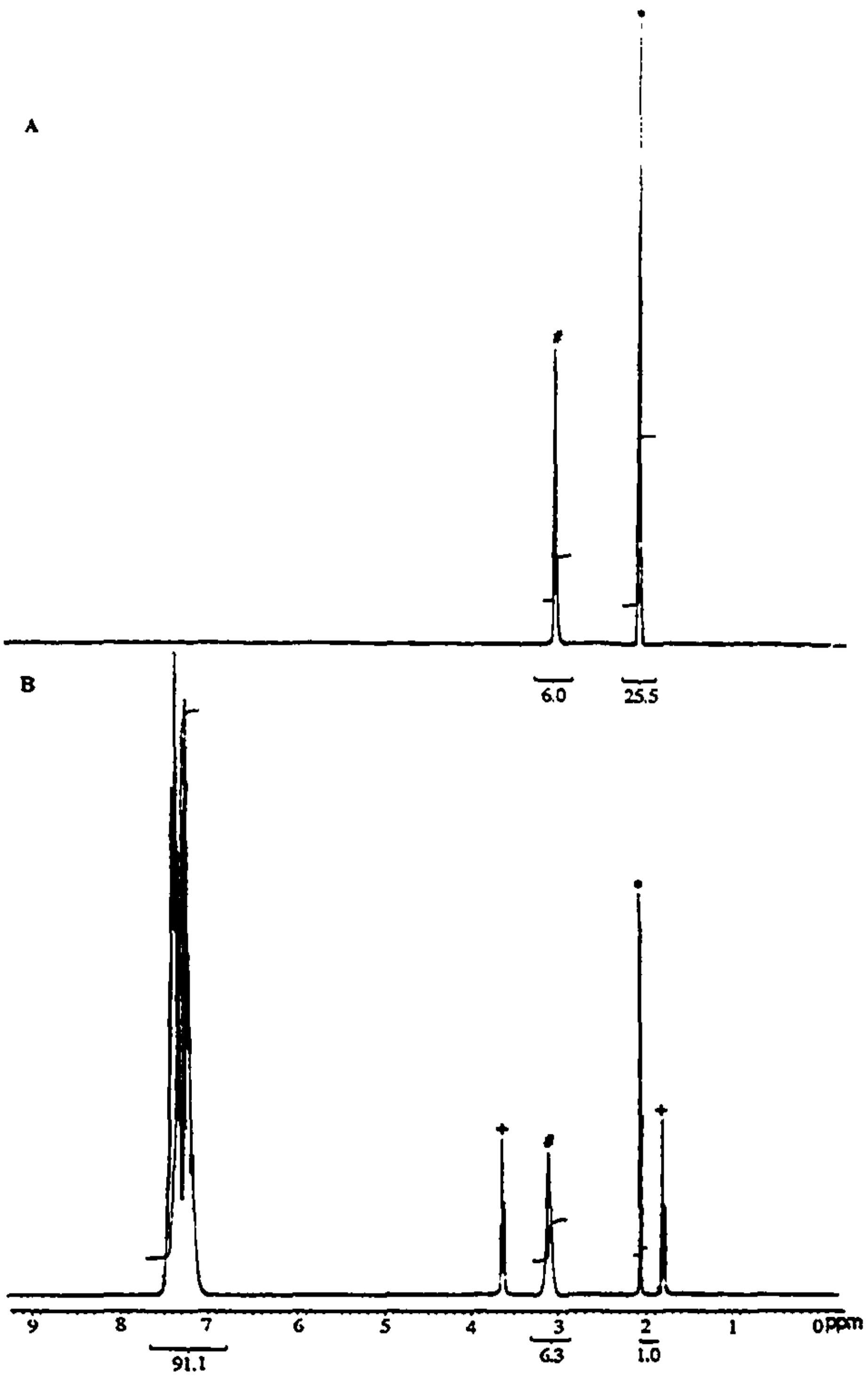


Figure 5.4: ^{1}H NMR spectrum of a) Acetone-d_6 saturated with SO_2. b) Products of the reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ and SO_2 in acetone-d_6. (*= solvent peak, #= water peak, += THF impurity).

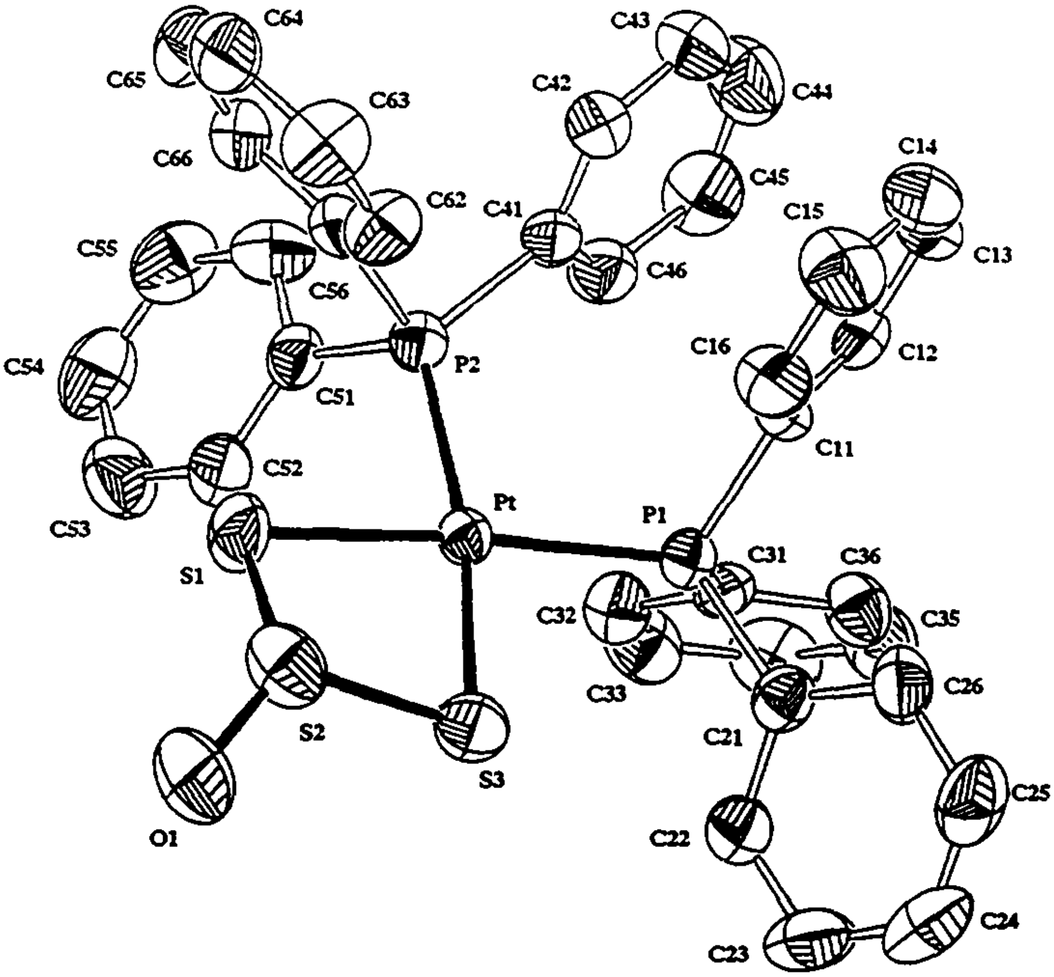


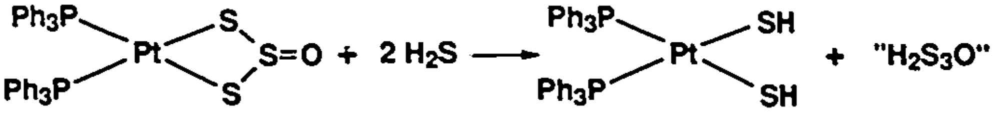
Figure 5.5: ORTEP drawing of $(PPh_3)_2Pt(S_3O)$, 17.

Table 5.2: Selected Structural parameters of some platinum complexes containing a 4-membered ring.

Complex (Reference)	Pt-S (Å)	C-S (Å)	S-Pt-S (°)	S-C-S (°)
$PtI_2(S_2CNMe_2)_2$ (422)	2.36(1)	1.73(4)	73.6(4)	111(2)
	2.35(1)	1.69(4)	73.3(4)	116(2)
	2.33(1)	1.63(4)		
	2.35(1)	1.67(4)		
$(PPh_3)_2Pt(\mu\text{-}S_2C)\text{-}Pt(Cl)(PPh_3)_2$ (423)	2.353(5)	1.709(21)	72.4(2)	109.9(9)
	2.361(5)	1.692(20)		
$(PPh_3)_2Pt(S_2CF).HF$ (424)	2.322(4)	1.82(2)	74.7	108
	2.340(5)	1.67(2)		
$(PPh_3)_2Pt(S_2CO)$ (425)	2.347(3)	1.755(16)	75.2(2)	106.6(7)
	2.326(4)	1.803(14)		
$(PPhMe_2)_2Pt(S_2CH_2)$ (426)	2.301(5)	1.815(19)	76.1(2)	102.1(9)
	2.390(5)	1.837(20)		
$(PPh_3)_2Pt(S_3O)$[a]	2.341(3)	(S-SO) 2.110(4) 2.17(1)	80.73(9)	(S-SO-S) 91.2(5)
	2.318(2)	2.042(4) 2.05(1)		93.2(2)

a) S=O bond lengths are 1.436(7) and 1.20(1) Å.

Compound 17 reacted at room temperature with H_2S over a ten hour period in THF to give the starting thiolo complex, *cis*-$(PPh_3)_2Pt(SH)_2$ (Equation 5.9).



(5.9)

The low isolated yield of this reaction (17%) is attributed to the decomposition of the thiolo complex when stirred for a long time in organic solvents.[265] The ^{31}P NMR spectrum of the reaction mixture showed a strong peak at 43.0 ppm due to the presence of $SPPh_3$ which resulted from the decomposition of the thiolo complex. The other product of the above reaction designated as "H_2S_3O" was not isolated nor detected.

The complex *trans*-$(PPh_3)_2Pt(SH)_2$[266] did not react with SO_2 under the same reaction conditions as used for the analogous *cis* complex, only the starting compound was recovered from the reaction mixture.

Claus Chemistry

The reaction of SO_2 with H_2S to produce sulfur was catalyzed by certain platinum complexes shown in Table 5.3 under mild homogeneous conditions. The reaction was carried out in a dry methylene chloride solution at room temperature in a very dry 100 mL Schlenk flask. The flask was previously treated with dimethyldichlorosilane to silylate the hydroxyl groups that are usually present on the glass surface (untreated glass catalyzed the reaction). The molar ratio of the catalyst to SO_2 was 1:20. The gases were added slowly using syringes and the reaction mixture was stirred for 3 hours. The sulfur was identified by thin layer chromatography and mass spectroscopy.

Table 5.3: Yields of the catalytic reaction of SO_2 and H_2S.[a]

Catalyst	% yield of Sulfur	Catalyst	% yield of Sulfur
Control[b] Un-catalyzed	8	*cis*- $(PPh_3)_2Pt(SCHMe_2)_2$	98
cis- $(PPh_3)_2Pt(SH)_2$	92	$(PPh_3)_2Pt(S_3O)$ **17**	93
trans- $(PPh_3)_2Pt(SH)_2$	9	*cis*- $(PPh_3)_2PtCl_2$	50

a) Ratio of H_2S:SO_2 is 2:1, volume used: H_2S= 50 mL; SO_2= 25 mL.
b) Based on three reactions.

Table 5.3 showed that the complexes *cis*-$(PPh_3)_2Pt(SH)_2$, *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$, and $(PPh_3)_2Pt(S_3O)$ are good catalysts for Claus chemistry. However, the *trans*-$(PPh_3)_2Pt(SH)_2$ did not catalyze this reaction and the chloro complex *cis*-$(PPh_3)_2PtCl_2$ was found to be a poor Claus catalyst. The catalytic activity of *cis*-$(PPh_3)_2Pt(SH)_2$ was tested by adding more of the gases. Addition of further aliquots of the gases showed that the catalyst remained active although with each addition this activity was reduced, as the amount of sulfur produced decreased with each addition.

DISCUSSION

The reaction of SO_2 with thiolates is well documented for $Cu(PPh_2Me)_3SPh$,[159] $CpW(CO)_2(PPh_3)SR$,[160] $CpRu(PPh_3)(L)SR$[161,162] and for (N,N'-bis(mercaptoethyl-1,5-diazacyclooctane)Ni.[407] In the cases of $Cu(PPh_2Me)_3SR$[159] and $CpRu(PPh_3)(CO)SR$[161] the products contain pyramidal SO_2 fragments reversibly bonded to the thiolate sulfur atom, while with the Ni compound[407] the product is stable and was structurally characterized. In the case of the tungsten complexes,[160] the adducts, $CpW(CO)_2(PPh_3)(S(SO)_2R)$, were believed to be under fast exchange conditions on the NMR time scale, therefore, the observed NMR spectrum was an average of the two species. On the other hand, the complexes $CpRu(PPh_3)_2SR$ gave $CpRu(PPh_3)_2(S(SO_2)R)$ and $CpRu(PPh_3)(SO_2)(S(SO_2)SR)$ upon treatment with SO_2.[161,162]

A platinum adduct, $(PPh_3)_2Pt(SPh)_2 \cdot 2SO_2$ similar to those reported here was reported from the reaction of $(PPh_3)_2Pt(SPh)_2$ with liquid SO_2.[159] This adduct possesses a high SO_2 dissociation pressure, in which the ratio of SO_2 to metal complex was found to be 1.72:1. This earlier result is in agreement with the instability of adducts **16a-c** toward loss of SO_2.

Treatment of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 gave $(PPh_3)_2Pt(S_3O)$, **17**, as shown in Equation 5.8. To our knowledge, this reaction is the first example of a direct interaction between a compound which contains an SH group and SO_2 in which a S-S bond is formed and, also, an oxygen atom is transferred to produce H_2O. This mimics a possible fundamental steps in the commercial Claus process.

The reaction of $(PPh_3)_2Pt(S_3O)$ with H_2S (Equation 5.9) produced *cis*-$(PPh_3)_2Pt(SH)_2$. The other product, which is designated as "H_2S_3O", was neither detected nor isolated. In a recent publication,[427] *ab initio* MO calculations on the isomers of "H_2S_3O" were carried out since it is believed to be a key intermediate in the Claus Process. The results of these calculations showed that the most stable form is a six atom chain with the oxygen attached to the end of a linear S3 moiety (Figure 5.6). This compound is expected to readily react with H_2S to form water and elemental sulfur. The compound should also spontaneously decompose to S_2O and H_2S as shown in Equation 5.10.[427]

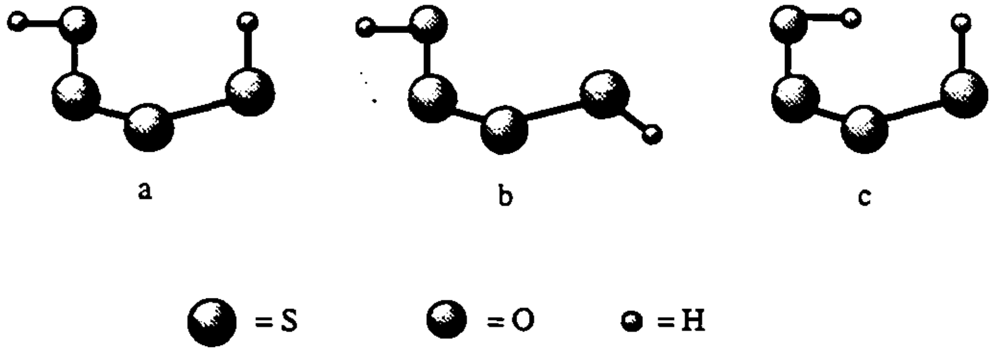


Figure 5.6: Three rotamers of the most stable isomer of "H_2S_3O".[427]

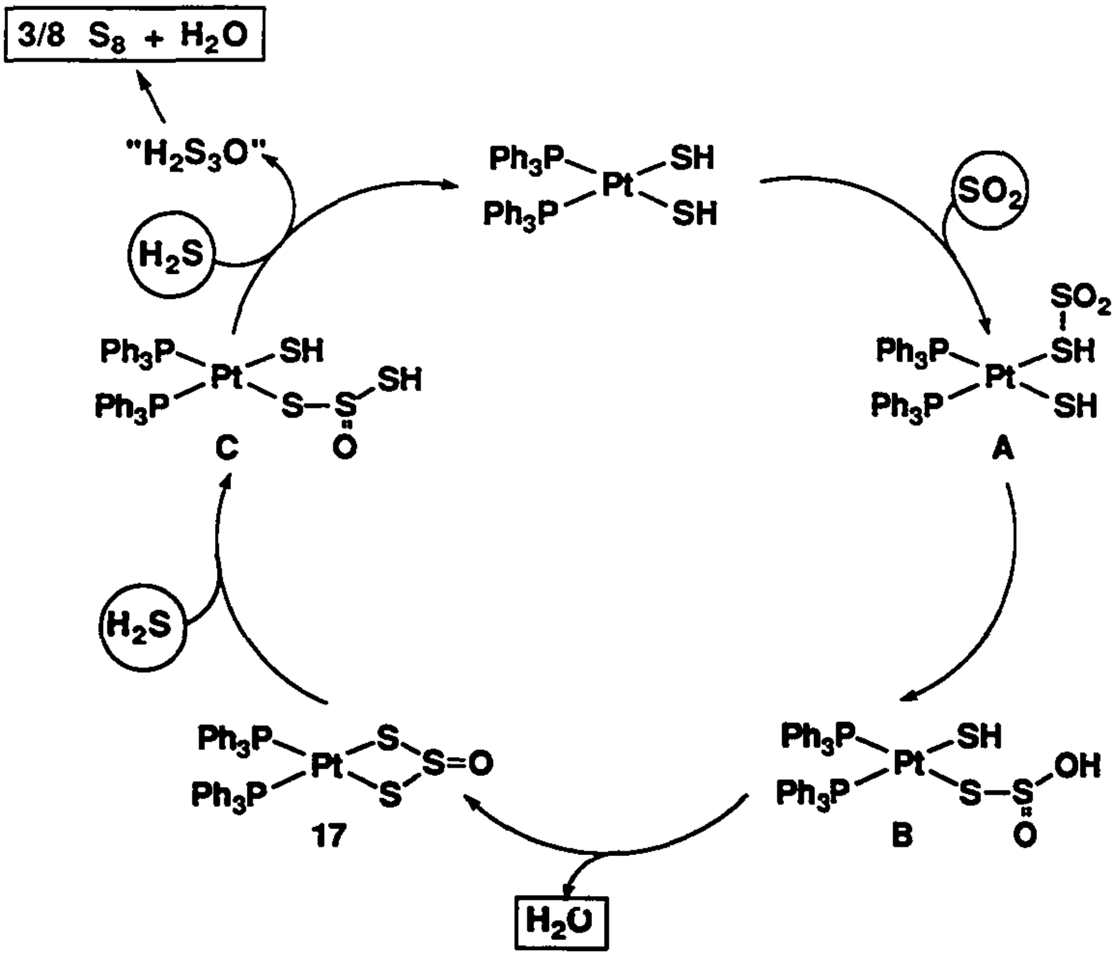
$$H_2S_3O \longrightarrow H_2S + S_2O \quad \Delta U_{298} = -54.0\ \mathrm{kJmol^{-1}} \qquad (5.10)$$

In the reaction of **17** with H_2S, no sulfur was formed but $SPPh_3$ was detected in the ^{31}P NMR spectrum of the reaction mixture. This sulfide may be formed by the reaction of PPh_3 (formed from the decomposition of *cis*-$(PPh_3)_2Pt(SH)_2$) with sulfur (or with "H_2S_3O"). Sulfur may be produced in this reaction either by decomposition of "H_2S_3O" (Equation 5.10) or its reaction with H_2S.

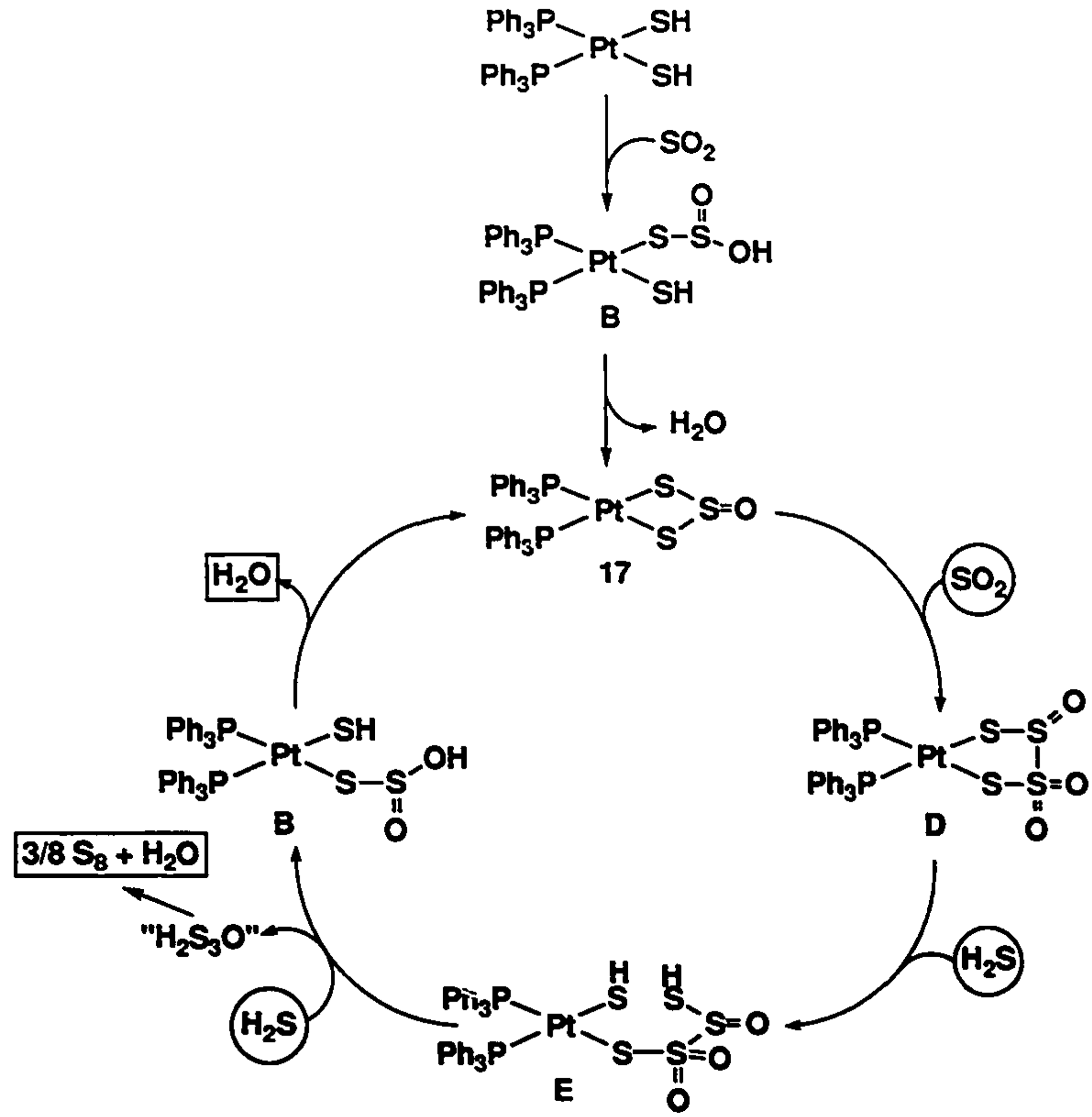
In terms of the Claus Process, the results presented in this chapter showed that the complexes *cis*-$(PPh_3)_2Pt(SH)_2$, *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$ and $(PPh_3)_2Pt(S_3O)$ catalyze the Claus reaction under mild homogeneous conditions. The ^{31}P NMR spectra of the solid obtained from the catalytic reactions showed the presence of peaks corresponding to the catalyst and, in the cases of *cis*-$(PPh_3)_2Pt(SH)_2$ and *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$ compound **17** was also observed. In all the cases, a peak for triphenylphosphine sulfide was also present.

The reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 gives some information about the mechanism of the Claus process. Taking model B as a guide, the formation of **17** shows two steps of the Claus reaction, one is sulfur-sulfur bond formation and the other is oxygen atom transfer from SO_2 to form water. The reaction of **17** with H_2S regenerates the starting thiolo complex, *cis*-$(PPh_3)_2Pt(SH)_2$, indicating that this complex catalyzes the Claus reaction. It also indicates that **17** is an intermediate in this reaction and also acts as a catalyst.

Two proposed catalytic cycles of the Claus reaction can be written as shown in Schemes 5.7 and 5.8. Scheme 5.7 shows the catalytic cycle based on *cis*-$(PPh_3)_2Pt(SH)_2$ as a catalyst while Scheme 5.8 shows the cycle based on $(PPh_3)_2Pt(S_3O)$, **17**, as a catalyst.



Scheme 5.7



Scheme 5.8

In Scheme 5.7 the reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 may give adduct **A**, $(PPh_3)_2Pt(SH)(S(SO_2)H)$, which has an SO_2 bound to the sulfur atom of the thiolo group, similar to the adducts observed for the dithiolate systems (Equation 5.7). This adduct undergoes proton transfer (from sulfur to oxygen) to give **B**, $(PPh_3)_2Pt(SH)(SS(O)OH)$ which loses H_2O to give **17**. Reaction of H_2S with **17** gives **C**,

$(PPh_3)_2Pt(SH)(SS(O)SH)$, which further reacts with H_2S to give the starting complex, *cis*-$(PPh_3)_2Pt(SH)_2$ and "H_2S_3O". The latter decomposes to give elemental sulfur and water.

Scheme 5.8 shows another possible cycle based on **17** as a catalyst. Insertion of SO_2 molecule in to the S-S(O) bond gives **D**, $(PPh_3)_2Pt(SS(O)S(O)_2S)$, which reacts with H_2S to give **E**, $(PPh_3)_2Pt(SH)(SS(O)S(O)_2SH)$. The latter reacts with another molecule of H_2S to give **B** and "H_2S_3O" which decomposes to sulfur and water. Intermediate **B** loses H_2O to regenerate **17**.

The only isolated intermediates in either cycle are *cis*-$(PPh_3)_2Pt(SH)_2$ and compound **17**. Proposed intermediate **C** arises from the reaction of H_2S with **17**. It is homologue of proposed intermediate **B** which might be generated from the reaction of **17** with H_2O. Analogous compounds such as $(PPh_3)_2Pt(SH)(SS(O)OR)$ and $(PPh_3)_2Pt(SH)(SS(O)SR)$ which might be more stable than intermediates **B** and **C** might be obtained from the reaction of **17** with alcohols or thiols, respectively. These are natural targets for future studies. Examples of proposed intermediates **D** and **E** are unknown. The complex $(PPh_3)_2Pt(S_4)$ is known[428] and its oxidation might lead to intermediate **D** or other similar oxidized forms.

CHAPTER 6

REACTIONS OF $(PPh_3)_2Pt(SR)_2$ WITH CS_2 (*cis*: R= H, CMe_3, $CHMe_2$; *trans*: R= 4-C_6H_4Me)

INTRODUCTION

Thioxanthate complexes, MS_2CSR, are known for many transition metals including Cu, Cr, Mo, W, Mn, Re, Pd, Fe, Co, Ru and Ni,[95,163-169,176] however, only one example of a platinum thioxanthate is known, namely, $[Pt(SCMe_3)(S_2CSMe_3)]_2$.[102] Metal thioxanthate complexes can be prepared *via* the reaction of a metal thiolates with CS_2.[163-169] The reaction of metal halides with thioxanthato anions, $RSCS_2^-$,[163,164,429,430] which are prepared by the treatment of the thiolate anion with CS_2, also gives thioxanthato complexes.[431]

The thioxanthato ligand can bind to the metal atom in either a monodentate (e.g. $CpNi(PBu_3)(S_2CSR)$)[167] or a bidentate fashion (e.g. $(PPh_3)_2CuS_2CSEt$)[166] (Figure 6.1).

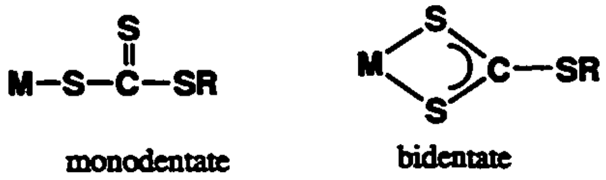
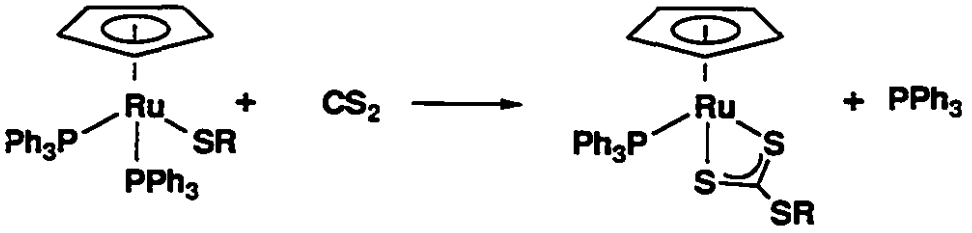


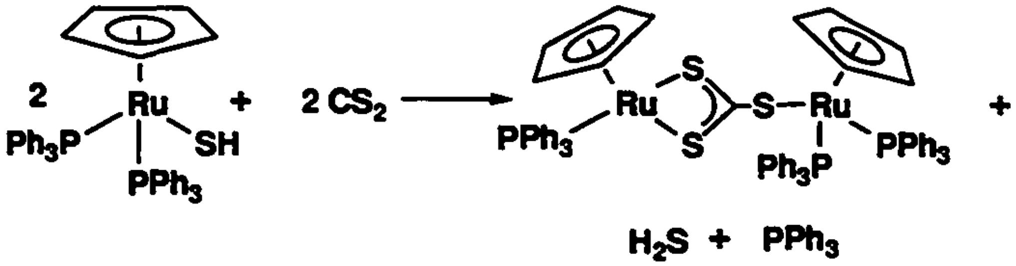
Figure 6.1: Coordination modes of thioxanthato ligand.

The complexes $CpRu(PPh_3)_2SR$ reacted readily at room temperature with CS_2 to give the thioxanthato complexes, $CpRu(PPh_3)(S_2CSR)$, wherein CS_2 had inserted into the Ru-S bond (Equation 1.27).[176]


(1.27)

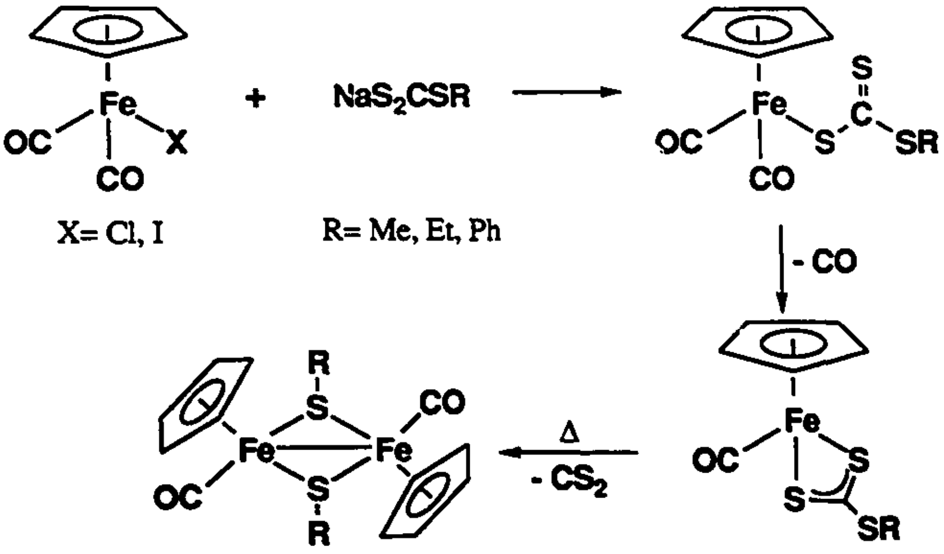
R= C_3H_7, $CHMe_2$, 4-C_6H_4Me.

The analogous thiolo complex, $CpRu(PPh_3)_2SH$, reacted slowly with CS_2 to give a red product formulated as $Cp_2Ru_2(PPh_3)_3CS_3$ as shown in equation 6.1.[176]


(6.1)

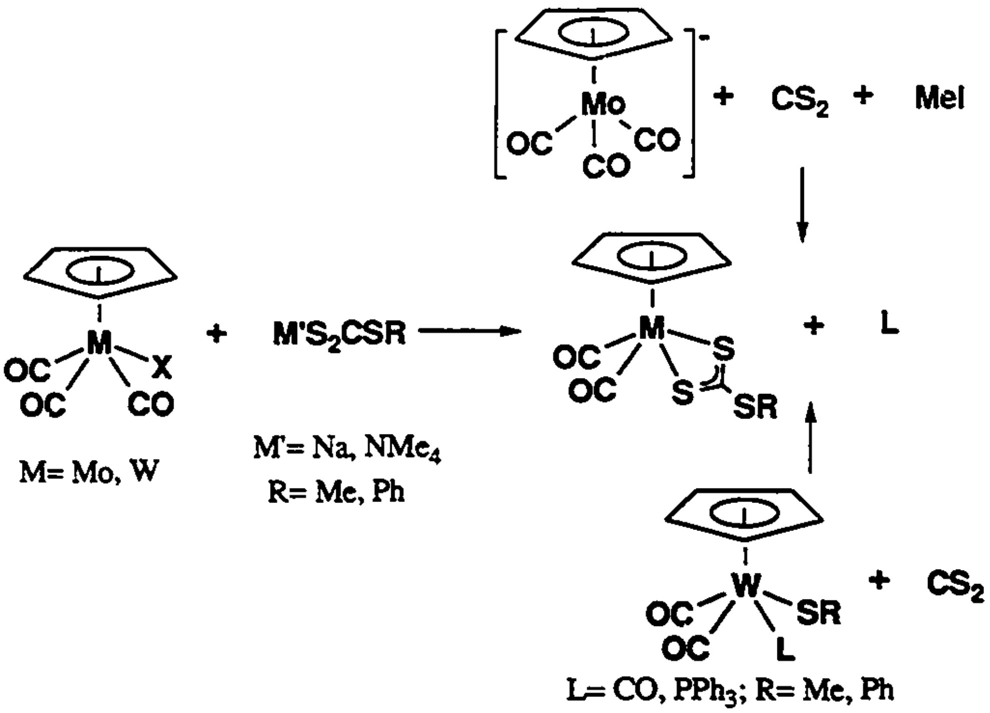
Other examples of thiolato complexes that undergo insertion reaction with CS_2 were given in Chapter one (Equations 1.25-1.28).[163-169]

Numerous thioxanthato complexes have been produced by the reaction of an organometallic halide with thioxanthate salts.[163,164,429,430] Scheme 6.1 represents an example of this method. Cyclopentadienyldicarbonyliron halides reacted at room temperature with NaS_2CSR to give $CpFe(CO)_2S_2CSR$, which have a monodentate $RSCS_2$ ligand. The latter complexes slowly converted in solution to $CpFe(CO)S_2CSR$. These complexes underwent elimination of CS_2 molecule in refluxing toluene to give the dimers $[CpFe(CO)(\mu\text{-}SR)]_2$.[429]



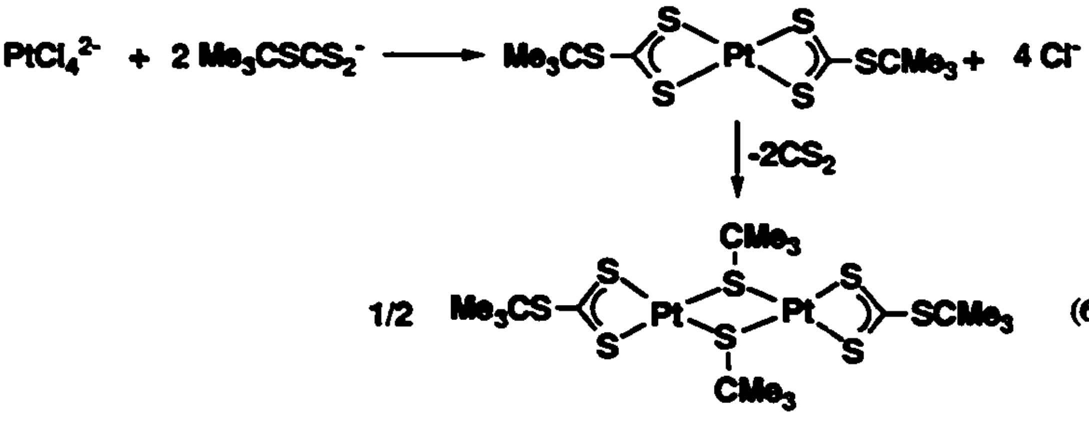
Scheme 6.1

The analogous reaction of $CpM(CO)_3Cl$ led to $CpM(CO)_2(S_2CSR)$ where M is Mo or W (Scheme 6.2).[430] The complex $CpMo(CO)_2(S_2CSMe)$ was also prepared by the treatment of the anion $[CpMo(CO)_3]^-$ with excess CS_2 followed by addition of methyl iodide.[432] The complexes $CpW(CO)_3S_2CSR$ were also reported to form from the reaction of $CpW(CO)_2(L)SR$ with CS_2, where L= CO[75] and PPh_3.[95]



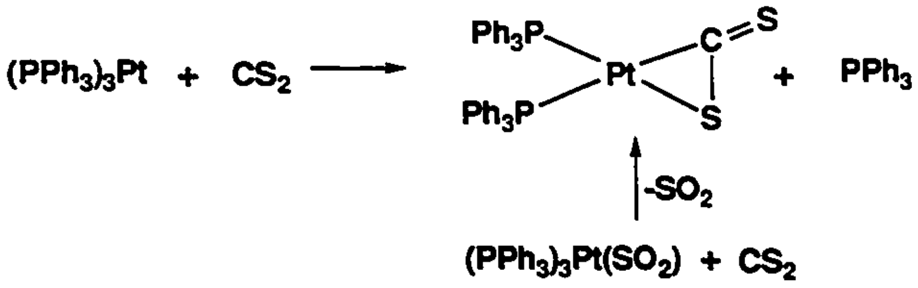
Scheme 6.2

The only known platinum thioxanthate complex, $[Pt(\mu\text{-}SCMe_3)(S_2CSMe_3)]_2$, was prepared by the reaction of NaS_2CSCMe_3 with K_2PtCl_4 in water (Equation 6.2).[102] This complex was prepared among a series of thioxanthates of Ni(II) and Pd(II) that underwent spontaneous CS_2 elimination to form dimeric thiolato bridged complexes.[101,102]



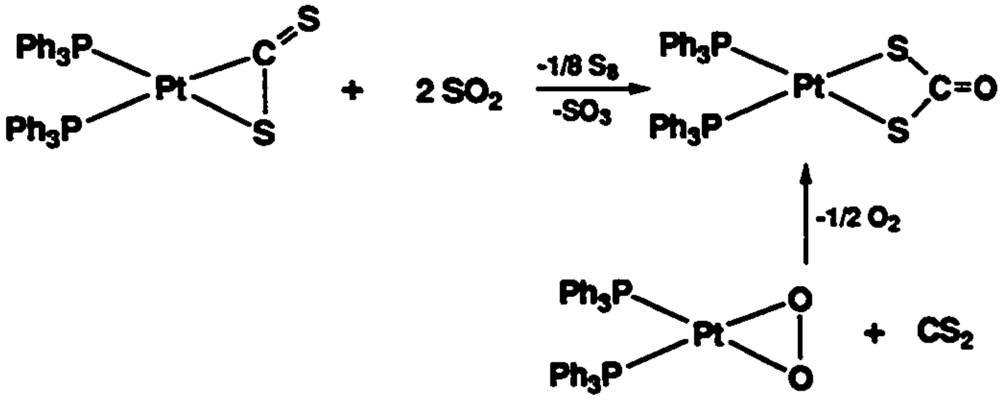
(6.2)

The reactions of various platinum complexes with CS_2 have been reported.[416,433,434] The complex $(PPh_3)_3Pt$ reacted with CS_2 to give $(PPh_3)_2Pt(\eta^2\text{-}CS_2)$ which was structurally characterized.[433] The same complex was also prepared by simple displacement of SO_2 from the complex $(PPh_3)_3Pt(SO_2)$ (Scheme 6.3).[416]



Scheme 6.3

If the reaction of $(PPh_3)_3Pt(SO_2)$ and CS_2 (shown in Scheme 6.3) was carried out under SO_2 atmosphere the dithiocarbonato complex, $(PPh_3)_2Pt(S_2CO)$, was isolated.[416] This complex was also obtained from the reaction of SO_2 with $(PPh_3)_2Pt(\eta^2\text{-}CS_2)$[416] or CS_2 with the complex $(PPh_3)_2Pt(O_2)$ (Scheme 6.4).[434]



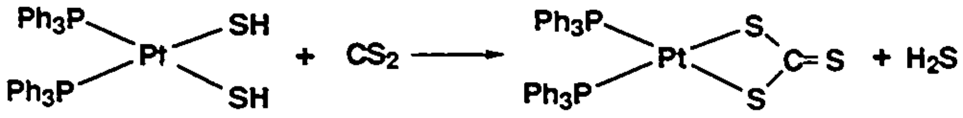
Scheme 6.4

The reactivity of the complexes $(PPh_3)_2Pt(SR)_2$ towards SO_2, which was discussed in Chapter 5, led to the treatment of these complexes with small molecules such as CO_2, COS and CS_2. The importance of the reactions of these molecules stems from the interest in CO_2 as a potential feed stock for organic molecules containing one carbon atom[435-437] and as an important molecule in solar energy conversion.[438,439]

The complexes $(PPh_3)_2Pt(SR)_2$ inserted one CS_2 molecule in the platinum-sulfur bond to form the mixed thiolato-thioxanthato complexes $(PPh_3)Pt(SR)(S_2CSR)$. The structure of $(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$ was determined by x-ray crystallography. The complex *cis*-$(PPh_3)_2Pt(SH)_2$ reacted with CS_2 to give the known complex, $(PPh_3)_2Pt(S_2CS)$, which contains a trithiocarbonato group.

RESULTS

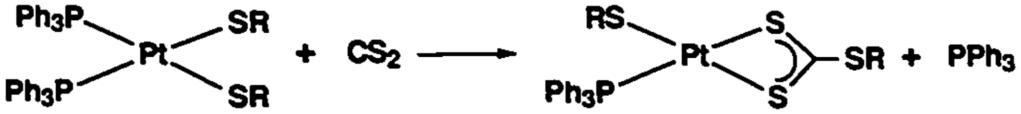
Treatment of the complex *cis*-$(PPh_3)_2Pt(SH)_2$ with CS_2 at room temperature gave $(PPh_3)_2Pt(S_2CS)$, **18**, in 85% yield with evolution of H_2S (Equation 6.3). The yellow complex is stable to air in both the solid state and in solution. The compound was characterized by spectroscopic techniques and elemental analysis. Its IR spectrum showed a strong band at 1060 cm^{-1} which is characteristic of C=S stretching frequency. The ^1H NMR spectrum of **18** showed a multiplet in the aromatic region. The ^{31}P NMR spectrum showed a singlet at 18.3 ppm with platinum satellites ($J_{P\text{-}Pt}$= 3146 Hz). This chemical shift is similar to that observed for $(PPh_3)_2Pt(S_3O)$ (18.5 ppm, $J_{P\text{-}Pt}$= 3200 Hz) and lower than that of the starting thiolo complex *cis*-$(PPh_3)_2Pt(SH)_2$ (21.4 ppm, $J_{P\text{-}Pt}$= 2980 Hz)



(6.3)

18

The thiolato complexes $(PPh_3)_2Pt(SR)_2$ reacted cleanly with CS_2 at room temperature to give $(PPh_3)Pt(SR)(S_2CSR)$, where R= CMe_3; **19a**, 4-C_6H_4Me; **19b**, $CHMe_2$; **19c** in isolated yields ranging from 78% to 86% (Equation 6.4).



(6.4)

R= CMe_3; **19a**, R= 4-C_6H_4Me; **19b**, $CHMe_2$; **19c**

The dark red complexes **19a-c** are stable in air as solids as well as in solution. The IR spectra of these complexes showed a strong band in the range 980-988 cm^{-1} characteristic of the C-S (of CS_3) stretching frequency of the thioxanthato ligand.[372] The C-S bands of both the thiolato and thioxanthato ligands appeared in the ranges 768-805 and 922-943 cm^{-1}.[431] The NMR spectral data of **19a-c** are presented in Table 6.1. The ^1H NMR spectra of **19a-c** showed a multiplet peak in the aromatic region integrating for one PPh_3 ligand and two different R groups in a 1:1 ratio. Resonances for the alkyl groups (SR and S_2CSR) were shifted to low field compared to those of the starting thiolates. The only exception is the methine proton of the isopropyl group of **19c** which is shifted to higher field for both the thiolato and thioxanthato ligands. The shift to lower field was also observed when the spectra of $CpW(CO)_2(PPh_3)SR$ and $CpW(CO)_2S_2CSR$ were compared.[95] In contrast, a shift to higher field was observed in the ruthenium system

CpRu(PPh$_3$)S$_2$CSR (Equation 1.27).[176] These data are consistent with equation 6.4 wherein only one CS$_2$ molecule was incorporated *via* the insertion into one of the two Pt-SR bonds.

Table 6.1: NMR data in ppm of (PPh$_3$)Pt(SR)(S$_2$CSR) and (PPh$_3$)$_2$Pt(SR)$_2$.

R	(PPh$_2$)Pt(SR)(S$_2$CSR)			(PPh$_3$)$_2$Pt(SR)$_2$	
	^{1}H NMR^{a,b}		^{31}P NMR^a (J$_{Pt-P}$ Hz)	^{1}H NMR^{a,b}	^{31}P NMR^a (J$_{Pt-P}$ Hz)
$C\underline{Me}_3$	1.35	1.61	17.1 (3780)	1.32	23.4 (2830)
$CH\underline{Me}_2$	1.32^c	1.42^c	17.8	1.30^c	23.8
$C\underline{H}Me_2{}^d$	4.06	2.99	(3780)	4.13	(2852)
$4\text{-}C_6H_4\underline{Me}$	2.24	2.34	16.8	2.19	22.3
$4\text{-}C_6\underline{H}_4Me$	6.88^c	7.25^c	(3730)	6.70^c	(2954)
	7.12^c	2.29^c		7.10^c	

a) In CDCl$_3$ solution. b) Phenyl resonances of PPh$_3$ appeared as two multiplets in the ranges 7.08-7.40 ppm and 7.45-7.60 ppm in the ratio 3:2. c) Doublet. d) Septet.

The x-ray structure determination of (PPh$_3$)Pt(S-C$_6$H$_4$Me)(S$_2$CS-4-C$_6$H$_4$Me), **19b**, confirmed that the compound had a thiolato and a thioxanthato ligand as determined by IR, NMR and analytical data. An ORTEP drawing is presented in Figure 6.2.[233] The crystal data, atom coordinates, bond lengths and bond angles are given in Appendix 5, Tables A5.1-A5.4 respectively. The structure is consistent with those reported for similar complexes.[95,176] The 16 electron complex, **19b**, possesses a square planar geometry.

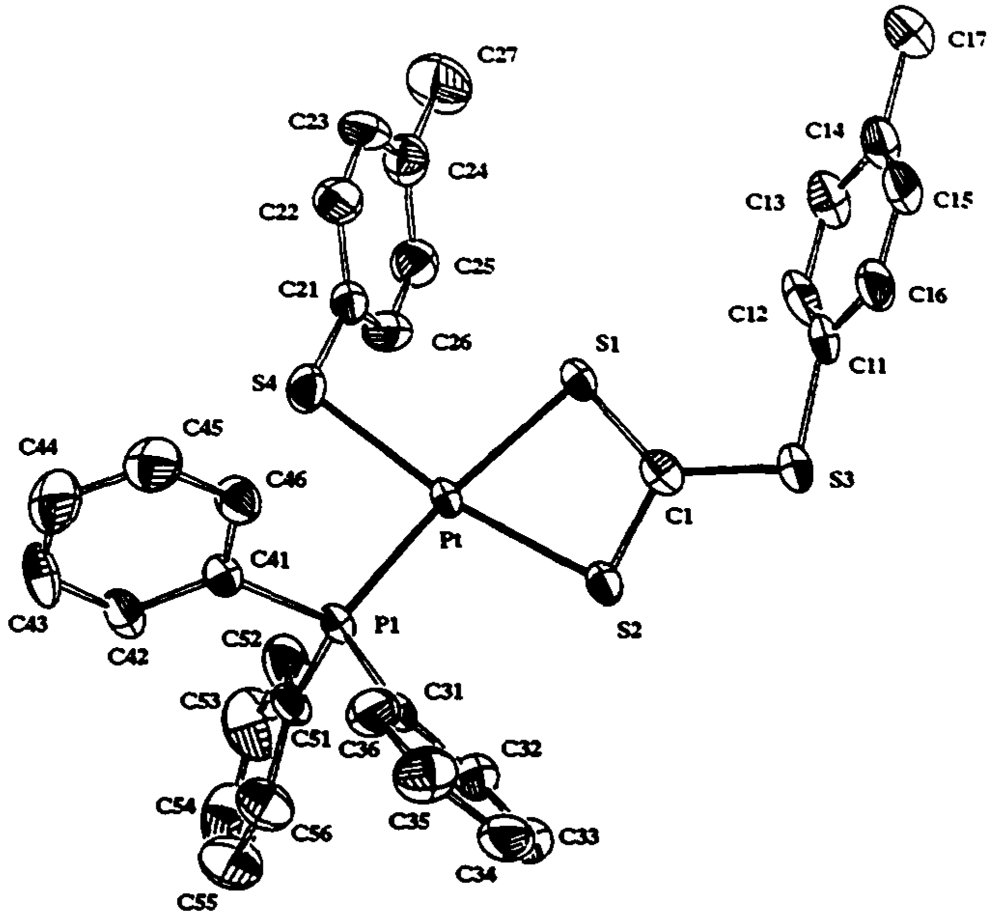


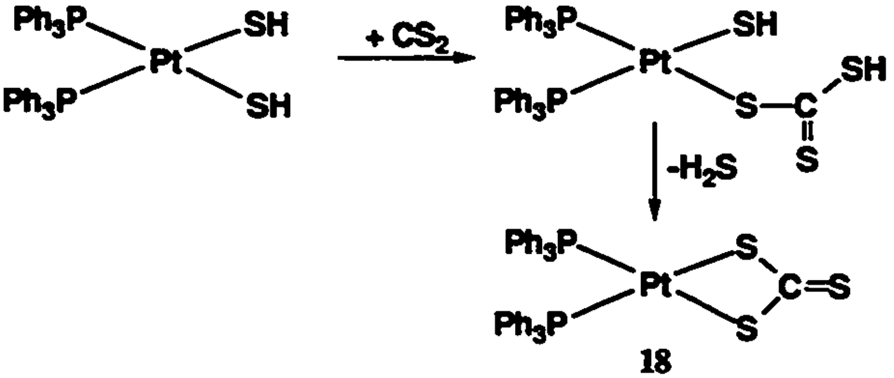
Figure 6.2: ORTEP drawing of $(PPh_3)Pt(S_2CS\text{-}4\text{-}C_6H_4Me)(S\text{-}4\text{-}C_6H_4Me)$, **19b**.

The Pt-S bond lengths of the thioxanthato ligand are 2.381(2) and 2.326(2) Å which are in the range observed for complexes containing PtSCS rings (Chapter 5, Table 5.2). These distances are longer than the Pt-SR bond length of (2.296(2) Å). The SPtS and SCS angles are similar to those observed for complexes containing PtSCS rings (Table 5.2).

The complexes *cis*-$(PPh_3)_2Pt(SH)_2$ and *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$ did not react with CO_2 or COS at room temperature in solution (THF, CH_2Cl_2).

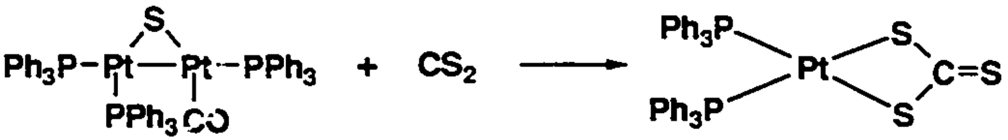
DISCUSSION

The complex *cis*-$(PPh_3)_2Pt(SH)_2$ reacted slowly with CS_2 with the evolution of H_2S gas to give the known trithiocarbonato complex, $(PPh_3)_2Pt(S_2CS)$, **18**. A reasonable reaction sequence for this conversion is shown in Scheme 6.5. This sequence involves an insertion of one molecule of CS_2 into the Pt-S bond to give an intermediate, $(PPh_3)_2Pt(SH)(S_2CSH)$, with a monodentate ligand followed by H_2S elimination to give **18**. A similar mechanism for the reaction of $CpRu(PPh_3)_2SH$ with CS_2 to give $Cp_2Ru_2(PPh_3)_3CS_3$ has been proposed.[176] These reaction mechanisms are very similar to one of those proposed for the Claus chemistry described in Chapter 5 (Scheme 5.6)



Scheme 6.5

Complex **18** is known and was made by two different methods. The reaction of CS_2 with either $(PPh_3)_2PtCl_2$[440] or $(PPh_3)_3Pt_2(CO)(\mu\text{-}S)$[441] (Equation 6.6) gave **18**.



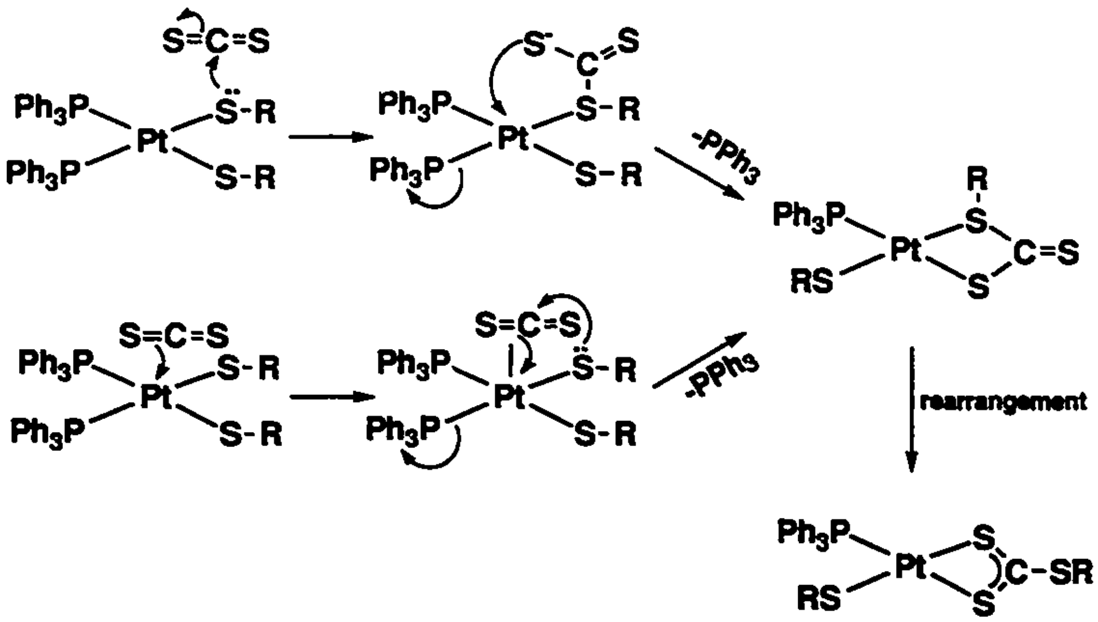
18

Scheme 6.6

Upon dissolution in CS_2 the yellow complexes $(PPh_3)_2Pt(SR)_2$ gave red solutions from which the complexes $(PPh_3)Pt(SR)(S_2CSR)$, **19a-c** were isolated. These complexes were formed by a simple CS_2 insertion into one of the Pt-S bonds with the loss of a PPh_3 ligand. The rate of reaction of the complexes containing electron donating groups (CMe_3, $CHMe_2$) was much faster than that of the complex with an electron withdrawing group (4-C_6H_4Me). This is consistent with the observed rates for the reaction of CS_2 with $CpRu(PPh_3)_2SR$ and $CpW(CO)_2(PPh_3)SR$ where R is $CHMe_2$, CH_2Ph, 4-C_6H_4Me.[85]

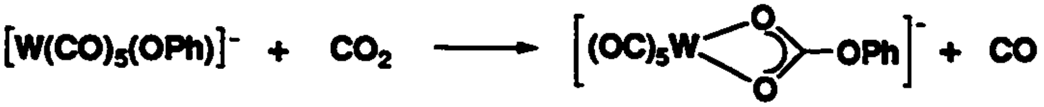
The reaction of CS_2 with $(PPh_3)_2Pt(SR)_2$ under different conditions was monitored by using NMR spectroscopy. These reactions showed that there was no evidence for the presence of any intermediate such as a monodentate thioxanthate complex. Increasing the CS_2 concentration increases the reaction rate. The reaction is retarded by the presence of added excess of PPh_3. Purging the reaction mixtures with CO did not slow down the reaction, although, peaks for a new species appeared. A similar observation was also made for a mixture of the platinum thiolates when treated with CO alone.

The above observations suggest that electrophilic attack by free CS_2 on the sulfur atom of the thiolato ligand or on the platinum center are possible pathways to **19a-c** (Scheme 6.7). In a related system,[442,443] the reaction of CO_2 with $[W(CO)_5OPh]^-$ (Equation 6.5) was not inhibited by CO which is consistent with free insertion.



19

Scheme 6.7



$$[W(CO)_5(OPh)]^- + CO_2 \longrightarrow \left[(OC)_5W(O_2C{-}OPh)\right]^- + CO \qquad (6.5)$$

The mechanisms of the analogous reactions of CS_2 with $CpRu(PPh_3)_2SR$[166] or $CpW(CO)_2(PPh_3)SR$[85] were studied. The results of these studies showed that these reactions were inhibited by the addition of PPh_3 or CO and pre-coordenation of CS_2 was proposed.

CHAPTER 7

EXPERIMENTAL SECTION

GENERAL METHODS

All experiments were performed under nitrogen using vacuum line and Schlenk techniques.[444] Flasks were charged with solids and then evacuated and filled with nitrogen. Tetrahydrofuran, hexanes, benzene and toluene were refluxed over sodium/benzophenone and distilled under nitrogen just prior to use. Methylene chloride was refluxed over phosphorus pentoxide and distilled under nitrogen. Absolute ethanol and spectrograde acetone were degassed by repeated evacuation (three times) followed by purging with nitrogen. Deuterated solvents (Isotec, Merck, and Cambridge Isotope) were used as received. Solvents and liquid reagents were transferred by syringes. Ruthenium thiolates $CpRu(PPh_3)(L)SR$ (L = PPh_3, CO)[176], platinum thiolates $(PPh_3)_2Pt(SR)_2$ (R= H[426], CMe_3, $CHMe_2$, and 4-C_6H_4Me),[80] the complex $CpRu(PPh_3)_2Cl$[445] and methylthiophthalimide[90] were all prepared according to published procedures. Allylthiol (Aldrich) was distilled before use. The reagents (Aldrich) $NOBF_4$, HBF_4 (85% in diethylether), the salt $[MeSSMe_2]BF_4$, MeLi (1.4 M in diethylether), NH_4PF_6, MeI and CS_2 were used as received. The gases (Matheson) H_2S and SO_2 were used as received unless otherwise specified.

Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Varian XL-200 or a JEOL-270 spectrometer. Samples were prepared under nitrogen. Chemical shifts are in ppm relative to TMS at 0 ppm. The ^{31}P NMR spectra were obtained on a Varian XL-300 or a JEOL-270 spectrometer using 85% phosphoric acid as the external reference at 0 ppm. Infrared spectra were recorded on an Analect AQS-20 Fourier-transform infrared (FT-IR) spectrophotometer calibrated using a He/Ne laser (632.8 nm). The detector was triglycine sulfate (TGS) with standard resolution of 4 cm^{-1}. All bands were reported in cm^{-1} with an accuracy of ±1 cm^{-1}. Low resolution mass spectra were measured on a KRATOS MS25RFA mass spectrometer. High resolution mass spectra were measured on a ZAB 2F HS mass spectrometer at the McGill University Biomedical Mass Spectrometry Unit. Elemental analyses were performed by either Guelph Chemical Laboratories, Guelph, Ontario or by Canadian Microanalytical Service Ltd., Delta, British Columbia. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and were uncorrected.

PREPARATION OF COMPLEXES

η^5–Cyclopentadienyl(nitrosyl)(triphenylphosphine)(2-methyl-2-propylthiolato)ruthenium(IV) tetrafluoroborate, $[CpRu(PPh_3)(NO)SCMe_3]BF_4$, 1a. In a 100-mL Schlenk flask, $CpRu(PPh_3)_2SCMe_3$ (0.51 g, 0.66 mmol) was dissolved in THF (20.0 mL), $NOBF_4$ (0.093 g, 0.82 mmol) was added and the solution was stirred overnight. During that time the color became dark orange-brown and a dark red precipitate formed. The supernatant was removed with a syringe and the precipitate was washed with diethyl ether (3 x 5.0 mL) and hexanes (3 x 5.0 mL). The resulting solid was recrystallized from methylene chloride/hexanes to give dark red crystals (0.43 g, 84%). mp: 198-199 °C (dec.). IR (CH_2Cl_2): $\nu_{(NO)}$= 1822(s) cm^{-1}. ^1H NMR (acetone-*d*$_6$): 1.39 (s, 9H, $C(CH_3)_3$), 6.30 (s, 5H, Cp), 7.64 (m, 15H, PPh_3). Anal. Calcd. for

($C_{27}H_{29}BF_4NOPRuS$): 51.12% C, 4.61% H, 2.21% N, 5.05% S. Found: 51.15% C, 4.65% H, 2.26% N, 5.28% S.

η^5–Cyclopentadienyl(nitrosyl)(triphenylphosphine)(4-methylbenzenethiolato)ruthenium(IV) tetrafluoroborate, [CpRu(PPh_3)(NO)S-4-C_6H_4Me]BF_4, 1b. In a 100-mL Schlenk flask, CpRu(PPh_3)$_2$S-4-C_6H_4Me (0.40 g, 0.50 mmol) was dissolved in THF (15.0 mL), $NOBF_4$ (0.070 g, 0.60 mmol) was added and the solution was stirred overnight. During that time the color became dark orange-brown and an orange precipitate formed. The supernatant was removed with a syringe and the precipitate was washed with diethyl ether (3 x 5.0 mL) and hexanes (3 x 5.0 mL). The resulting solid was recrystallized from acetone/ethanol to give orange-red crystals (0.36 g, 90%). mp: 218-220 °C (dec.). IR (CH_2Cl_2): $\nu_{(NO)}$= 1817(s) cm^{-1}. ^1H NMR (acetone-d_6): 2.31 (s, 3H, 4-$C_6H_4C\underline{H}_3$), 6.10 (s, 5H, Cp), 7.10 (d, 2H, 4-$C_6\underline{H}_4CH_3$), 7.47 (d, 2H, 4-$C_6\underline{H}_4CH_3$), 7.72 (m, 15H, PPh_3). Anal. Calcd. for ($C_{30}H_{27}BF_4NOPRuS$): 53.90% C, 4.07% H, 2.10% N, 4.80% S. Found: 53.66% C, 4.02% H, 2.07% N, 4.93% S.

η^5–Cyclopentadienyl(nitrosyl)(triphenylphosphine)(2-propylthiolato)-ruthenium(IV) tetrafluoroborate, [CpRu(PPh_3)(NO)SCHMe_2]BF_4, 1c. In a 100-mL Schlenk flask, CpRu(PPh_3)$_2$SCHMe_2 (0.38 g, 0.50 mmol) was dissolved in THF (15.0 mL), $NOBF_4$ (0.070 g, 0.60 mmol) was added and the solution was stirred overnight. During that time the color became dark brown and a brown precipitate formed. The precipitate was isolated by removing the mother liquor which was concentrated under vacuum to about 3.0 mL and diethyl ether (15.0 mL) was added to precipitate more solid. The combined solids were washed with diethyl ether (3 x 5.0 mL) and hexanes (3 x 5.0 mL). Then, they were dried under vacuum overnight to give an orange-brown powder (0.18 g, 58%) which slowly decomposed in the solid state that this interfered with the elemental analysis. mp: 184-186 °C (dec.). IR (CH_2Cl_2): $\nu_{(NO)}$= 1821(m) cm^{-1}. ^1H

NMR (CD_2Cl_2): 1.26 (coupled doublets, 3H, $CH(C\underline{H}_3)_2$), 1.30 (coupled doublets, 3H, $CH(C\underline{H}_3)_2$), 2.95 (septet, 1H, $C\underline{H}(CH_3)_2$), 5.89 (s, 5H, Cp), 7.50 (m, 15H, PPh_3). ^1H NMR (acetone-d_6): 1.31 (d, 6H, $CH(C\underline{H}_3)_2$), 3.22 (septet, 1H, $C\underline{H}(CH_3)_2$), 6.31 (s, 5H, Cp), 7.62 (m, 15H, PPh_3). Anal. Calcd. for ($C_{26}H_{27}BF_4NOPRuS$): 50.34% C, 4.39% H, 2.26% N, 4.80% S. Found: 47.79% C, 3.82% H, 2.23% N, 5.01% S.

Bis(η^5–cyclopentadienyl)bis(triphenylphosphine)dicarbonyl(μ-4-methylbenzenedisulfide)diruthenium(II) ditetrafluoroborate,

$[(CpRu(PPh_3)CO)_2S_2(4\text{-}C_6H_4Me)_2][BF_4]_2$, 2. In a 100-mL Schlenk flask, $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$ (0.18 g, 0.31 mmol) was dissolved in THF (15.0 mL), $NOBF_4$ (0.044 g, 0.37 mmol) was added and the solution was stirred for 3 hours. During that time a yellow precipitate formed. The supernatant was removed with a syringe and the precipitate was washed with diethyl ether (3 x 5.0 mL) and hexanes (3 x 5.0 mL). The resulting solid was recrystallized from methylene chloride/hexanes to give yellow crystals (0.18 g, 87%). mp: 185-187 °C. IR (CH_2Cl_2): $\nu_{(CO)}$= 2002(s), 1980(m) cm^{-1}. ^1H NMR (CD_2Cl_2); isomer A: 2.48 (s, 3H, $4\text{-}C_6H_4C\underline{H}_3$), 5.12 (s, 5H, Cp), 6.80 (m, 11H, PPh_3), 7.40 (m, 8H, $4\text{-}C_6\underline{H}_4CH_3$, PPh_3); isomer B: 2.33 (s, 3H, $4\text{-}C_6H_4C\underline{H}_3$), 5.02 (s, 5H, Cp), 6.80 (m, 11H, PPh_3), 7.40 (m, 8H, $4\text{-}C_6\underline{H}_4CH_3$, PPh_3); A:B= 4:1 Anal. Calcd. for ($C_{62}H_{54}B_2F_8O_2P_2Ru_2S_2$): 55.86% C, 4.08% H, 4.81% S. Found: 56.15% C, 4.14% H, 4.98% S.

η^5–Cyclopentadienyl(carbonyl)(triphenylphosphine)(2-methyl-2-propyldisulfide)ruthenium(II) tetrafluoroborate,

$[(CpRu(PPh_3)(CO)S_2(CMe_3)_2]BF_4$, 3. In a 100-mL Schlenk flask, $CpRu(PPh_3)(CO)SCMe_3$ (0.20 g, 0.37 mmol) was dissolved in THF (20.0 mL), $NOBF_4$ (0.047 g, 0.40 mmol) was added and the solution was stirred for 1 hour. During that time a yellow precipitate formed. The supernatant was removed with a syringe and the precipitate was washed with diethyl ether (3 x 5.0 mL) and hexanes (3 x 5.0 mL). The resulting solid was recrystallized from methylene chloride/hexanes to give yellow crystals

(0.082 g, 62%). mp: 155-156 °C (dec.). IR (CH_2Cl_2): $\nu_{(CO)}$= 1984(s) cm^{-1}. ^{1}H NMR (acetone-d_6): 1.15 (s, 9H, SSC(C$\underline{H}_3$)$_3$), 1.42 (s, 9H, SC(C$\underline{H}_3$)$_3$), 5.64 (s, 5H, Cp), 7.45 (m, 6H, PPh_3), 7.63 (m, 9H, PPh_3). Anal. Calcd. for ($C_{32}H_{38}BF_4OPRuS_2$): 53.25% C, 5.31% H, 8.89% S. Found: 52.40% C, 5.11% H, 8.20% S.

η^5–Cyclopentadienylbis(triphenylphosphine)(2-methyl-2-propylthiol)-ruthenium(II) tetrafluoroborate, [CpRu(PPh_3)$_2$($HSCMe_3$)]BF_4, 4a. In a 100-mL Schlenk flask, CpRu(PPh_3)$_2$$SCMe_3$ (0.20 g, 0.25 mmol) was dissolved in THF (20.0 mL) and $HBF_4.Et_2O$ (0.052 mL, 0.30 mmol) was added. The reaction mixture was stirred for 30 minutes. A yellow precipitate formed and was isolated by the removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3 x 5.0 mL) and recrystallized from methylene chloride/hexanes to give orange crystals (0.19 g, 88%). mp: 144-146 °C. IR (KBr Disk): $\nu_{(SH)}$= 2505(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): 1.39 (s, 9H, C(C$\underline{H}_3$)$_3$), 2.60 (t, 1H, S$\underline{H}$), 4.69 (s, 5H, Cp), 6.95 (m, 12H, PPh_3), 7.40 (m, 18H, PPh_3). Anal. Calcd. for ($C_{45}H_{45}BF_4P_2RuS$): 62.28% C, 5.23% H, 3.69% S. Found: 61.86% C, 5.20% H, 3.34% S.

η^5–Cyclopentadienylbis(triphenylphosphine)(4-methylbenzenethiol)-ruthenium(II) tetrafluoroborate, [CpRu(PPh_3)$_2$(HS-4-C_6H_4Me)]BF_4, 4b. In a 100-mL Schlenk flask, CpRu(PPh_3)$_2$S-4-C_6H_4Me (0.20 g, 0.25 mmol) was dissolved in THF (15.0 mL) and $HBF_4.Et_2O$ (0.052 mL, 0.30 mmol) was added. The reaction mixture was stirred for 5 minutes. To the resulting yellow solution, absolute ethanol (10.0 mL) was added. Concentration of the solution under vacuum to about 5.0 mL followed by standing gave a yellow precipitate. The precipitate, isolated after removal of the mother liquor with a syringe, was washed with hexanes (3 x 5.0 mL). Recrystallization from methylene chloride/hexanes gave yellow air sensitive crystals, that were unsuitable for elemental analysis (0.20 g, 80%). mp: 138-140 °C. IR (KBr Disk): $\nu_{(SH)}$= 2514(w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.38 (s, 3H, 4-C_6H_4C$\underline{H}_3$), 4.44 (s, 5H, Cp), 4.93 (t, 1H, S<u>H</u>), 6.92 (m, 16H, PPh_3, $C_6\underline{H}_4CH_3$), 7.21 (m, 18H, PPh_3). Anal. Calcd. for ($C_{48}H_{43}BF_4P_2RuS$): 63.92% C, 4.80% H, 3.55% S. Found: 56.40% C, 4.25% H, 3.55% S.

η^5–Cyclopentadienylbis(triphenylphosphine)(2-propylthiol)ruthenium(II) tetrafluoroborate, [CpRu(PPh_3)$_2$($HSCHMe_2$)]BF_4, 4c. In a 100-mL Schlenk flask, $CpRu(PPh_3)_2SCHMe_2$ (0.20 g, 0.26 mmol) was dissolved in THF (10.0 mL) and $HBF_4.Et_2O$ (0.054 mL, 0.31 mmol) was added. The reaction mixture was stirred for 30 minutes. A yellow precipitate was formed while stirring and was isolated by the removal the mother liquor with a syringe. The precipitate was washed with hexanes (3 x 5.0 mL) and recrystallized from methylene chloride/hexanes to give orange crystals (0.18 g, 81%). mp: 185-187 °C. IR (KBr Disk): $\nu_{(SH)}$= 2512(w) cm^{-1}. ^1H NMR (CD_2Cl_2): 1.32 (d, 6H, $CH(C\underline{H}_3)_2$), 2.72 (septet, 1H, $C\underline{H}(CH_3)_2$), 2.93 (m, 1H, S<u>H</u>), 4.62 (s, 5H, Cp), 6.95 (m, 12H, PPh_3), 7.22 (m, 18H, PPh_3). Anal. Calcd. for ($C_{44}H_{43}BF_4P_2RuS$): 61.90% C, 5.08% H, 3.76% S. Found: 61.71% C, 5.34% H, 4.12% S.

η^5–Cyclopentadienylbis(triphenylphosphine)(dimethylsulfide)ruthenium(II) tetrafluoroborate, [CpRu(PPh_3)$_2$$SMe_2$]$BF_4$, 5. In a 100-mL Schlenk flask, $CpRu(PPh_3)_2SR$, (R= CMe_3 or 4-C_6H_4Me or $CHMe_2$), (0.25 mmol) was dissolved in THF (10.0 mL). The salt [$MeSSMe_2$]BF_4 (0.055 g, 0.28 mmol) was added and the resulting mixture was stirred for 3 hours. During that time, a yellow precipitate was formed and isolated by removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3 x 5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals. Yield 85% (R= CMe_3); 70% (R= 4-C_6H_4Me); 80% (R= $CHMe_2$). mp: 181-183 °C. ^1H NMR (CD_2Cl_2): 2.26 (s, 6H, $C\underline{H}_3$), 4.47 (s, 5H, Cp), 7.03 (m, 12H, PPh_3), 7.38 (m, 18H, PPh_3). Anal. Calcd. for ($C_{43}H_{41}BF_4P_2RuS$): 61.50% C, 4.92% H, 3.82% S. Found: 61.17% C, 4.91% H, 3.99 S% .

η^5–Cyclopentadienylbis(triphenylphosphine)phthalimidoruthenium(II), $CpRu(PPh_3)_2(phth)$, 6. In a 100-mL Schlenk flask, $CpRu(PPh_3)_2SCMe_3$ or $CpRu(PPh_3)_2SCHMe_2$ (0.65 mmol) was dissolved in THF (30.0 mL). Methylthiophthalimide (0.13 g, 0.65 mmol) was added as a solid. The resulting mixture was stirred at room temperature for 2 days. The volume was concentrated to 3.0 mL under vacuum and the concentrate placed on an alumina column (20 mm x 30 cm). Elution with hexanes removed PPh_3. Elution with THF in hexanes (1:2) gave a yellow fraction which was collected and reduced to 15.0 mL and cooled to 0 °C overnight. Yellow crystals of the title complex were produced. Yield 78% (R= CMe_3); 84% (R= $CHMe_2$). mp: 126-127 °C. IR (KBr Disk): $\nu_{(CO)}$= 1651(s) cm^{-1}. ^1H NMR ($CDCl_3$): 4.32 (s, 5H, Cp), 7.15 (m, 34H, PPh_3, $C_6\underline{H}_4$). Anal. Calcd. for ($C_{49}H_{39}NO_2P_2Ru$): 70.32% C, 4.70% H, 1.67% N. Found: 69.52% C, 5.16% H, 1.63% N. A red fraction was also collected by eluting the column with THF in hexanes (2:1). Recrystallization of the crude solid from methylene chloride/hexanes gave red crystals of **7a** where R= CMe_3 or **7b** where R= $CHMe_2$ (see below).

Bis(η^5–cyclopentadienyl)(diphthalimido)(μ-methylthiolato)(μ-2-methyl-2-propylthiolato)diruthenium(II), (μ-SMe)(μ-$SCMe_3$)[CpRu(phth)]$_2$, 7a. Yield (0.070 g, 43%). mp: 162-164 °C. IR (KBr Disk): $\nu_{(CO)}$= 1658(s) cm^{-1}. ^1H NMR ($CDCl_3$): 1.90 (s, 9H, $C(C\underline{H}_3)_3$), 3.44 (s, 3H, $SC\underline{H}_3$), 5.22 (s, 10H, Cp), 7.41 (m, 4H, $C_6\underline{H}_4$), 7.47 (m, 4H, $C_6\underline{H}_4$). Anal. Calcd. for ($C_{31}H_{30}N_2O_4Ru_2S_2$): 48.92% C, 3.97% H, 3.86% N, 8.68% S. Found: 49.00% C, 4.12% H, 3.51% N, 8.16% S.

Bis(η^5–cyclopentadienyl)(diphthalimido)(μ-methylthiolato)(μ-2-propylthiolato)diruthenium(II), (μ-SMe)(μ-$SCHMe_2$)[CpRu(phth)]$_2$, 7b. Yield (0.05 g, 31%). mp: 171-173 °C. IR (KBr Disk): $\nu_{(CO)}$= 1663(s) cm^{-1}. ^1H NMR (CD_2Cl_2): 1.98 (d, 6H, $CH(C\underline{H}_3)_2$), 3.25 (septet, 1H, $C\underline{H}(CH_3)_2$), 3.39 (s, 3H, $SC\underline{H}_3$), 5.17 (s, 10H, Cp), 7.48 (m, 8H, $C_6\underline{H}_4$). Anal. Calcd. for ($C_{30}H_{28}N_2O_4Ru_2S_2$): 48.23% C, 3.78% H, 3.75%N, 8.58% S. Found: 48.09% C, 3.73% H, 3.33% N, 6.98% S.

η^5–Cyclopentadienyl(triphenylphosphine)(phthalimido)(methyl-4-methylbenzenedisulfide)ruthenium(II), $CpRu(PPh_3)(phth)(MeSS\text{-}4\text{-}C_6H_4Me)$, 8. In a 100-mL Schlenk flask, $CpRu(PPh_3)_2S\text{-}4\text{-}C_6H_4Me$ (0.50 g, 0.62 mmol) was dissolved in THF (30.0 mL). Methylthiophthalimide (0.14 g, 0.68 mmol) was added as a solid. The resulting mixture was stirred at room temperature for 6 days. The volume was concentrated to 3.0 mL under vacuum and placed on an alumina column (20 mm x 30 cm). Elution with hexanes removed PPh_3. Elution with THF in hexanes (1:2) gave an orange fraction which was collected and stripped to dryness. Elution with THF in hexanes (2:1) gave a red fraction. The ^1H NMR spectrum of the residue from the orange band demonstrated the presence of two compounds. Also, the ^1H NMR spectrum of the residue from the red band revealed the presence of several compounds as indicated by the number of Cp-peaks. The red band was discarded and the orange product was redissolved in THF and was chromatographed on another alumina column (10 mm x 20 cm). Elution with THF in hexanes (1:5) gave a yellow band which was collected and reduced to 10 mL. Storage at 0 °C overnight gave the complex as a yellow solid (23.0 mg, 15%). mp: 97-99 °C. IR (KBr Disk): $\nu_{(CO)}$= 1652(s) cm^{-1}. ^1H NMR (C_6D_6): 2.02 (s, 3H, $4\text{-}C_6H_4C\underline{H}_3$), 2.15 (s, 3H, $C\underline{H}_3$), 4.33 (s, 5H, Cp), 6.94 (d, 2H, $C_6\underline{H}_4CH_3$), 6.95 (d, 2H, $C_6\underline{H}_4CH_3$), 6.97 (m, 8H, PPh_3, $C_6\underline{H}_4$), 7.45 (m, 11H, PPh_3, $C_6\underline{H}_4$). Mass spectrum (FAB in NBA): m/e 744 ($M^{\cdot+}$), 598 ($M^{\cdot+}$-phth), 428 ($M^{\cdot+}$-(phth+$MeSSC_6H_4Me$)), 166 ($M^{\cdot+}$-(phth+$MeSSC_6H_4Me$+PPh_3)). High resolution mass spectrum (FAB, Glycerol) for $C_{39}H_{34}O_2NS_2P^{102}Ru$: 746.0892100 (Calcd.: 746.0890342). Elution with THF in hexanes (1:2) gave a red fraction which was collected and stripped to dryness. Recrystallization from methylene chloride/hexanes gave red crystals of 9 (see below).

Bis(η^5–cyclopentadienyl)bis(4-methylbenzenethiolato)(μ-methylthiolato)(μ-4-methylbenzenethiolato)diruthenium(II), (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)]$_2$, 9. Yield (30.0 mg, 10%). mp: 160-162 °C. ^{1}H NMR (CD_2Cl_2): 1.79 (s, 3H, $C_6H_4C\underline{H}_3$), 2.22 (s, 6H, $C_6H_4C\underline{H}_3$), 2.33 (s, 3H, $C\underline{H}_3$), 5.05 (s, 10H, Cp), 6.85 (d, 2H, $C_6\underline{H}_4CH_3$), 7.10 (d, 2H, $C_6\underline{H}_4CH_3$), 7.30 (m, 8H, $C_6\underline{H}_4CH_3$). Mass spectrum (FAB in NBA): m/e 750 ($M^{\cdot+}$), 627 ($M^{\cdot+}$-SC_6H_4Me), 504 ($M^{\cdot+}$-2(SC_6H_4Me)), 489 ($M^{\cdot+}$-(2(SC_6H_4Me)+Me)), 289 ($M^{\cdot+}$-(CpRu+2(SC_6H_4Me)+SMe)). High resolution mass spectrum (FAB, Glycerol) for $C_{32}H_{34}O_2NS_4{}^{102}Ru_2$: 750.9707100 (Calcd.: 750.9708586).

η^5–Cyclopentadienylbis(triphenylphosphine)(2-propenyl-1-thiolato)-ruthenium(II), CpRu(PPh_3)$_2$$SCH_2CH=CH_2$, 10. A 3-neck round bottom flask equipped with a reflux condenser was charged with THF (100.0 mL) and cooled to -78 °C in an ethanol/dry ice bath. Methyllithium (2.05 mL, 1.4 M in ether, 2.87 mmol) was added followed by allylthiol (0.23 mL, 2.87 mmol). The cooling bath was removed and the solution was warmed to 0 °C. The flask was immersed in a water bath at 40 °C for 15 minutes. The complex CpRu(PPh_3)$_2$Cl (1.00 g, 1.44 mmol) was added and the resulting slurry was refluxed for 30 minutes. The volume of the mixture was concentrated under vacuum to about 50 mL and ethanol (100.0 mL) was added. Further concentration to about 30 mL, followed by standing, gave the product as an orange solid which was collected by decanting the mother liquor. The solid was washed with ethanol and hexanes several times and dried in vacuo overnight (0.90 g, 81%). mp: 128-130 °C. ^{1}H NMR (C_6D_6): 3.06 (d, 2H, $C\underline{H}_2CH=CH_2$), 4.38 (s, 5H, Cp), 5.02 (dd, 1H, $CH_2CH=C\underline{H}_2$), 5.28 (dd, 1H, $CH_2CH=C\underline{H}_2$), 6.80 (m, 1H, $CH_2C\underline{H}=CH_2$), 7.30 (m, 18H, PPh_3), 7.40 (m, 12H, PPh_3). Anal. Calcd. for ($C_{44}H_{40}P_2RuS$): 69.17% C, 5.28% H, 4.20% S. Found: 69.32% C, 5.21% H, 4.36% S.

η^5–Cyclopentadienyl(carbonyl)(triphenylphosphine)(2-propenyl-1-thiolato)-ruthenium(II), $CpRu(PPh_3)(CO)SCH_2CH=CH_2$, 11. In a 100-mL Schlenk flask, **10**, (0.50 g, 0.65 mmol) was dissolved in THF (50.0 mL). CO gas was bubbled through the solution for one hour and the resulting yellow mixture was stirred under CO atmosphere for 5 hours. The solution was reduced in volume to 2.0 mL and chromatographed on alumina (20 mm x 30 cm). Elution with hexanes removed PPh_3. Elution with THF in hexanes (1:2) gave yellow fraction which was collected and stripped to dryness. The resulting yellow solid was recrystallized from THF/hexanes to give yellow crystals (0.30 g, 87%). mp 149-150 °C. IR (KBr Disk): $\nu_{(CO)}$= 1908(s), 1921(sh) cm^{-1}. ^1H NMR (C_6D_6): 3.24 (d, 2H, $C\underline{H_2}CH=CH_2$), 4.70 (s, 5H, Cp), 5.00 (dd, 1H, $CH_2CH=C\underline{H_2}$), 5.21 (dd, 1H, $CH_2CH=C\underline{H_2}$), 6.21 (m, 1H, $CH_2C\underline{H}=CH_2$), 7.09 (m, 9H, PPh_3), 7.69 (m, 6H, PPh_3). Anal. Calcd. for ($C_{27}H_{25}OP_2RuS$): 61.22% C, 4.76% H. Found: 60.20% C, 4.76 % H.

η^5–Cyclopentadienyl(triphenylphosphine)(2-propenyl-1-thioxanthato)-ruthenium(II), $CpRu(PPh_3)S_2CSCH_2CH=CH_2$, 12. A solution of **10** (0.50 g, 0.65 mmol) in toluene (100.0 mL) was treated with CS_2 (40.0 mL) and stirred for 30 minutes. The solvent was removed under vacuum and the remaining solid was dissolved in THF (3.0 mL) and was chromatographed on alumina (20 mm x 30 cm). Elution with hexanes removed PPh_3. Elution with THF in hexanes (1:2) gave a brown fraction which was collected and stripped to dryness. The resulting brown solid was recrystallized from THF/hexanes to give dark red crystals (0.34 g, 90%). mp 132-133 °C. IR (KBr Disk): $\nu_{(CS\ of\ CS3)}$= 991 (s) cm^{-1}, $\nu_{(CS\ of\ SR)}$= 692(s) cm^{-1}. ^1H NMR (C_6D_6): 3.43 (d, 2H, $C\underline{H_2}CH=CH_2$), 4.29 (s, 5H, Cp), 4.86 (dd, 1H, $CH_2CH=C\underline{H_2}$), 4.94 (dd, 1H, $CH_2CH=C\underline{H_2}$), 5.61 (m, 1H, $CH_2C\underline{H}=CH_2$), 7.03 (m, 9H, PPh_3), 7.60 (m, 6H, PPh_3). Anal. Calcd. for ($C_{27}H_{25}PRuS_3$): 56.12% C, 4.36% H. Found: 56.53% C, 4.56% H.

Tris(η^5–cyclopentadienyl)di(μ_3-sulfido)(μ-2-propenyl-1-thiolato)-triruthenium, $(\mu_3\text{-S})_2(\mu\text{-SCH}_2\text{CH=CH}_2)[\text{CpRu}]_3$, 13. A solution of **10** (0.50 g, 0.65 mmol) in toluene (50.0 mL) was prepared in a Schlenk flask fitted with a reflux condenser. The solution was refluxed for 3 hours and was allowed to cool. The solution was reduced in volume to about 3 mL and was chromatographed on alumina (20 mm x 30 cm). Elution with hexanes removed PPh_3. Elution with THF in hexanes (1:4) gave brown fraction which was collected and stripped to dryness. Recrystallization from benzene/hexanes gave brown crystals (0.058 g, 42%). mp 177-179 °C. ^{1}H NMR (C_6D_6): 2.79 (d, 2H, $\text{C}\underline{\text{H}}_2\text{CH=CH}_2$), 4.46 (s, 10H, Cp), 4.78 (s, 5H, Cp), 4.95 (dd, 1H, $\text{CH}_2\text{CH=C}\underline{\text{H}}_2$), 5.01 (dd, 1H, $\text{CH}_2\text{CH=C}\underline{\text{H}}_2$), 5.93 (m, 1H, $\text{CH}_2\text{C}\underline{\text{H}}\text{=CH}_2$). Anal. Calcd. for ($\text{C}_{18}\text{H}_{20}\text{Ru}_3\text{S}_3$): 33.99% C, 3.17% H, 15.12% S. Found: 34.51% C, 3.28% H, 14.52% S.

η^5–Cyclopentadienyl(carbonyl)(triphenylphosphine)(methyl-2-propenyl-disulfideruthenium(II) hexafluorophosphate, $[\text{CpRu(PPh}_3\text{)(CO)(CH}_3\text{SCH}_2\text{CH=CH}_2\text{)]PF}_6$, 14. In a 100-mL Schlenk flask, **11** (0.20 g, 0.38 mmol) was dissolved in THF (10.0 mL). Methyl iodide (0.056 g, 0.40 mmol) was added followed by ammonium hexafluorophosphate (0.065 g, 0.40 mmol). The reaction mixture was stirred for 3 hours. A yellow precipitate was formed during that time which was collected by the removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3 x 5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals (0.19 g, 73%). mp: 181-183 °C. IR (KBr Disk): $\nu_{(\text{CO})}$= 1991(s) cm^{-1}. ^{1}H NMR (acetone-d_6): 2.36 (s, 3H, $\text{C}\underline{\text{H}}_3$), 3.50 (m, 2H, $\text{C}\underline{\text{H}}_2\text{CH=CH}_2$), 5.29 (m, 1H, $\text{CH}_2\text{CH=C}\underline{\text{H}}_2$), 5.36 (m, 1H, $\text{CH}_2\text{CH=C}\underline{\text{H}}_2$), 5.56 (s, 5H, Cp), 5.70 (m, 1H, $\text{CH}_2\text{C}\underline{\text{H}}\text{=CH}_2$), 7.44 (m, 9H, PPh_3), 7.63 (m, 6H, PPh_3). Anal. Calcd. for ($\text{C}_{28}\text{H}_{28}\text{F}_6\text{OP}_2\text{RuS}$): 48.76% C, 4.09% H. Found: 48.01% C, 4.16 % H.

η^5–Cyclopentadienyl(carbonyl)(triphenylphosphine)(2-propene-1-thiol)-ruthenium(II) tetrafluoroborate, $[CpRu(PPh_3)(CO)(HSCH_2CH{=}CH_2)]BF_4$, 15. In a 100-mL Schlenk flask, **11** (0.20 g, 0.38 mmol) was dissolved in THF (10.0 mL) and $HBF_4.Et_2O$ (0.069 mL, 0.40 mmol) was added. The reaction mixture was stirred for 30 minutes. The solution was reduced in volume to 3.0 mL and 10.0 mL of diethyl ether was added. A yellow precipitate was formed which was collected by the removal of the mother liquor with a syringe. The precipitate was washed with hexanes (3 x 5.0 mL) and recrystallized from methylene chloride/hexanes to give yellow crystals (0.19 g, 81%). mp: 162-164 °C. IR (KBr Disk): $\nu_{(CO)}$= 1991(s), 1979(m) cm^{-1}, $\nu_{(SH)}$= 2508(w) cm^{-1}. ^1H NMR (acetone-d_6): 3.40 (m, 3H, $C\underline{H_2}CH{=}CH_2$, $S\underline{H}$), 5.25 (dd, 1H, $CH_2CH{=}C\underline{H_2}$), 5.35 (dd, 1H, $CH_2CH{=}C\underline{H_2}$), 5.56 (s, 5H, Cp), 5.80 (m, 1H, $CH_2C\underline{H}{=}CH_2$), 7.42 (m, 9H, PPh_3), 7.56 (m, 6H, PPh_3). Anal. Calcd for ($C_{27}H_{26}BF_4OPRuS$): 52.52% C, 4.24% H. Found: 52.30% C, 4.35 % H.

***cis*-Bis(triphenylphosphine)di(2-methyl-2-proylthiolato(S-sulfur dioxide))-platinum(II), *cis*-$(PPh_3)_2Pt(S(SO_2)CMe_3)_2$, 16a.** In a 25-mL Schlenk tube, *cis*-$(PPh_3)_2Pt(SCMe_3)_2$, (0.050 g, 0.057 mmol) was dissolved in methylene chloride (2.0 mL). The yellow solution was treated with SO_2 gas for 5 minutes to give red solution. Hexanes (10.0 mL saturated with SO_2) was added carfully so as to form a layer over the CH_2Cl_2 solution (layering) and the flask was allowed to stand at -16 °C for 6 days. A mixture of yellow and red crystals formed which was isolated by the removal of the mother liquor with a syringe. The crystals were dried with a gentle flow of SO_2. The solid was found to be a mixture of the title compound and the starting Pt thiolate as indicated by the NMR spectra. **17a**: IR (KBr Disk): $\nu_{(SO)}$= 1280(m, br), 1095(s) cm^{-1}. ^1H NMR ($CDCl_3$): 1.11 (s, 9H, $C(C\underline{H_3})_3$), 7.40 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$): 20.5 ($J_{Pt\text{-}P}$= 2930 Hz). The title complex was never isolated in pure form due to rapid loss of SO_2.

***trans*-Bis(triphenylphosphine)di(4-methylbenzenethiolato(S-sulfur dioxide))platinum(II), *trans*-$(PPh_3)_2Pt(S(SO_2)$-4-$C_6H_4Me)_2$, 16b.** In a 25-mL Schlenk tube, *trans*-$(PPh_3)_2Pt(S$-4-$C_6H_4Me)_2$, (0.050 g, 0.052 mmol) was dissolved in methylene chloride (2.0 mL). The yellow solution was treated with SO_2 gas for 5 minutes and the solution became red. The solution was layered with hexanes (10.0 mL) saturated with SO_2 and left at -16 °C for 2 days. A red crystalline solid, which easily loses SO_2, was isolated by the removal of the mother liquor with a syringe. The crystals were dried with a gentle flow of SO_2 (0.049 g, 86%). mp: lost SO_2 at 78 °C melted at 177-180 °C. IR (KBr Disk): $\nu_{(SO)}$= 1282 (m, br), 1091(s) cm^{-1}. ^1H NMR ($CDCl_3$): 2.19 (s, 3H, $C_6H_4C\underline{H}_3$), 6.74 (d, 2H, $C_6\underline{H}_4CH_3$), 7.26 (m, 17H, PPh_3, $C_6\underline{H}_4CH_3$). ^{31}P NMR ($CDCl_3$): 21.2 ($J_{Pt\text{-}P}$= 2980 Hz). Anal. Calcd. for ($C_{50}H_{44}O_4P_2PtS_4$): 54.89% C, 4.05% H, 11.72% S. Found: 57.49% C, 4.30% H, 10.76% S.

***cis*-Bis(triphenylphosphine)di(2-propylthiolato(S-sulfur dioxide))-platinum(II), $(PPh_3)_2Pt(S(SO_2)CHMe_2)_2$, 16c.** In a 25-mL Schlenk tube, *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$, (0.050 g, 0.057 mmol) was dissolved in methylene chloride (2.0 mL). The yellow solution was treated with SO_2 gas for 5 minutes and the solution became red. The solution was then layered with hexanes (10.0 mL) that was saturated with SO_2 and left at -16 °C for 7 days. A red crystalline solid, sensitive to loss of SO_2, was isolated by the removal of the mother liquor with a syringe. The crystals were dried with a gentle flow of SO_2 (0.045 g, 78%). mp: lost SO_2 at 62 °C melted at 134-138 °C. IR (KBr Disk): $\nu_{(SO)}$= 1285(m, br), 1093(s) cm^{-1}. ^1H NMR ($CDCl_3$): 1.22 (d, 6H, $CH(C\underline{H}_3)_2$), 3.68 (septet, 1H, $C\underline{H}(CH_3)_2$), 7.33 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$): 20.3 ($J_{Pt\text{-}P}$= 2926 Hz). Anal. Calcd. for ($C_{42}H_{44}O_4P_2PtS_4$): 50.54% C, 4.44% H, 12.85% S. Found: 52.05%C, 4.61%H, 10.30%S.

Bis(triphenylphosphine)(2-oxotrisulfido)platinum(II), $(PPh_3)_2PtS_3O$, 17. In a 100-mL Schlenk flask, *cis*-$(PPh_3)_2Pt(SH)_2$, (0.050 g, 0.064 mmol) was dissolved in methylene chloride (5.0 mL). The pale yellow solution was treated with SO_2 gas for 30 minutes at room temperature and stirred for an additional 3 hours. The volatiles were removed under vacuum and the resulting yellow solid was recrystallized from methylene chloride/hexanes. The yellow crystals were isolated by the removal of the mother liquor with a syringe (0.043 g, 82%). mp: 262-263 °C. IR (Nujol): $\nu_{(SO)}$= 1065(s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.26 (m, PPh_3). ^{31}P NMR ($CDCl_3$): 18.5 (J_{Pt-P}= 3200 Hz). Mass Spectrum (FAB in NBA): m/e 832 ($M^{\cdot+}$), 784 ($M^{\cdot+}$-SO), 752 ($M^{\cdot+}$-S_2O), 720 ($M^{\cdot+}$-S_3O). Anal. Calcd. for ($C_{36}H_{30}OP_2PtS_3 \cdot CH_2Cl_2$): 48.47% C, 3.52% H, 10.49% S. Found: 47.98% C, 3.53% H, 14.45% S.

Reaction of 17 with H_2S. In a 100-Schlenk flask, **17** (0.10 g, 0.12 mmol) was dissolved in THF (10.0 mL). The resulting mixture was treated with H_2S for 2 hours and stirred under H_2S atmosphere for an additional 8 hours. The reaction was monitored by ^{31}P NMR to ensure complete consumption of **17**. Then the mixture was purged with nitrogen for 30 minutes. The volume was reduced to 1.0 mL. Upon standing, a white solid precipitated which was collected by removal of the mother liquor by a syringe and washed with hexanes three times. The solid was characterized by ^1H and ^{31}P NMR spectroscopy and found to be *cis*-$(PPh_3)_2Pt(SH)_2$ (0.0021 g, 17%).

Bis(triphenylphosphine)(trithiocarbonato)platinum(II), $(PPh_3)_2Pt(S_2CS)$, 18. In a 100-mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *cis*-$(PPh_3)_2Pt(SH)_2$ (0.010 g, 0.128 mmol). The solution became yellow after it was stirred overnight. The volatile compounds were removed under vacuum. Recrystallization of the residue from methylene chloride/hexanes gave yellow crystals (0.090 g, 85%). mp: 265-267 °C. IR (KBr Disk): $\nu_{(C=S)}$= 1060(s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.20 (m, PPh_3).

^{31}P NMR ($CDCl_3$): 18.3 ($J_{Pt\text{-}P}$= 3146 Hz). Anal. Calcd. for ($C_{37}H_{30}P_2PtS_3 \cdot CH_2Cl_2$): 50.00% C, 3.53% H, 10.54% S. Found 49.81% C, 3.65% H, 10.02% S.

Triphenylphosphine(2-methyl-2-propylthiolato)(2-methyl-2-propylthioxanthato)platinum(II), (PPh_3)Pt(S_2CSCMe_3)($SCMe_3$), 19a. In a 100-mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *cis*-$(PPh_3)_2Pt(SCMe_3)_2$ (0.05 g, 0.056 mmol). The solution became dark red almost immediately and the stirring was continued for 4 hours. The volatile compounds were removed under vacuum. Recrystallization of the crude residue from hot hexanes gave purple crystals (0.031 g, 78%). mp: 160-162 °C. IR (KBr Disk): $\nu_{(CS\text{ of }CS3)}$= 988(m), $\nu_{(CS\text{ of }SR)}$= 768(s), 922(m) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.35 (s, 9H, SC($\underline{C}\underline{H}_3$)$_3$), 1.61 (s, 9H, SC($CH_3$)$_3$), 7.37 (m, 9H, PPh_3), 7.67 (m, 6H, PPh_3). ^{31}P NMR ($CDCl_3$): 17.1 ($J_{Pt\text{-}P}$ = 3780 Hz). Anal. Calcd. for ($C_{27}H_{33}PPtS_4$): 45.56% C, 4.67% H, 18.02% S. Found 45.50% C, 4.86% H, 15.93% S.

Triphenylphosphine(4-methylbenzenethiolato)(4-methylbenzenethioxanthato)platinum(II), (PPh_3)Pt(S_2CS-4-C_6H_4Me)(S-4-C_6H_4Me), 19b. In a 100-mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *trans*-$(PPh_3)_2Pt(S\text{-}4\text{-}C_6H_4Me)_2$ (0.05 g, 0.052 mmol). The solution became dark red after it was stirred overnight. The volatile compounds were removed under vacuum. Recrystallization of the residue from methylene chloride/hexanes gave red crystals (0.035 g, 86%). mp: 196-198 °C. IR (KBr Disk): $\nu_{(CS\text{ of }CS3)}$= 980(s), $\nu_{(CS\text{ of }SR)}$= 805(s), 943(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.24 (s, 3H, $SC_6H_4C\underline{H}_3$), 2.34 (s, 3H, $SC_6H_4C\underline{H}_3$), 6.88 (d, 2H, $SC_6\underline{H}_4CH_3$), 7.12 (d, 2H, $SC_6\underline{H}_4CH_3$), 7.25 (d, 2H, $SC_6\underline{H}_4Me$), 7.29 (d, 2H, $SC_6\underline{H}_4Me$), 7.45 (m, 9H, PPh_3), 7.60 (m, 6H, PPh_3). ^{31}P NMR ($CDCl_3$): 16.8 ($J_{Pt\text{-}P}$= 3730 Hz). Anal. Calcd. for ($C_{33}H_{29}PPtS_4$): 50.82% C, 3.75% H, 16.45% S. Found: 49.77% C, 3.55% H, 15.08% S.

Triphenylphosphine(2-propylthiolato)(2-propylthioxanthato)platinum(II), $(PPh_3)Pt(S_2CSCHMe_2)(SCHMe_2)$, 19c. In a 100-mL Schlenk flask, carbon disulfide (10.0 mL) was added to a solid sample of *cis*-$(PPh_3)_2Pt(SCHMe_2)_2$ (0.050 g, 0.057 mmol). The solution became dark red almost immediately and the stirring was continued for 4 hours. The volatile compounds were removed under vacuum. Recrystallization of the residue from hot hexanes gave purple crystals (0.031 g, 79%). mp: 129-131 °C. IR (KBr Disk): $\nu_{(CS\ of\ CS3)}$= 985(s) , $\nu_{(CS\ of\ SR)}$= 799(s), 925(m) cm^{-1}. ^1H NMR ($CDCl_3$): 1.32 (d, 6H, $SCH(CH_3)_2$), 1.42 (d, 6H, $SCH(CH_3)_2$), 2.99 (septet, 1H, $SCH(CH_3)_2$), 4.06 (septet, 1H, $SCH(CH_3)_2$), 7.28 (m, 9H, PPh_3), 7.62 (m, 6H, PPh_3). ^{31}P NMR ($CDCl_3$): 17.8 ($J_{Pt\text{-}P}$= 3780 Hz). Anal. Calcd. for ($C_{25}H_{29}PPtS_4$): 43.91% C, 4.27% H, 18.76% S. Found: 44.53% C, 4.33% H, 18.40% S.

CATALYTIC REACTION OF H_2S WITH SO_2

Drying of gases: H_2S was dried by passage through a column of P_2O_5. SO_2 was purified by bubbling through concentrated sulfuric acid and then by passage through a column of P_2O_5.

Reaction vessel: the reactions were carried out in silylated Schlenk flasks (100 mL). Silylation was done by treatment of the flask with dimethyldichlorosilane (30 mL) for 12 hours under nitrogen atmosphere. Then the dimethyldichlorosilane was removed by a syringe and the flask was dried under vacuum overnight.

Solvent: methylene chloride was distilled over P_2O_5 under nitrogen, then passed through an activated alumina column and collected under nitrogen.

Sulfur Identification: sulfur produced from these reactions was identified by thin layer chromatography (TLC) and mass spectroscopy. TLC was performed using CS_2 in hexanes (1:1) as eluent using pure sulfur as reference. The R_f value (0.69) was compared to that of a pure sulfur (0.69). The plate was visualized by dipping it in a solution of ammonium molybdate (2.5 g) and cerium sulfate (1.0 g) in 10% aqueous sulfuric acid (100 mL).

Control: the reaction of SO_2 with H_2S in methylene chloride without a catalyst under the same condition of the catalyzed reaction was used as a control. This reaction was repeated three times on three different days.

Procedure: The flask was charged with the solid catalyst (5.15×10^{-2} mmol), evacuated, filled with N_2 twice and weighed. The solvent (20.0 mL) was added by a syringe. H_2S (2.06 mmol, 50.0 mL) was bubbled slowly (syringe) into the mixture, followed by the addition (syringe) of SO_2 (1.03 mmol, 25.0 mL). The resulting solution was stirred at room temperature for 3 hours, then purged with nitrogen gas for 30 minutes. The supernatant was removed under vacuum and the resulting solid was dried under vacuum for 4 days. The flask and its contents was weighed again to estimate the amount of sulfur formed. Details of the experiments are presented in Table 7.1.

In the experiment where *cis*-$(PPh_3)_2Pt(SH)_2$ was used as a catalyst, the residue was redissolved in methylene chloride (20.0 mL). Again the gases (50.0 mL of H_2S and 25.0 mL of SO_2) were bubbled through the solution which was stirred for 3 hours. After the work up (as above) an additional 0.080 g of sulfur was produced (total of 0.172 g). If the cycle is repeated an additional 0.064 g of sulfur was obtained (total of 0.236 g).

Table 7.1: Data of the catalytic reaction of SO_2 and H_2S.

Catalyst	Amount of Catlyst used (g)	Amount of Sulfur produced (g)
Non-catalyzed	0	0.008
cis-$(PPh_3)_2Pt(SH)_2$	0.040	0.092
trans-$(PPh_3)_2Pt(SH)_2$	0.040	0.009
cis-$(PPh_3)_2Pt(SHMe_2)_2$	0.045	0.098
$(PPh_3)_2Pt(S_3O)$ **17**	0.043	0.093
cis-$(PPh_3)_2PtCl_2$	0.041	0.050

Original Contributions to Knowledge

1. When the electron rich complexes $CpRu(PPh_3)_2SR$ were reacted with a variety of electrophiles, either the ruthenium atom or the sulfur atom acted as the center for attack. In all the cases, NO^+ attacked the metal to give $[CpRu(PPh_3)(NO)SR]^+$,while H^+ attacked the sulfur atom of the thiolato ligands to give $[CpRu(PPh_3)_2(HSR)]^+$. The MeS^+ moiety can attack both the metal center and the sulfur atom producing two different compounds. Reducing the electron density on the starting complexes by replacing the PPh_3 with CO resulted in a change in the site of attack by NO^+. Thus $CpRu(PPh_3)(CO)SR$ reacted with NO^+ to give dimers containing disulfide ligands wherein oxidative coupling of the thiolato ligands has occurred. This demonstrates an interesting ability to control the site of oxidation by tuning the ligand in a complex.

2. Allyl thiol was desulfurized using $CpRu(PPh_3)_2Cl$. Heating the S-bonded allyl thiolate complex, $CpRu(PPh_3)_2SCH_2CH{=}CH_2$ gave $(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH{=}CH_2)[CpRu]_3$. This process is of particular practical interest in view of the fact that thiols are significant contaminants of crude oil.

3. The reaction of *cis*-$(PPh_3)_2Pt(SH)_2$ with SO_2 gave $(PPh_3)_2PtS_3O$ and H_2O, a reaction which mimics Claus chemistry. This is the first reaction in which a compound containing the thiolo group, (SH), reacted with SO_2 forming a sulfur-sulfur bond and transferring an oxygen atom to give a water molecule. These steps are fundamental in Claus chemistry.

4. Both *cis*-$(PPh_3)_2Pt(SH)_2$ and $(PPh_3)_2PtS_3O$ are Claus chemistry catalysts. These are the first such homogeneous catalysts of which we are aware. This provides insight into the possible nature of Claus chemistry and opens a new area of future study.

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APPENDIX 1

Structural Analysis of [CpRu(PPh$_3$)(NO)SCMe$_3$]BF$_4$.

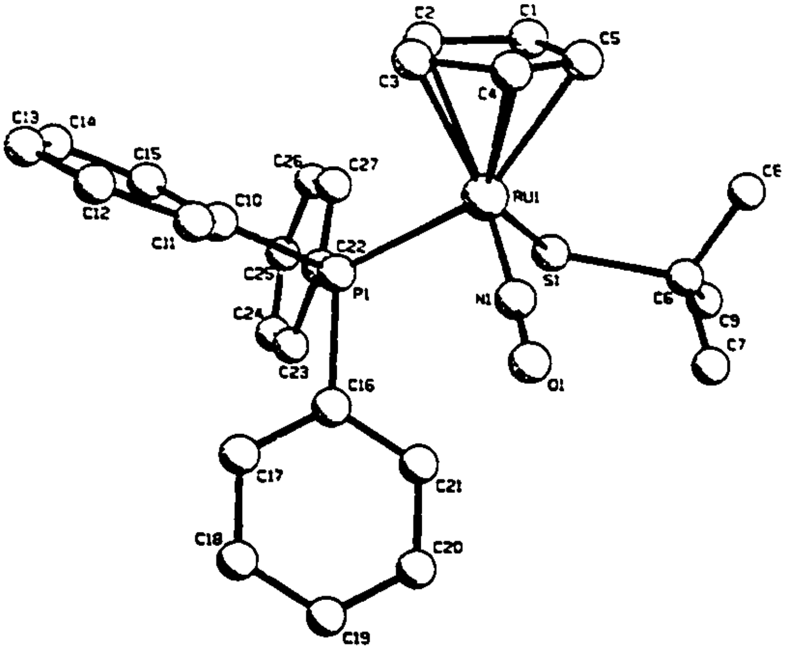

Table A1.1: Crystal data for $[CpRu(PPh_3)(NO)SCMe_3]BF_4$.

Space Group: monoclinic $P2_1/c$

Cell Dimensions:

a = 16.380(2) Å	b = 17.135(3) Å	c = 10.137(2) Å

β = 91.06(2)°
Volume = 2937.5(1) $Å^3$

Empirical formula: $C_{27}H_{29}BF_4NOPRuS$

Cell dimensions were obtained from 25 reflections with 2θ angle in the range 30.0-35.0°.

Crystal dimensions: 0.470 x 0.125 x 0.500 mm

FW = 634.44 Z = 4 F(000) = 1288

D_{calc} = 1.481 g.cm^{-3}, μ = 7.11 mm^{-1}, λ = 0.71069 Å, $2\theta_{(max)}$ = 47.1°

The intensity data were collected on a Rigaku AFC5R diffractometer, using the ω/2θ scan mode.
T = 22 °C.

No. of reflections measured	8980
No. of unique reflections	4721
No.of reflections with $I_{net} > 3.0\sigma(I_{net})$	2626

A psi correction was made for absorption.

Data set was solved by Patterson methods.
The last least squares cycle was calculated with 313 variable parameters and 2626 out of 8980 reflections.
Weights based on counting-statistics were used.

The residuals are as follows:-
For significant reflections, R = 0.043 Rw = 0.047
GoF = 1.50

where

$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$

$Rw = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/\Sigma(wFo^2)]}$

$GoF = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/(\text{No.of obsvn.} - \text{No.of params.})]}$

The maximum shift/σ ratio was 0.18.

In the last D-map, the deepset hole was -0.67 e$^-$/Å^3, and the highest peak 0.60 e$^-$/Å^3.

Table A1.2: Atom coordinates, x, y, z and B_{iso} for $[CpRu(PPh_3)(NO)SCMe_3]BF_4$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Ru(1)	0.18827(03)	0.04526(04)	0.23761(06)	2.91(2)
S(1)	0.31672(11)	0.10904(11)	0.2148(02)	3.26(9)
P(1)	0.25327(10)	-0.05445(11)	0.1163(02)	2.82(8)
O(1)	0.1984(04)	-0.0404(04)	0.4831(06)	8.6(4)
N(1)	0.2008(04)	-0.0044(04)	0.3878(06)	4.4(3)
C(1)	0.1271(05)	0.1491(06)	0.1384(14)	7.0(6)
C(2)	0.1079(07)	0.0802(09)	0.0684(09)	7.2(7)
C(3)	0.0623(06)	0.0344(06)	0.1543(12)	6.2(6)
C(4)	0.0566(05)	0.0715(06)	0.2708(10)	5.4(5)
C(5)	0.0970(05)	0.1405(06)	0.2632(11)	5.6(5)
C(6)	0.3399(05)	0.1760(05)	0.3532(07)	4.0(4)
C(7)	0.3532(08)	0.1309(07)	0.4802(09)	9.5(7)
C(8)	0.2757(06)	0.2384(06)	0.3708(11)	7.9(6)
C(9)	0.4200(05)	0.2150(05)	0.3136(09)	5.8(5)
C(10)	0.1816(04)	-0.1160(04)	0.0273(07)	3.2(4)
C(11)	0.1210(05)	-0.1551(05)	0.0944(08)	4.5(4)
C(12)	0.0669(05)	-0.2051(05)	0.0315(11)	5.4(5)
C(13)	0.0735(05)	-0.2152(05)	-0.1025(11)	5.5(5)
C(14)	0.1297(06)	-0.1744(06)	-0.1736(09)	6.2(6)
C(15)	0.1837(05)	-0.1259(05)	-0.1074(08)	5.2(5)
C(16)	0.3104(04)	-0.1214(04)	0.2236(07)	3.4(4)
C(17)	0.3089(05)	-0.2016(04)	0.2023(09)	4.7(4)
C(18)	0.3557(05)	-0.2500(05)	0.2826(11)	5.8(5)
C(19)	0.4015(06)	-0.2199(06)	0.3840(10)	6.1(6)
C(20)	0.4042(05)	-0.1416(06)	0.4054(09)	5.9(5)
C(21)	0.3580(05)	-0.0917(05)	0.3253(08)	4.5(4)
C(22)	0.3266(04)	-0.0253(04)	-0.0086(07)	3.2(4)
C(23)	0.4004(05)	-0.0658(04)	-0.0202(08)	4.2(4)
C(24)	0.4502(05)	-0.0471(06)	-0.1233(10)	5.8(5)
C(25)	0.4298(07)	0.0096(07)	-0.2127(10)	7.1(6)
C(26)	0.3574(07)	0.0499(06)	-0.1982(09)	7.3(6)
C(27)	0.3061(05)	0.0334(05)	-0.0950(08)	5.5(5)
B(1)	0.0948(08)	0.1130(08)	0.6745(13)	7.7(3)
F(1)	0.0413(10)	0.1338(10)	0.7558(13)	10.6(6)
F(2)	0.1052(09)	0.1753(07)	0.5777(12)	6.5(3)
F(3)	0.0664(12)	0.0515(07)	0.592(02)	12.5(6)
F(4)	0.1684(09)	0.0955(11)	0.719(02)	17(1)
F(5)	0.1196(05)	0.0453(03)	0.7379(07)	9.4(2)
F(6)	0.0207(04)	0.1019(05)	0.6195(08)	11.1(3)
F(7)	0.1497(05)	0.1371(05)	0.5921(07)	13.2(4)
F(8)	0.0863(05)	0.1688(04)	0.7763(06)	8.8(2)

B_{iso} is the Mean of Principal Axes of the Thermal Ellipsoid.

Table A1.3: Anisotropic thermal factors for $[\mathrm{CpRu(PPh_3)(NO)SCMe_3}]\mathrm{BF_4}$. U(i,j) values × 100. E.S.Ds. refer to the last digit printed.

atom	U11	U22	U33	U12	U13	U23
Ru(1)	3.29(03)	4.29(03)	3.45(03)	0.44(03)	-0.03(02)	-0.00(04)
S(1)	3.71(11)	4.85(12)	3.81(11)	-0.20(09)	0.17(09)	-0.43(09)
P(1)	3.43(10)	3.56(11)	3.74(10)	0.05(09)	-0.02(08)	0.16(09)
O(1)	14.6(07)	12.3(06)	5.9(04)	3.6(05)	3.4(04)	4.7(05)
N(1)	6.4(05)	6.6(05)	3.9(04)	1.3(04)	1.1(03)	0.5(04)
C(1)	4.2(06)	8.3(08)	14.0(11)	2.0(05)	-0.4(07)	6.8(08)
C(2)	7.7(08)	15.1(12)	4.5(06)	7.0(08)	-0.2(05)	0.1(07)
C(3)	5.1(06)	7.3(07)	11.0(09)	0.8(05)	-3.7(06)	-1.4(07)
C(4)	4.5(05)	8.6(08)	7.6(07)	1.1(05)	0.2(05)	0.9(06)
C(5)	4.6(06)	7.0(07)	9.5(08)	1.8(05)	-1.6(05)	-3.0(06)
C(6)	5.7(05)	5.6(05)	3.8(05)	-0.9(04)	-0.2(04)	-0.9(04)
C(7)	19.0(13)	12.4(09)	4.5(06)	-7.8(09)	-4.5(07)	1.7(06)
C(8)	8.3(07)	7.7(07)	14.0(10)	-0.8(06)	0.5(07)	-6.4(07)
C(9)	6.0(06)	7.3(06)	8.7(07)	-1.9(05)	-1.6(05)	-1.5(05)
C(10)	4.0(04)	3.0(04)	5.1(05)	0.2(03)	-0.6(04)	-0.0(04)
C(11)	6.3(06)	5.3(06)	5.5(05)	-1.0(04)	-0.8(05)	0.9(04)
C(12)	5.1(06)	5.7(06)	9.8(08)	-0.7(04)	-1.3(05)	1.1(06)
C(13)	5.0(06)	5.9(06)	10.0(08)	0.3(05)	-2.2(06)	-2.3(06)
C(14)	7.0(07)	9.6(08)	7.1(07)	0.2(06)	-1.3(06)	3.9(06)
C(15)	5.6(06)	7.9(06)	6.3(06)	-1.0(05)	-0.2(05)	-2.3(05)
C(16)	3.3(04)	5.0(05)	4.7(05)	0.5(04)	0.3(04)	0.8(04)
C(17)	5.2(05)	3.9(05)	8.5(07)	0.2(04)	-0.7(05)	1.2(05)
C(18)	6.0(06)	5.0(05)	10.9(08)	0.2(05)	-0.9(06)	2.2(06)
C(19)	6.0(07)	7.4(07)	9.9(08)	0.9(05)	-0.7(06)	4.0(06)
C(20)	6.5(06)	8.3(07)	7.7(07)	0.4(05)	-2.2(05)	2.5(06)
C(21)	5.7(06)	5.1(05)	6.2(06)	1.3(04)	-0.9(05)	0.5(04)
C(22)	4.2(05)	3.9(05)	3.9(04)	-0.1(03)	0.5(03)	- 0.7(03)
C(23)	4.8(05)	5.2(06)	6.0(05)	-1.1(04)	1.7(04)	-1.8(04)
C(24)	5.5(06)	8.4(07)	8.2(07)	-1.9(06)	2.5(05)	-3.2(06)
C(25)	9.7(09)	11.5(09)	6.1(07)	-3.7(07)	4.9(06)	-1.9(06)
C(26)	11.9(09)	9.9(08)	6.0(06)	-0.0(08)	3.4(06)	2.0(06)
C(27)	8.3(07)	7.4(07)	5.4(05)	1.0(05)	2.3(05)	0.9(05)
B(1)	9.7(04)					
F(1)	13.4(07)					
F(2)	8.3(04)					
F(3)	15.8(08)					
F(4)	21.9(12)					
F(5)	11.9(03)					
F(6)	14.0(03)					
F(7)	16.8(05)					
F(8)	11.1(03)					

Table A1.4: Selected bond lengths (Å) and angles (deg) for [CpRu(PPh3)(NO)SCMe3]BF$_4$.

Ru(1)-S(1)	2.386(2)	C(6)-C(9)	1.53(1)
Ru(1)-P(1)	2.369(2)	C(10)-C(11)	1.39(1)
Ru(1)-N(1)	1.753(6)	C(10)-C(15)	1.38(1)
Ru(1)-C(1)	2.27(1)	C(11)-C(12)	1.38(1)
Ru(1)-C(2)	2.22(1)	C(12)-C(13)	1.38(2)
Ru(1)-C(3)	2.22(1)	C(13)-C(14)	1.37(1)
Ru(1)-C(4)	2.235(9)	C(14)-C(15)	1.38(1)
Ru(1)-C(5)	2.23(1)	C(16)-C(17)	1.39(1)
S(1)-C(6)	1.846(8)	C(16)-C(21)	1.38(1)
P(1)-C(10)	1.808(7)	C(17)-C(18)	1.38(1)
P(1)-C(16)	1.827(7)	C(18)-C(19)	1.36(1)
P(1)-C(22)	1.831(7)	C(19)-C(20)	1.36(1)
O(1)-N(1)	1.148(9)	C(20)-C(21)	1.39(1)
C(1)-C(2)	1.41(2)	C(22)-C(23)	1.40(1)
C(1)-C(5)	1.38(2)	C(22)-C(27)	1.37(1)
C(2)-C(3)	1.40(2)	C(23)-C(27)	1.38(1)
C(3)-C(4)	1.35(2)	C(24)-C(25)	1.37(1)
C(4)-C(5)	1.36(1)	C(25)-C(26)	1.38(2)
C(6)-C(7)	1.51(1)	C(26)-C(27)	1.38(1)
C(6)-C(8)	1.51(1)		

S(1)-Ru(1)-P(1)	82.79(7)	Ru(1)-S(1)-C(6)	112.3(3)
S(1)-Ru(1)-N(1)	102.6(2)	Ru(1)-P(1)-C(10)	112.7(2)
S(1)-Ru(1)-C(1)	88.9(2)	Ru(1)-P(1)-C(16)	112.0(2)
S(1)-Ru(1)-C(2)	108.2(3)	Ru(1)-P(1)-C(22)	118.0(2)
S(1)-Ru(1)-C(3)	144.7(3)	P(1)-C(22)-C(23)	120.1(5)
S(1)-Ru(1)-C(4)	141.1(3)	P(1)-C(22)-C(27)	119.0(6)
S(1)-Ru(1)-C(5)	105.7(2)	C(10)-P(1)-C(16)	104.5(3)
P(1)-Ru(1)-N(1)	93.1(2)	C(10)-P(1)-C(22)	104.0(3)
P(1)-Ru(1)-C(1)	122.3(3)	C(16)-P(1)-C(22)	104.3(3)
P(1)-Ru(1)-C(2)	93.4(3)	Ru(1)-N(1)-O(1)	170.7(7)
P(1)-Ru(1)-C(3)	99.5(3)	Ru(1)-C(1)-C(2)	70.0(6)
P(1)-Ru(1)-C(4)	131.8(3)	Ru(1)-C(1)-C(5)	70.8(6)
P(1)-Ru(1)-C(5)	153.7(3)	Ru(1)-C(2)-C(1)	73.4(6)
N(1)-Ru(1)-C(1)	144.1(4)	Ru(1)-C(2)-C(3)	71.6(6)
N(1)-Ru(1)-C(2)	149.1(4)	Ru(1)-C(3)-C(2)	71.7(6)
N(1)-Ru(1)-C(3)	112.5(4)	Ru(1)-C(3)-C(4)	72.9(6)
N(1)-Ru(1)-C(4)	93.7(3)	Ru(1)-C(4)-C(3)	71.9(5)
N(1)-Ru(1)-C(5)	108.8(3)	Ru(1)-C(4)-C(5)	72.1(5)
C(1)-Ru(1)-C(2)	36.6(5)	Ru(1)-C(5)-C(1)	73.7(6)
C(1)-Ru(1)-C(3)	59.9(4)	Ru(1)-C(5)-C(4)	72.4(6)
C(1)-Ru(1)-C(4)	59.3(4)	S(1)-C(6)-C(7)	110.7(6)
C(1)-Ru(1)-C(5)	35.6(4)	P(1)-C(10)-C(11)	120.1(6)
C(2)-Ru(1)-C(3)	36.7(4)	P(1)-C(10)-C(15)	122.6(6)
C(2)-Ru(1)-C(4)	60.2(4)	P(1)-C(16)-C(17)	121.4(6)
C(2)-Ru(1)-C(5)	60.3(4)	P(1)-C(16)-C(21)	119.3(6)
C(3)-Ru(1)-C(4)	35.1(4)	P(1)-C(22)-C(20)	120.2(8)
C(3)-Ru(1)-C(5)	59.1(4)	P(1)-C(22)-C(23)	120.1(5)
C(4)-Ru(1)-C(5)	35.4(4)		

APPENDIX 2

Structural Analysis of (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)]$_2$.

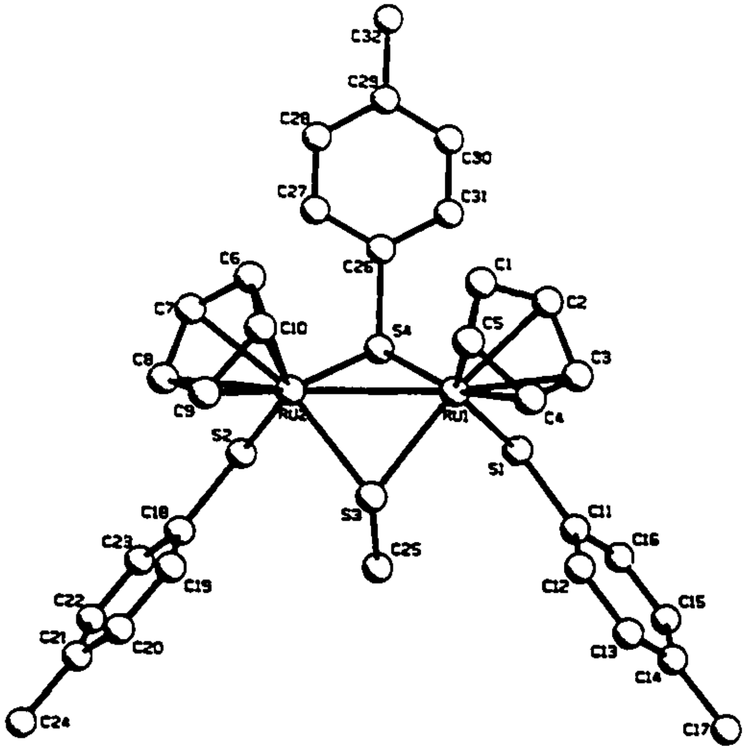

Table A2.1: Crystal data for $(\mu\text{-SMe})(\mu\text{-4-SC}_6\text{H}_4\text{Me})[\text{CpRu(S-4-C}_6\text{H}_4\text{Me})]_2$.

Space Group: monoclinic $P2_1/c$

Cell Dimensions:
$a = 8.805(2)$ Å $b = 13.668(3)$ Å $c = 26.026(6)$ Å
$\beta = 108.86(2)°$
Volume = 2963.8(12) Å^3

Empirical formula: $C_{32}H_{34}Ru_2S_4$

Cell dimensions were obtained from 24 reflections with 2θ angle in the range 24.00-29.00°.

Crystal dimensions: 0.500 x 0.130 x 0.110 mm

FW = 749.22 Z = 4 F(000) = 1512

$D_{calc} = 1.678$ g.cm^{-3}, $\mu = 12.92$ mm^{-1}, $\lambda = 0.71069$ Å, $2\theta_{(max)} = 45°$

The intensity data were collected on a Rigaku AFC5R diffractometer, using the $\omega/2\theta$ scan mode.
T = 19 °C.

No. of reflections measured	4386
No. of unique reflections	4077
No.of reflections with $I_{net} > 3.0\sigma(I_{net})$	2656

Data set was solved by heavy atom method.
The last least squares cycle was calculated with 344 variable parameters and 2656 out of 4386 reflections.
Weights based on counting-statistics were used.

The residuals are as follows:-
For significant reflections, R = 0.043 Rw = 0.040
GoF = 1.27

where $R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$

$Rw = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/\Sigma(wFo^2)]}$

$GoF = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/(\text{No.of obsvn.} - \text{No.of params.})]}$

The maximum shift/σ ratio was 0.02.

In the last D-map, the deepset hole was -0.042 e$^-$/Å^3, and the highest peak 0.042 e$^-$/Å^3.

Table A2.2: Atom coordinates, x, y, z and B_{iso} for (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)]$_2$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Ru(1)	0.39910(08)	0.20363(06)	0.11592(03)	3.06(3)
Ru(2)	0.50603(08)	0.12861(06)	0.22083(03)	2.94(3)
S(1)	0.5069(03)	0.1270(02)	0.05237(10)	4.1(1)
S(2)	0.7016(03)	0.00103(18)	0.23694(10)	3.8(1)
S(3)	0.6493(03)	0.22846(18)	0.18006(09)	3.4(1)
S(4)	0.3927(03)	0.04068(18)	0.14118(09)	3.3(1)
C(1)	0.1590(16)	0.2589(11)	0.1085(08)	7.4(8)
C(3)	0.2798(18)	0.3051(11)	0.0480(05)	6.5(7)
C(4)	0.3377(13)	0.3604(08)	0.0940(07)	5.8(6)
C(5)	0.266(02)	0.3315(11)	0.1315(05)	6.8(7)
C(6)	0.2999(12)	0.1396(09)	0.2508(05)	5.3(6)
C(7)	0.4094(15)	0.0765(08)	0.2831(05)	5.4(6)
C(8)	0.5500(13)	0.1267(11)	0.3091(04)	5.7(6)
C(9)	0.5295(17)	0.2226(10)	0.2942(05)	6.2(7)
C(10)	0.3726(18)	0.2317(09)	0.2577(05)	6.5(7)
C(11)	0.6169(10)	0.2081(08)	0.0250(03)	3.7(4)
C(12)	0.6635(11)	0.3015(08)	0.0423(03)	4.0(5)
C(13)	0.7524(11)	0.3577(07)	0.0179(04)	4.1(5)
C(14)	0.7970(11)	0.3225(08)	-0.0251(04)	3.9(5)
C(15)	0.7507(11)	0.2285(08)	-0.0426(04)	4.2(5)
C(16)	0.6632(10)	0.1723(07)	-0.0182(04)	3.8(5)
C(17)	0.8930(12)	0.3863(09)	-0.0510(04)	5.5(6)
C(18)	0.8865(10)	0.0332(07)	0.2866(03)	3.4(4)
C(19)	0.9301(11)	0.1270(07)	0.3059(04)	3.9(4)
C(20)	1.0766(11)	0.1426(07)	0.3445(04)	4.1(5)
C(21)	1.1879(11)	0.0689(08)	0.3660(04)	3.5(4)
C(22)	1.1432(11)	-0.0239(08)	0.3445(04)	4.0(5)
C(23)	0.9992(11)	-0.0408(07)	0.3062(04)	3.7(4)
C(24)	1.3463(11)	0.0894(08)	0.4095(04)	4.6(5)
C(25)	0.8116(10)	0.1688(08)	0.1647(04)	4.8(5)
C(26)	0.1934(10)	-0.0032(06)	0.1323(03)	3.0(4)
C(27)	0.1586(10)	-0.0553(07)	0.1723(04)	3.8(4)
C(29)	-0.1133(10)	-0.0820(07)	0.1147(04)	3.4(4)
C(30)	-0.0758(11)	-0.0352(08)	0.0743(04)	4.5(5)
C(31)	0.0759(12)	0.0051(08)	0.0824(04)	4.5(5)
C(32)	-0.2816(10)	-0.1202(07)	0.1058(04)	4.8(5)

B_{iso} is the Mean of Principal Axes of the Thermal Ellipsoid.

Table A2.3: Anisotropic thermal factors for (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)]$_2$. U(i,j) values × 100. E.S.Ds. refer to the last digit printed.

atom	U11	U22	U33	U12	U13	U23
Ru(1)	3.17(04)	4.16(05)	4.26(05)	0.30(04)	1.17(04)	0.32(04)
Ru(2)	3.32(04)	4.20(05)	3.73(05)	-0.26(04)	1.24(04)	-0.16(04)
S(1)	5.93(17)	4.97(17)	5.32(17)	-1.00(14)	2.54(14)	-1.12(14)
S(2)	4.38(15)	3.75(15)	5.34(17)	-0.14(12)	0.35(13)	0.17(13)
S(3)	3.43(14)	4.14(16)	5.14(16)	-0.48(11)	1.26(12)	0.38(12)
S(4)	3.57(13)	4.56(16)	4.35(15)	-0.13(12)	1.05(11)	-0.26(13)
C(1)	4.6(08)	7.9(11)	16.8(17)	2.8(07)	5.3(10)	5.3(11)
C(2)	6.1(10)	7.1(10)	11.1(12)	2.0(08)	-4.5(09)	-0.7(10)
C(3)	10.1(11)	7.8(10)	6.5(09)	4.7(09)	2.2(08)	3.3(08)
C(4)	6.0(08)	3.8(07)	10.9(11)	1.5(06)	1.0(08)	1.7(08)
C(5)	11.5(12)	9.2(11)	5.5(08)	5.9(09)	3.1(09)	2.3(08)
C(6)	4.6(07)	6.7(09)	8.9(09)	0.8(07)	2.6(06)	-1.7(08)
C(7)	8.2(09)	7.4(09)	6.6(08)	-2.1(08)	4.9(07)	0.1(07)
C(8)	5.6(07)	12.2(12)	4.0(07)	1.5(08)	1.5(06)	-1.6(08)
C(9)	11.0(11)	7.7(10)	6.3(09)	-5.3(09)	4.8(08)	-3.6(08)
C(10)	12.6(12)	7.1(10)	6.3(09)	4.6(09)	5.2(09)	1.1(07)
C(11)	3.7(05)	6.8(07)	3.0(06)	0.1(05)	0.6(04)	0.4(05)
C(12)	5.7(07)	6.0(07)	3.4(06)	-0.4(06)	1.5(05)	-1.8(06)
C(13)	5.6(07)	5.3(07)	4.8(07)	-1.0(06)	2.0(05)	-0.8(06)
C(15)	4.5(06)	7.7(09)	4.0(06)	0.7(06)	1.4(05)	-0.9(06)
C(14)	3.9(06)	7.5(08)	3.3(06)	-0.2(06)	0.8(05)	0.5(06)
C(16)	4.1(06)	5.3(07)	5.2(07)	-0.9(05)	1.5(05)	-1.2(05)
C(17)	5.8(07)	10.3(10)	5.3(07)	-0.7(07)	2.5(06)	0.5(07)
C(18)	3.9(05)	4.6(07)	4.5(06)	-0.4(05)	1.3(05)	-0.0(05)
C(19)	3.9(06)	3.9(06)	6.0(07)	0.5(05)	0.4(05)	0.1(06)
C(20)	5.2(07)	4.2(07)	5.9(07)	-0.3(05)	1.7(06)	-1.4(06)
C(21)	4.2(06)	6.1(07)	3.3(06)	-0.7(06)	1.3(05)	0.5(05)
C(22)	4.2(06)	6.0(08)	3.9(06)	0.7(05)	-0.2(05)	2.2(06)
C(23)	5.8(07)	3.2(06)	5.0(07)	0.2(05)	1.7(05)	0.9(05)
C(24)	4.0(06)	7.3(08)	4.9(07)	0.2(05)	-0.0(05)	0.2(06)
C(25)	3.4(06)	8.1(09)	6.8(07)	0.7(06)	1.9(05)	2.1(06)
C(26)	3.8(05)	3.5(06)	3.5(06)	0.2(04)	0.3(05)	0.3(05)
C(27)	4.2(06)	5.1(07)	3.5(06)	-0.3(05)	-0.7(05)	-0.1(05)
C(28)	5.1(06)	5.3(07)	5.1(07)	-2.0(05)	1.2(05)	0.2(05)
C(29)	3.9(06)	3.5(06)	5.8(07)	0.6(05)	1.7(05)	-0.7(05)
C(30)	3.9(06)	6.3(08)	5.4(07)	-0.6(06)	-0.7(05)	-0.4(06)
C(31)	6.0(07)	7.9(08)	3.1(06)	-0.4(06)	1.4(05)	0.2(06)
C(32)	3.2(06)	6.1(07)	8.5(08)	0.0(05)	1.4(05)	-0.6(06)

Table A2.4: Selected bond lengths (Å) and angles (deg) for (μ-SMe)(μ-S-4-C_6H_4Me)[CpRu(S-4-C_6H_4Me)$]_2$.

Ru(1)-Ru(2)	2.780(1)	C(6)-C(7)	1.36(1)
Ru(1)-S(1)	2.398(3)	C(6)-C(10)	1.40(2)
Ru(1)-S(3)	2.319(2)	C(7)-C(8)	1.39(1)
Ru(1)-S(4)	2.328(3)	C(8)-C(9)	1.36(2)
Ru(1)-C(1)	2.19(1)	C(9)-C(10)	1.41(2)
Ru(1)-C(2)	2.21(1)	C(11)-C(12)	1.37(1)
Ru(1)-C(3)	2.23(1)	C(11)-C(16)	1.40(1)
Ru(1)-C(4)	2.24(1)	C(12)-C(13)	1.39(1)
Ru(1)-C(5)	2.22(1)	C(13)-C(14)	1.39(1)
Ru(2)-S(2)	2.391(3)	C(14)-C(15)	1.38(1)
Ru(2)-S(3)	2.333(2)	C(14)-C(17)	1.51(1)
Ru(2)-S(4)	2.324(3)	C(15)-C(16)	1.38(1)
Ru(2)-C(6)	2.20(1)	C(18)-C(19)	1.39(1)
Ru(2)-C(7)	2.180(9)	C(18)-C(23)	1.39(1)
Ru(2)-C(8)	2.20(1)	C(19)-C(20)	1.37(1)
Ru(2)-C(9)	2.25(1)	C(20)-C(21)	1.39(1)
Ru(2)-C(10)	2.24(1)	C(21)-C(22)	1.39(1)
S(1)-C(11)	1.766(9)	C(21)-C(24)	1.51(1)
S(2)-C(18)	1.776(9)	C(22)-C(23)	1.35(1)
S(3)-C(25)	1.799(9)	C(26)-C(27)	1.37(1)
S(4)-C(26)	1.797(9)	C(26)-C(31)	1.38(1)
C(1)-C(2)	1.37(2)	C(27)-C(28)	1.37(1)
C(1)-C(5)	1.36(2)	C(28)-C(29)	1.39(1)
C(2)-C(3)	1.41(2)	C(29)-C(30)	1.36(1)
C(3)-C(4)	1.37(2)	C(29)-C(32)	1.52(1)
C(4)-C(5)	1.38(2)	C(30)-C(31)	1.40(1)

Ru(2)-Ru(1)-S(1)	115.62(7)	S(3)-Ru(2)-C(6)	138.6(4)
Ru(2)-Ru(1)-S(3)	53.53(6)	S(3)-Ru(2)-C(7)	158.1(3)
Ru(2)-Ru(1)-S(4)	53.22(6)	S(3)-Ru(2)-C(8)	122.9(4)
Ru(2)-Ru(1)-C(1)	103.0(4)	S(3)-Ru(2)-C(9)	97.9(3)
Ru(2)-Ru(1)-C(2)	135.5(6)	S(3)-Ru(2)-C(10)	105.2(4)
Ru(2)-Ru(1)-C(3)	158.9(4)	S(4)-Ru(2)-C(6)	100.7(3)
Ru(2)-Ru(1)-C(4)	125.5(4)	S(4)-Ru(2)-C(7)	109.6(3)
Ru(2)-Ru(1)-C(5)	98.2(3)	S(4)-Ru(2)-C(8)	143.5(4)
S(1)-Ru(1)-S(3)	93.71(9)	S(4)-Ru(2)-C(9)	161.0(4)
S(1)-Ru(1)-S(4)	80.10(9)	S(4)-Ru(2)-C(10)	125.0(4)
S(1)-Ru(1)-C(1)	132.4(6)	C(6)-Ru(2)-C(7)	36.2(4)
S(1) -Ru(1)-C(2)	97.0(5)	C(6)-Ru(2)-C(8)	61.2(4)
S(1)-Ru(1)- C(3)	85.1(3)	C(6)-Ru(2)-C(9)	61.4(4)
S(1)-Ru(1)-C(4)	111.1(4)	C(6)-Ru(2)-C(10)	36.7(4)
S(1)-Ru(1)-C(5)	145.4(3)	C(7)-Ru(2)-C(8)	36.9(4)
S(3)-Ru(1)-S(4)	92.34(8)	C(7)-Ru(2)-C(9)	60.5(4)
S(3)-Ru(1)-C(1)	132.6(6)	C(7)-Ru(2)-C(10)	60.1(4)
S(3)-Ru(1)-C(2)	157.5(4)	C(8)-Ru(2)-C(9)	35.5(4)
S(3)-Ru(1)- C(3)	125.1(5)	C(8)-Ru(2)-C(10)	60.0(4)
S(3)-Ru(1)-C(4)	97.9(3)	C(9)-Ru(2)-C(10)	36.5(4)
S(3)-Ru(1)-C(5)	100.9(4)	Ru(1)-S(1)-C(11)	113.2(4)
S(4)-Ru(1)- C(1)	104.1(4)	Ru(2)-S(2)-C(18)	112.7(3)
S(4)-Ru(1)-C(2)	108.9(4)	Ru(1)-S(3)-Ru(2)	73.41(7)
S(4)-Ru(1)-C(3)	140.6(5)	Ru(1)-S(3)-C(25)	114.3(3)

S(4)-Ru(1)-C(4)	164.1(3)
S(4)- Ru(1)-C(5)	129.8(5)
C(1)-Ru(1)-C(2)	36.1(5)
C(1)-Ru(1)-C(3)	61.4(5)
C(1)-Ru(1)-C(4)	60.1(4)
C(1)-Ru(1)-C(5)	36.0(5)
C(2)-Ru(1)-C(3)	37.1(5)
C(2) -Ru(1)-C(4)	59.7(4)
C(2)-Ru(1)-C(5)	60.0(5)
C(3)-Ru(1)-C(4)	35.7(4)
C(3)-Ru(1)-C(5)	60.8(4)
C(4)-Ru(1)-C(5)	36.1(4)
Ru(1)-Ru(2)-S(2)	115.93(7)
Ru(1)-Ru(2)-S(3)	53.06(6)
Ru(1)-Ru(2)-S(4)	53.36(7)
Ru(1)-Ru(2)-C(6)	105.5(3)
Ru(1)-Ru(2)-C(7)	139.6(4)
Ru(1)-Ru(2)-C(8)	156.6(4)
Ru(1)-Ru(2)-C(9)	122.1(4)
Ru(1)-Ru(2)-C(10)	97.5(3)
S(2)-Ru(2)-S(3)	92.39(9)
S(2)-Ru(2)-S(4)	81.75(9)
S(2)-Ru(2)-C(6)	128.1(4)
S(2)-Ru(2)-C(7)	93.6(3)
S(2)-Ru(2)-C(8)	86.3(3)
S(2)-Ru(2)-C(9)	113.8(4)
S(2)-Ru(2)-C(10)	146.3(3)
S(3)-Ru(2)-S(4)	92.08(9)
Ru(2)-S(3)-C(25)	114.9(3)
Ru(1)-S(4)-Ru(2)	73.41(8)
Ru(1)-S(4)-C(26)	113.3(3)
Ru(2)-S(4)-C(26)	114.0(3)
Ru(1)-C(1)-C(2)	72.6(7)
Ru(1)-C(1)-C(5)	72.8(7)
Ru(1)-C(2)-C(1)	71.3(7)
Ru(1)-C(2)-C(3)	72.0(7)
Ru(1)-C(3)-C(2)	70.9(7)
Ru(1)-C(3)-C(4)	72.7(7)
Ru(1)-C(4)-C(3)	71.6(7)
Ru(1)-C(4)-C(5)	71.0(7)
Ru(1)-C(5)-C(1)	71.1(7)
Ru(1)-C(5)-C(4)	72.8(7)
Ru(2)-C(6)-C(7)	71.0(6)
Ru(2)-C(6)-C(10)	73.2(6)
Ru(2)-C(7)-C(6)	72.7(6)
Ru(2)-C(7)-C(8)	72.5(6)
Ru(2)-C(8)-C(7)	70.6(6)
Ru(2)-C(8)-C(9)	74.7(7)
Ru(2)-C(9)-C(8)	70.2(7)
Ru(2)-C(9)-C(10)	71.2(6)
Ru(2)-C(10)-C(6)	70.1(6)
Ru(2)-C(10)-C(9)	72.3(7)
S(1)-C(11)-C(12)	126.7(8)
S(1)-C(11)-C(16)	116.3(8)
S(4)-C(26)-C(27)	121.5(7)
S(4)-C(26)-C(31)	119.9(7)

APPENDIX 3

Structural Analysis of $(\mu_3\text{-S})_2(\mu\text{-SCH}_2\text{CH=CH}_2)[\text{CpRu}]_3$.

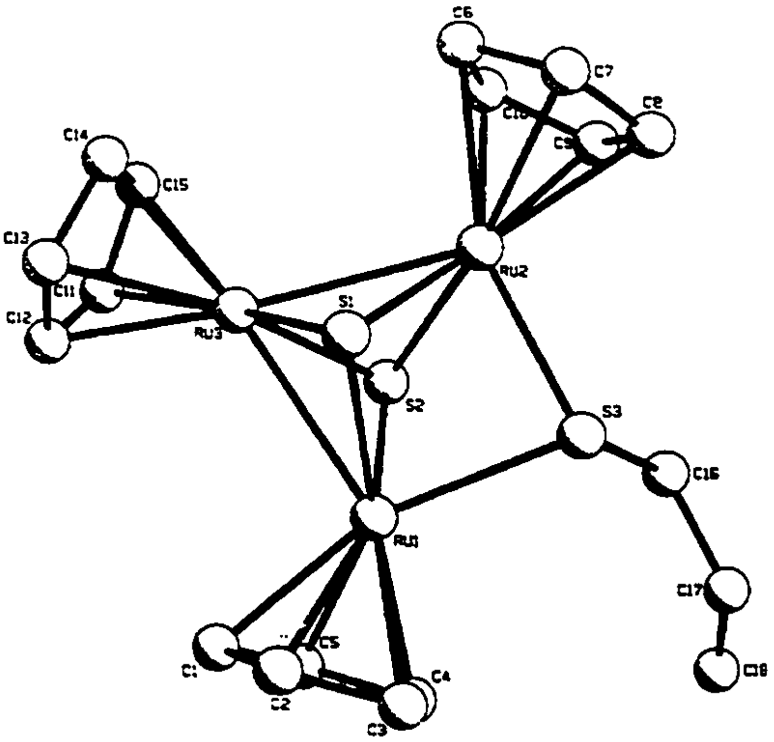

Table A3.1: Crystal data for $(\mu_3\text{-S})_2(\mu\text{-SCH}_2\text{CH=CH}_2)[\text{CpRu}]_3$.

Space Group: monoclinic $P2_1/c$

Cell Dimensions:
a = 12.458(2) Å b = 10.876(1) Å c = 15.817(2) Å
β = 116.36(1)°
Volume = 1920.3(5) Å^3

Empirical formula: $C_{18}H_{20}Ru_3S_3$

Cell dimensions were obtained from 20 reflections with 2θ angle in the range 95.0-100.0°.

Crystal dimensions: 0.100 x 0.010 x 0.500 mm

FW = 635.75 Z = 4 F(000) = 1232

D_{calc} = 2.199 g.cm^{-3}, μ = 223.57 mm^{-1}, λ = 1.54178 Å, $2\theta_{(max)}$ = 110°

The intensity data were collected on a Rigaku AFC5R diffractometer, using the $\omega/2\theta$ scan mode.
T = 20 °C.

No. of reflections measured	2726
No. of unique reflections	2588
No.of reflections with $I_{net} > 3.0\sigma(I_{net})$	1919

A psi correction was made for absorption.

Data set was solved by Patterson methods.
The last least squares cycle was calculated with 195 variable parameters and 1919 out of 2726 reflections.
Weights based on counting-statistics were used.

The residuals are as follows:-
For significant reflections, R = 0.049 Rw = 0.058
GoF = 1.67

where $R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$

$Rw = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/\Sigma(wFo^2)]}$

$GoF = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/(\text{No.of obsvn.} - \text{No.of params.})]}$

The maximum shift/σ ratio was 0.03.

In the last D-map, the deepset hole was -1.24 e$^-$/Å^3, and the highest peak 1.04 e$^-$/Å^3.

Table A3.2: Atom coordinates, x, y, z and B_{iso} for $(\mu_3\text{-S})_2(\mu\text{-SCH}_2\text{CH=CH}_2)[\text{CpRu}]_3$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Ru(1)	-0.25707(08)	-0.24189(09)	0.12515(06)	2.72(4)
Ru(2)	-0.20299(10)	0.02291(09)	0.06272(06)	3.25(4)
Ru(3)	-0.18219(09)	-0.03348(09)	0.24080(06)	3.03(4)
S(1)	-0.0799(03)	-0.1242(03)	0.1727(02)	3.0(1)
S(2)	-0.3487(03)	-0.0498(03)	0.1065(02)	3.5(1)
S(3)	-0.2592(03)	-0.1688(03)	-0.0189(02)	3.2(1)
C(1)	-0.2641(14)	-0.3682(13)	0.2334(09)	4.3(6)
C(2)	-0.1914(14)	-0.4215(13)	0.1959(11)	4.6(6)
C(3)	-0.2599(18)	-0.4399(14)	0.1006(11)	5.2(7)
C(4)	-0.3777(15)	-0.3966(14)	0.0761(10)	5.2(7)
C(5)	-0.3793(15)	-0.3529(16)	0.1588(12)	5.4(7)
C(6)	-0.101(03)	0.201(02)	0.0955(10)	3.8(5)
C(7)	-0.0782(16)	0.140(02)	0.027(02)	3.6(5)
C(8)	-0.187(03)	0.123(02)	-0.0527(11)	3.8(6)
C(9)	-0.2782(12)	0.173(03)	-0.034(02)	6.6(8)
C(10)	-0.225(03)	0.221(02)	0.058(03)	5.0(6)
C(11)	-0.2453(17)	0.037(03)	0.3415(13)	8(1)
C(12)	-0.167(02)	-0.0569(16)	0.3833(10)	5.2(8)
C(13)	-0.055(02)	-0.0266(18)	0.3932(10)	6(1)
C(14)	-0.0649(15)	0.0910(16)	0.3548(10)	4.8(7)
C(15)	-0.182(02)	0.1260(14)	0.3230(11)	5.7(8)
C(16)	-0.4152(13)	-0.1504(14)	-0.1098(08)	4.0(6)
C(17)	-0.4632(17)	-0.2673(18)	-0.1619(13)	6.4(9)
C(18)	-0.554(02)	-0.323(03)	-0.1752(15)	10(1)
C(6A)	-0.0780(15)	0.171(03)	0.068(03)	5.3(8)
C(7A)	-0.136(04)	0.125(03)	-0.024(03)	6(1)
C(8A)	-0.259(03)	0.148(03)	-0.0583(12)	3.4(6)
C(9A)	-0.277(02)	0.208(03)	0.013(03)	4.1(7)
C(10A)	-0.165(04)	0.222(03)	0.0909(13)	4.2(7)

B_{iso} is the Mean of Principal Axes of the Thermal Ellipsoid.

Table A3.3: Anisotropic thermal factors for $(\mu_3\text{-S})_2(\mu\text{-CH}_2\text{CH=CH}_2)[\text{CpRu}]_3$. U(i,j) values × 100. E.S.Ds. refer to the last digit printed.

atom	U11	U22	U33	U12	U13	U23
Ru(1)	3.49(06)	3.48(06)	3.14(06)	0.06(05)	1.27(04)	-0.23(04)
Ru(2)	5.40(07)	3.54(06)	3.32(06)	0.54(05)	1.84(05)	02.8(04)
Ru(3)	4.74(07)	3.80(06)	3.01(06)	-0.13(05)	1.74(05)	-0.51(04)
S(1)	3.72(17)	3.55(18)	3.88(17)	-0.2[illegible](15)	1.53(14)	-0.05(13)
S(2)	4.09(19)	5.0(02)	3.80(17)	1.02(17)	1.52(15)	-0.58(15)
S(3)	4.26(19)	4.6(02)	3.14(17)	0.59(16)	1.51(15)	-0.45(14)
C(1)	7.1(11)	4.8(09)	4.3(08)	-1.3(08)	0.24(08)	1.1(07)
C(2)	6.7(10)	4.0(09)	6.9(10)	1.0(08)	3.3(09)	1.6(07)
C(3)	10.4(15)	3.6(08)	6.7(10)	0.2(09)	4.6(11)	0.3(08)
C(4)	7.0(11)	5.2(10)	5.4(09)	-4.0(09)	1.0(09)	-0.5(08)
C(5)	6.2(11)	7.3(12)	8.0(12)	-0.6(10)	3.9(10)	0.9(10)
C(11)	6.5(12)	1.9(03)	5.9(12)	-2.2(16)	3.9(10)	-7.0(14)
C(12)	10.8(15)	7.2(12)	3.0(08)	-4.5(12)	4.3(10)	-2.7(08)
C(13)	11.3(17)	8.5(14)	2.3(07)	0.0(13)	0.8(09)	-1.4(08)
C(14)	6.2(11)	7.7(12)	4.3(08)	-1.7(10)	2.3(08)	-2.3(08)
C(15)	11.4(16)	4.5(10)	6.0(10)	0.4(11)	4.2(11)	-1.2(08)
C(16)	4.6(08)	5.8(09)	3.4(07)	0.5(08)	0.5(06)	-0.4(07)
C(17)	6.3(11)	8.6(14)	8.3(13)	-0.3(11)	2.3(10)	1.3(10)
C(18)	10.9(18)	16(02)	9.1(16)	-4(02)	1.2(14)	3.2(15)
C(6)	4.9(06)					
C(7)	4.6(06)					
C(8)	4.8(07)					
C(9)	8.4(11)					
C(10)	6.3(08)					
C(6A)	6.7(10)					
C(7A)	7.3(12)					
C(8A)	4.3(08)					
C(9A)	5.2(08)					
C(10A)	5.4(09)					

Table A3.4: Selected bond lengths (Å) and angles (deg) for (μ_3-S)$_2$(μ-SCH$_2$CH=CH$_2$)-[CpRu]$_3$.

Ru(1)-Ru(3)	2.800(1)	Ru(3)-C(13)	2.22(1)
Ru(1)-S(1)	2.367(3)	Ru(3)-C(14)	2.21(1)
Ru(1)-S(2)	2.336(4)	Ru(3)-C(15)	2.17(2)
Ru(1)-S(3)	2.403(4)	S(3)-C(16)	1.84(1)
Ru(1)-C(1)	2.23(2)	C(1)-C(2)	1.41(3)
Ru(1)-C(2)	2.22(1)	C(1)-C(5)	1.41(2)
Ru(1)-C(3)	2.19(2)	C(2)-C(3)	1.32(2)
Ru(1)-C(4)	2.16(2)	C(3)-C(4)	1.42(3)
Ru(1)-C(5)	2.19(2)	C(4)-C(5)	1.40(3)
Ru(2)-Ru(3)	2.780(2)	C(6)-C(7)	1.40(4)
Ru(2)-S(1)	2.360(3)	C(6)-C(10)	1.40(5)
Ru(2)-S(2)	2.348(4)	C(7)-C(8)	1.40(4)
Ru(2)-S(3)	2.388(3)	C(8)-C(9)	1.40(5)
Ru(2)-C(6)	2.24(3)	C(9)-C(10)	1.40(5)
Ru(2)-C(7)	2.26(3)	C(6A)-C(7A)	1.40(6)
Ru(2)-C(8)	2.21(3)	C(6A)-C(10A)	1.40(6)
Ru(2)-C(9)	2.15(3)	C(7A)-C(8A)	1.40(5)
Ru(2)-C(10)	2.17(2)	C(8A)-C(9A)	1.40(5)
Ru(2)-C(6A)	2.22(3)	C(9A)-(10A)	1.40(4)
Ru(2)-C(7A)	2.20(5)	C(11)-C(12)	1.37(3)
Ru(2)-C(8A)	2.20(2)	C(11)-C(15)	1.36(4)
Ru(2)-C(9A)	2.21(3)	C(12)-C(13)	1.38(4)
Ru(2)-C(10A)	2.22(3)	C(13)-C(14)	1.40(3)
Ru(3)-S(1)	2.232(4)	C(14)-C(15)	1.49(2)
Ru(3)-S(2)	2.221(3)	C(16)-C(17)	1.49(2)
Ru(3)-C(11)	2.20(2)	C(17)-C(18)	1.22(4)
Ru(3)-C(12)	2.19(2)		

Ru(3)-Ru(1)-S(1)	50.3(1)	S(2)-Ru(2)-C(10)	104(1)
Ru(3)-Ru(1)-S(2)	50.26(7)	S(2)-Ru(2)-C(6A)	149(1)
Ru(3)-Ru(1)-S(3)	102.24(9)	S(2)-Ru(2)-C(7A)	156(1)
Ru(3)-Ru(1)-C(1)	96.5(3)	S(2)-Ru(2)-C(8A)	119(1)
Ru(3)-Ru(1)-C(2)	116.2(4)	S(2)-Ru(2)-C(9A)	99(1)
Ru(3)-Ru(1)-C(3)	152.6(4)	S(2)-Ru(2)-C(10A)	113(1)
Ru(3)-Ru(1)-C(4)	147.5(5)	S(3)-Ru(2)-C(6)	151.4(7)
Ru(3)-Ru(1)-C(5)	110.7(5)	S(3)-Ru(2)-C(7)	115.3(7)
S(1)-Ru(1)-S(2)	83.7(1)	S(3)-Ru(2)-C(8)	95.5(5)
S(1)-Ru(1)-S(3)	74.8(1)	S(3)-Ru(2)-C(9)	110.4(8)
S(1)-Ru(1)-C(1)	116.0(4)	S(3)-Ru(2)-C(10)	147.7(8)
S(1)-Ru(1)-C(2)	103.5(4)	S(3)-Ru(2)-C(6A)	133(1)
S(1)-Ru(1)-C(3)	121.9(6)	S(3)-Ru(2)-C(7A)	102(1)
S(1)-Ru(1)-C(4)	159.8(5)	S(3)-Ru(2)-C(8A)	99.6(7)
S(1)-Ru(1)-C(5)	150.9(4)	S(3)-Ru(2)-C(9A)	128.8(8)
S(2)-Ru(1)-S(3)	77.6(1)	S(3)-Ru(2)-C(10A)	161.0(6)
S(2)-Ru(1)-C(1)	117.7(5)	Ru(1)-Ru(3)-S(1)	54.72(8)
S(2)-Ru(1)-C(2)	154.3(5)	Ru(1)-Ru(3)-S(2)	54.0(1)
S(2)-Ru(1)-C(3)	152.9(5)	Ru(1)-Ru(3)-C(11)	129.2(7)
S(2)-Ru(1)-C(4)	115.4(5)	Ru(1)-Ru(3)-C(12)	115.4(5)
S(2)-Ru(1)-C(5)	99.8(5)	Ru(1)-Ru(3)-C(13)	127.3(5)

S(3)-Ru(1)-C(1)	161.0(4)
S(3)-Ru(1)-C(2)	128.0(5)
S(3)-Ru(1)-C(3)	99.5(5)
S(3)-Ru(1)-C(4)	101.8(5)
S(3)-Ru(1)-C(5)	134.3(4)
Ru(3)-Ru(2)-S(1)	50.7(1)
Ru(3)-Ru(2)-S(2)	50.47(7)
Ru(3)-Ru(2)-S(3)	103.2(1)
Ru(3)-Ru(2)-C(6)	99.6(5)
Ru(3)-Ru(2)-C(7)	127.5(7)
Ru(3)-Ru(2)-C(8)	160.8(5)
Ru(3)-Ru(2)-C(9)	135(1)
Ru(3)-Ru(2)-C(10)	102(1)
Ru(3)-Ru(2)- C(6A)	112(1)
Ru(3)-Ru(2)-C(7A)	149(1)
Ru(3)-Ru(2)- C(8A)	150.6(8)
Ru(3)-Ru(2)-C(9A)	114(1)
Ru(3)-Ru(2)-C(10A)	95.5(7)
S(1)-Ru(2)-S(2)	83.6(1)
S(1)-Ru(2)-S(3)	75.2(1)
S(1)-Ru(2)-C(6)	107.4(5)
S(1)-Ru(2)-C(7)	105.7(5)
S(1)-Ru(2)-C(8)	132.6(9)
S(1)-Ru(2)-C(9)	167.4(5)
S(1)-Ru(2)-C(10)	137.0(8)
S(1)-Ru(2)- C(6A)	104.4(7
S(1)-Ru(2)-C(7A)	120(1)
S(1)-Ru(2)-C(8A)	156(1)
S(1)-Ru(2)-C(9A)	155.9(8)
S(1)-Ru(2)-C(10A)	120.2(7)
S(2)-Ru(2)-S(3)	77.6(1)
S(2)-Ru(2)-C(6)	130.7(8)
S(2)-Ru(2)- C(7)	165.4(6)
S(2)-Ru(2)-C(8)	140.7(9)
S(2)-Ru(2)-C(9)	108.4(6)
Ru(1)-Ru(3)-C(14)	159.6(5)
Ru(1)-Ru(3)-C(15)	162.0(7)
Ru(2)-Ru(3)-S(1)	54.87(8)
Ru(2)-Ru(3)-S(2)	54.6(1)
Ru(2)-Ru(3)-C(11)	138.8(6)
Ru(2)-Ru(3)-C(12)	173.9(5)
Ru(2)-Ru(3)-C(13)	142.4(6)
Ru(2)-Ru(3)-C(14)	114.9(5)
Ru(2)-Ru(3)-C(15)	114.0(5)
S(1)-Ru(3)-S(2)	89.6(1)
S(1)-Ru(3)-C(11)	165.2(5)
S(1)-Ru(3)-C(12)	129.7(6)
S(1)-Ru(3)-C(13)	104.6(6)
S(1)-Ru(3)-C(14)	110.6(6)
S(1)-Ru(3)-C(15)	142.7(7)
S(2)-Ru(3)- C(11)	103.7(4)
S(2)-Ru(3)-C(12)	126.3(6)
S(2)-Ru(3)-C(13)	162.6(7)
S(2)-Ru(3)- C(14)	145.9(4)
S(2)-Ru(3)-C(15)	112.9(5)
Ru(1)-S(1)-Ru(2)	85.6(1)
Ru(1)-S(1)- Ru(3)	75.0(1)
Ru(1)-S(2)-Ru(2)	86.6(1)
Ru(1)-S(2)-Ru(3)	75.8(1)
Ru(1)-S(3)-Ru(2)	84.2(1)
Ru(1)-S(3)-C(16)	109.8(6)
Ru(2)-S(1)-Ru(3)	74.5(1)
Ru(2)-S(2)-Ru(3)	74.9(1)
Ru(2)-S(3)-C(16)	106.3(5)
S(1)-Ru(3)-Ru(2)	54.87(8)
S(1)-Ru(3)-Ru(1)	54.72(8)
S(2)-Ru(3)-Ru(1)	54.0(1)
Ru(2)-Ru(3)-Ru(1)	70.28(4)
S(3)-C(16)-C(17)	129(2)

APPENDIX 4

Structural Analysis of $(PPh_3)_2PtS_3O \cdot CH_2Cl_2$.

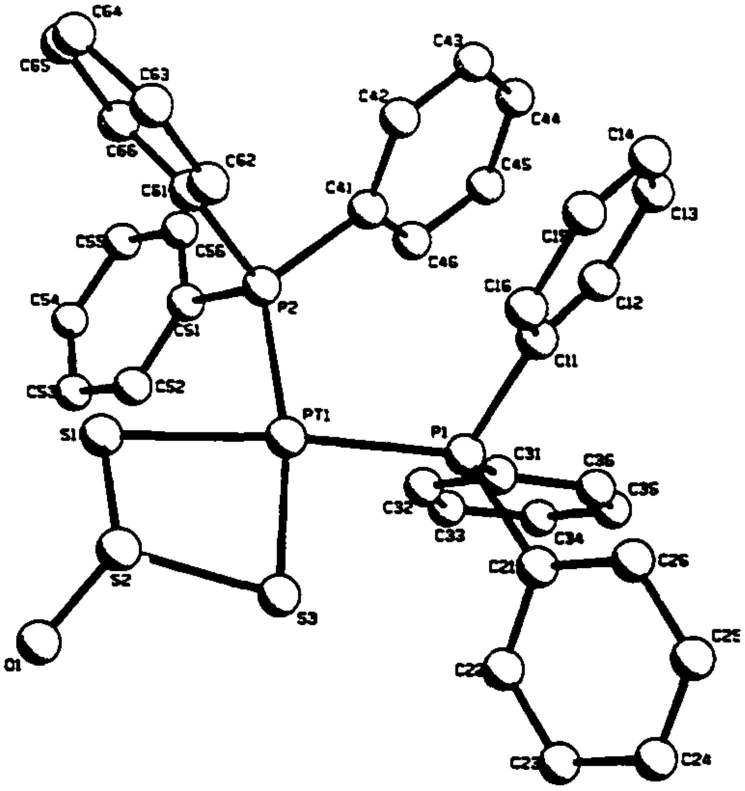

Table A4.1: Crystal data for $(PPh_3)_2PtS_3O{\bullet}CH_2Cl_2$.

Space Group: monoclinic $P\bar{1}$ (#2)

Cell Dimensions:

a = 10.852(3) Å	b = 13.411(3) Å	c = 13.847(7) Å
α = 80.76(3)°	β = 86.56(4)°	γ = 68.01(2)°

Volume = 1844(1) Å^3

Empirical formula: $C_{37}H_{32}Cl_2OP_2PtS_3$

Cell dimensions were obtained from 23 reflections with 2θ angle in the range 20.0-25.0°.

Crystal dimensions: 0.270 x 0.150 x 0.100 mm

FW = 916.78   Z = 2   F(000) = 904

D_{calc} = 1.651 g.cm^{-3}, μ = 42.66 cm^{-1}, λ = 0.71069 Å, $2\theta_{(max)}$ = 110°

The intensity data were collected on a Rigaku AFC5R diffractometer, using the $\omega/2\theta$ scan mode.
T = 20 °C.

No. of reflections measured	12970
No. of unique reflections	6485
No.of reflections with $I_{net} > 2.50\sigma(I_{net})$	4265

A psi correction was made for absorption.

Data set was solved by Patterson methods.
The last least squares cycle was calculated with 418 variable parameters and 4256out of 12970 reflections.
Weights based on counting-statistics were used.

The residuals are as follows:-
For significant reflections, R = 0.040 Rw = 0.037
GoF = 1.04

where
$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$
$Rw = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/\Sigma(wFo^2)]}$
$GoF = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/(\text{No.of obsvn. - No.of params.})]}$

The maximum shift/σ ratio was 0.356.

In the last D-map, the deepset hole was -1.07 e$^-$/Å^3, and the highest peak 0.77 e$^-$/Å^3.

Table A4.2: Atom coordinates, x, y, z and B_{iso} for $(PPh_3)_2PtS_3O{\bullet}CH_2Cl_2$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Pt(1)	0.16100(03)	0.06193(03)	0.23507(03)	2.65(2)
S(1)	0.3933(02)	-0.0096(02)	0.2440(02)	5.4(2)
S(2)	0.4034(03)	-0.1334(03)	0.1713(03)	4.9(3)
S(2A)	0.4053(13)	-0.1661(10)	0.2472(10)	5.0(3)
S(3)	0.2013(02)	-0.10943(18)	0.19650(18)	4.1(2)
P(1)	-0.0619(02)	0.11346(17)	0.21701(16)	2.8(2)
P(2)	0.1648(02)	0.22361(17)	0.26754(17)	3.1(2)
O(1)	0.4902(07)	-0.2396(06)	0.2146(06)	7.8(7)
C(11)	-0.1237(07)	0.2291(06)	0.1209(06)	2.9(6)
C(12)	-0.2241(08)	0.3255(07)	0.1343(06)	3.4(6)
C(13)	-0.2650(09)	0.4099(07)	0.0565(07)	4.3(7)
C(14)	-0.2075(10)	0.3968(08)	-0.0345(07)	5.3(9)
C(15)	-0.1048(11)	0.3026(09)	-0.0475(07)	6(1)
C(16)	-0.0629(09)	0.2169(07)	0.0299(07)	4.2(7)
C(21)	-0.1229(08)	0.0154(07)	0.1811(06)	3.2(6)
C(22)	-0.0983(08)	-0.0823(07)	0.2452(06)	4.0(7)
C(23)	-0.1484(10)	-0.1575(07)	0.2280(08)	5.2(9)
C(24)	-0.2288(11)	-0.1354(09)	0.1491(09)	6(1)
C(25)	-0.2544(10)	-0.0415(09)	0.0862(08)	5(1)
C(26)	-0.2022(08)	0.0353(07)	0.1004(07)	4.3(7)
C(31)	-0.1613(08)	0.1437(06)	0.3272(06)	2.8(6)
C(32)	-0.0983(08)	0.1276(07)	0.4143(07)	3.7(7)
C(33)	-0.1727(11)	0.1424(08)	0.5015(07)	4.9(8)
C(34)	-0.3075(10)	0.1729(08)	0.4973(07)	4.8(8)
C(35)	-0.3692(09)	0.1876(07)	0.4102(08)	4.6(8)
C(36)	-0.2985(08)	0.1731(07)	0.3253(06)	3.9(7)
C(41)	0.0189(08)	0.3517(06)	0.2542(06)	3.2(6)
C(42)	0.0009(09)	0.4314(07)	0.1743(07)	4.3(7)
C(43)	-0.1055(11)	0.5275(08)	0.1675(09)	5.6(9)
C(44)	-0.1995(11)	0.5459(09)	0.2402(10)	6(1)
C(45)	-0.1864(09)	0.4678(08)	0.3193(08)	5.1(8)
C(46)	-0.0746(09)	0.3705(07)	0.3275(07)	4.0(7)
C(51)	0.2236(07)	0.2173(07)	0.3900(06)	3.2(6)
C(52)	0.2848(08)	0.1180(07)	0.4478(07)	3.9(7)
C(53)	0.3384(09)	0.1133(08)	0.5389(07)	5.0(8)
C(54)	0.3290(10)	0.2064(10)	0.5718(07)	5(1)
C(55)	0.2656(11)	0.3049(09)	0.5163(08)	5(1)
C(56)	0.2129(09)	0.3115(07)	0.4253(07)	4.7(8)
C(61)	0.2833(08)	0.2595(06)	0.1839(06)	2.9(6)
C(62)	0.2930(09)	0.2353(07)	0.0896(07)	4.4(8)
C(63)	0.3807(10)	0.2602(08)	0.0240(07)	5.3(9)
C(64)	0.4599(09)	0.3108(08)	0.0508(08)	5.1(8)
C(65)	0.4484(09)	0.3388(08)	0.1408(08)	5.1(8)
C(66)	0.3597(08)	0.3127(07)	0.2095(06)	4.0(7)
C((S)1)	0.320(03)	0.615(02)	0.356(02)	11.9(7)
C((S)2)	0.328(04)	0.585(04)	0.296(03)	11(1)
Cl(1)	0.4427(06)	0.4951(05)	0.3658(05)	17.9(8)
Cl(2)	0.1662(06)	0.6134(04)	0.3605(05)	18.2(7)

B_{iso} is the Mean of Principal Axes of the Thermal Ellipsoid.

Table A4.3: Anisotropic thermal factors for $(PPh_3)_2PtS_3O{\cdot}CH_2Cl_2$. U(i,j) values × 100. E.S.Ds. refer to the last digit printed.

atom	U11	U22	U33	U12	U13	U23
Pt(1)	2.671(17)	3.050(18)	4.14(02)	-0.768(13)	-0.051(13)	0.00698(13)
S(1)	3.05(14)	5.03(16)	12.3(03)	-0.64(12)	-0.52(15)	-0.0252(16)
S(2)	5.1(02)	5.6(02)	6.6(03)	-0.28(17)	1.04(18)	-0.0160(19)
S(2A)	6.4(03)					
S(3)	5.11(15)	3.89(14)	6.68(17)	-1.24(12)	0.05(13)	-1.65(12)
P(1)	3.03(12)	3.77(13)	3.77(14)	-1.27(10)	0.04(10)	-0.60(10)
P(2)	3.32(13)	3.65(13)	4.64(15)	-1.27(11)	-0.25(11)	-0.63(11)
O(1)	5.0(05)	5.7(05)	16.3(08)	1.2(04)	-0.6(05)	-2.0(05)
C(11)	3.2(05)	2.9(05)	4.3(05)	-0.9(04)	-0.3(04)	0.4(04)
C(12)	3.3(05)	4.4(05)	6.0(06)	-2.2(04)	-0.2(04)	-0.04(05)
C(13)	4.7(06)	4.0(06)	7.0(07)	-1.3(05)	-0.6(05)	0.9(05)
C(14)	7.3(08)	6.9(08)	5.6(07)	-3.3(06)	-0.9(06)	2.0(06)
C(15)	6.8(08)	8.1(08)	5.7(07)	-2.1(06)	0.7(06)	0.1(06)
C(16)	5.1(06)	5.5(06)	5.1(06)	-1.6(05)	0.7(05)	-0.6(05)
C(21)	3.5(05)	4.3(05)	4.4(06)	-1.5(04)	0.4(04)	-1.0(04)
C(22)	4.4(05)	5.5(06)	5.5(06)	-2.2(05)	-0.3(05)	-0.1(05)
C(23)	7.2(08)	4.6(06)	8.7(09)	-3.2(06)	1.3(06)	-1.3(06)
C(24)	7.2(08)	7.5(08)	9.5(09)	-5.0(07)	2.4(07)	-3.6(07)
C(25)	6.4(07)	7.9(08)	7.7(08)	-3.2(06)	-1.1(06)	-3.3(07)
C(26)	4.3(06)	5.8(06)	5.8(07)	-1.5(05)	-1.2(05)	-0.6(05)
C(31)	3.9(05)	3.7(05)	3.5(05)	-2.0(04)	-0.0(04)	-0.3(04)
C(32)	4.4(05)	5.0(06)	4.8(06)	-15(04)	0.3(05)	-1.4(05)
C(33)	7.4(08)	6.4(07)	4.4(06)	-20(06)	-1.3(06)	-0.5(05)
C(34)	7.3(08)	6.4(07)	3.7(06)	-1.7(06)	2.0(06)	-1.4(05)
C(35)	4.7(06)	6.0(06)	6.3(07)	-1.3(05)	0.7(05)	-1.0(05)
C(36)	3.9(05)	5.3(06)	4.7(06)	-0.9(04)	0.3(05)	-0.5(05)
C(41)	3.8(05)	3.1(05)	5.5(06)	-1.2(04)	-0.4(04)	-0.9(04)
C(42)	4.3(06)	4.5(06)	7.3(07)	-1.5(05)	-0.7(05)	0.0(05)
C(43)	6.4(07)	4.3(06)	10.1(09)	-1.6(06)	-2.6(07)	0.4(06)
C(44)	5.5(07)	6.1(08)	10.3(10)	-0.4(06)	-0.8(07)	-1.9(07)
C(45)	5.1(06)	5.7(07)	8.7(08)	-0.9(05)	1.5(06)	-4.0(06)
C(46)	4.6(06)	4.1(05)	6.4(07)	-1.6(05)	0.2(05)	-0.9(05)
C(51)	3.0(05)	5.1(06)	4.1(05)	-1.8(04)	0.0(04)	-0.4(04)
C(52)	4.2(05)	5.4(06)	5.4(06)	-1.9(05)	-0.2(05)	-1.0(05)
C(53)	6.1(07)	6.9(07)	5.2(07)	-1.8(06)	-1.2(05)	0.4(06)
C(54)	6.4(07)	9.9(09)	5.1(07)	-4.3(07)	0.4(05)	-2.4(07)
C(55)	8.8(09)	7.9(08)	5.4(07)	-4.6(07)	-0.0(06)	-2.4(06)
C(56)	7.1(07)	4.5(06)	6.3(07)	-2.4(05)	0.4(06)	-0.9(05)
C(61)	3.5(05)	4.1(05)	3.4(05)	-1.2(04)	-0.2(04)	-0.5(04)
C(62)	5.8(06)	6.7(07)	4.8(06)	-3.0(05)	0.7(05)	-1.2(05)
C(63)	7.4(08)	8.1(08)	5.4(07)	-3.4(06)	1.4(06)	-2.2(06)
C(64)	3.6(06)	7.1(07)	7.8(08)	-1.6(05)	1.4(06)	-0.0(06)
C(65)	4.0(06)	7.8(08)	7.7(08)	-3.0(05)	0.2(06)	-0.0(06)
C(66)	4.5(06)	5.2(06)	5.5(06)	-1.9(05)	-1.0(05)	-0.4(05)
Cl(1)	20.3(06)	17.7(05)	31.8(08)	-9.3(05)	-6.1(06)	-0.8(05)
Cl(2)	23.1(06)	11.1(04)	32.4(08)	-5.2(04)	-7.3(06)	3.6(04)
C(S1)	15.1(09)					
C(S2)	13.5(14)					

Table A4.4: Selected bond lengths (Å) and angles (deg) for $(PPh_3)_2PtS_3O\bullet CH_2Cl_2$.

Pt(1)-S(1)	2.341(3)	C(24)-C(25)	1.36(1)
Pt(1)-S(3)	2.318(2)	C(25)-C(26)	1.39(1)
Pt(1)-P(1)	2.271(2)	C(31)-C(32)	1.37(1)
Pt(1)-P(2)	2.299(2)	C(31)-C(36)	1.39(1)
S(1)-S(2)	2.042(4)	C(32)-C(33)	1.41(1)
S(1)-S(2A)	2.05(1)	C(33)-C(34)	1.37(1)
S(2)-S(3)	2.110(4)	C(34)-C(35)	1.37(1)
S(2)-O(1)	1.436(7)	C(35)-C(36)	1.36(1)
S(2A)-S(3)	2.17(1)	C(41)-C(42)	1.38(1)
S(2A)-O(1)	1.20(1)	C(41)-C(46)	1.38(1)
P(1)-C(11)	1.815(8)	C(42)-C(43)	1.37(1)
P(1)-C(21)	1.821(8)	C(43)-C(44)	1.37(1)
P(1)-C(31)	1.825(8)	C(44)-C(45)	1.36(1)
P(2)-C(41)	1.841(8)	C(45)-C(46)	1.40(1)
P(2)-C(51)	1.825(8)	C(51)-C(52)	1.38(1)
P(2)-C(61)	1.826(8)	C(51)-C(56)	1.39(1)
C(11)-C(12)	1.37(1)	C(52)-C(53)	1.40(1)
C(11)-C(16)	1.39(1)	C(53)-C(54)	1.36(1)
C(12)-C(13)	1.39(1)	C(54)-C(55)	1.37(1)
C(13)-C(14)	1.38(1)	C(55)-C(56)	1.39(1)
C(14)-C(15)	1.37(1)	C(61)-C(62)	1.38(1)
C(15)-C(16)	1.40(1)	C(61)-C(66)	1.37(1)
C(21)-C(22)	1.40(1)	C(62)-C(63)	1.37(1)
C(21)-C(26)	1.38(1)	C(63)-C(64)	1.38(1)
C(22)-C(23)	1.37(1)	C(64)-C(65)	1.34(1)
C(23)-C(24)	1.36(1)	C(65)-C(66)	1.41(1)

S(1)-Pt(1)-S(3)	80.73(9)	C(11)-P(1)-C(31)	109.2(4)
S(1)-Pt(1)-P(1)	172.87(9)	C(21)-P(1)-C(31)	99.2(3)
S(1)-Pt(1)-P(2)	88.37(8)	Pt(1)-P(2)-C(41)	123.5(3)
S(3)-Pt(1)-P(1)	92.33(8)	Pt(1)-P(2)-C(51)	114.3(3)
S(3)-Pt(1)-P(2)	168.76(8)	Pt(1)-P(2)-C(61)	107.9(3)
P(1)-Pt(1)-P(2)	98.47(8)	C(41)-P(2)-C(51)	102.1(4)
Pt(1)-S(1)-S(2)	91.3(1)	P(2)-C(41)-C(42)	122.5(7)
Pt(1)-S(1)-S(2A)	93.3(4)	P(2)-C(41)-C(46)	119.2(7)
S(1)-S(2)-S(3)	93.2(2)	P(2)-C(51)-C(52)	120.5(7)
S(1)-S(2)-O(1)	115.0(4)	P(2)-C(51)-C(56)	120.8(7)
S(3)-S(2)-O(1)	112.1(4)	P(2)-C(61)-C(62)	118.5(6)
S(1)-S(2A)-S(3)	91.2(5)	P(2)-C(61)-C(66)	122.8(7)
S(1)-S(2A)-O(1)	129(1)	C(41)-P(2)-C(61)	101.8(4)
S(3)-S(2A)-O(1)	120(1)	C(51)-P(2)-C(61)	105.2(4)
Pt(1)-S(3)-S(2)	90.3(1)	P(1)-C(11)-C(12)	123.6(6)
Pt(1)-S(3)-S(2A)	90.7(3)	P(1)-C(11)-C(16)	116.4(6)
Pt(1)-P(1)-C(11)	110.5(3)	P(1)-C(21)-C(22)	117.3(6)
Pt(1)-P(1)-C(21)	117.6(3)	P(1)-C(21)-C(26)	124.3(7)
Pt(1)-P(1)-C(31)	115.9(3)	P(1)-C(31)-C(32)	119.1(6)
C(11)-P(1)-C(21)	103.2(4)	P(1)-C(31)-C(36)	120.8(6)

Table A4.5: Least square planes for $(PPh_3)_3PtS_3O\cdot CH_2Cl_2$.

Plane #1.

Atoms defining Plane	Distance	esd
C11	-0.0066	0.0073
C12	0.0024	0.0074
C13	0.0097	0.0087
C14	-0.0205	0.0097
C15	0.0154	0.0108
C16	0.0034	0.0090

Additional atoms	Distance
P1	-0.0149

Mean deviation from plane is 0.0097 Å·
Chi-Squared is 7.7.

Plane #2.

Atoms defining Plane	Distance	esd
C21	0.0006	0.0076
C22	-0.0091	0.0085
C23	0.0156	0.0097
C24	-0.0088	0.0100
C25	-0.0032	0.0101
C26	0.0058	0.0089

Additional atoms	Distance
P1	-0.1685

Mean deviation from plane is 0.0072 Å·
Chi-Squared is 4.6.

Plane #3.

Atoms defining Plane	Distance	esd
C31	-0.0058	0.0072
C32	0.0035	0.0083
C33	0.0034	0.0094
C34	-0.0054	0.0093
C35	-0.0002	0.0092
C36	0.0063	0.0085

Additional atoms	Distance
P1	0.1298

Mean deviation from plane is 0.0041 Å·
Chi-Squared is 1.8.

Plane #4.

Atoms defining Plane	Distance	esd
C41	-0.0005	0.0075
C42	-0.0098	0.0087
C43	0.0089	0.0097
C44	0.0063	0.0108
C45	-0.0154	0.0095

C46	0.0102	0.0084

Additional atoms	Distance
P2	0.0426

Mean deviation from plane is 0.0085 Å.
Chi-Squared is 6.0.

Plane #5.

Atoms defining Plane	Distance	esd
C51	0.0090	0.0074
C52	-0.0097	0.0082
C53	0.0004	0.0096
C54	0.0092	0.0095
C55	-0.0085	0.0102
C56	-0.0040	0.0092

Additional atoms	Distance
P2	0.1242

Mean deviation from plane is 0.0068 Å.
Chi-Squared is 4.2.

Plane #6.

Atoms defining Plane	Distance	esd
C61	0.0121	0.0076
C62	-0.0129	0.0093
C63	-0.0041	0.0104
C64	0.0160	0.0095
C65	-0.0112	0.0098
C66	-0.0059	0.0084

Additional atoms	Distance
P2	0.0055

Mean deviation from plane is 0.0104 Å.
Chi-Squared is 8.4.

Plane #7.

Atoms defining Plane	Distance	esd
Pt1	0.0000	
S1	0.0000	
S3	0.0000	

Additional atoms	Distance
O1	0.2231
S2	-0.25419
S2A	0.5251

Mean deviation from plane is 0.0000 Å.
Chi-Squared is 0.0.

Plane #8.

Atoms defining Plane	Distance	esd
S1	0.0000	
S2	0.0000	
S3	0.0000	

Additional atoms	Distance
Pt1	-0.6745
O1	1.1681

Mean deviation from plane is 0.0000 Å.
Chi-Squared is 0.0.

Plane #9.

Atoms defining Plane	Distance	esd
S1	0.0000	
S2	0.0000	
S3	0.0000	

Additional atoms	Distance
Pt1	0.6319
O1	-6.958

Mean deviation from plane is 0.0000 Å.
Chi-Squared is 0.0.

Dihedral angles between least-squres planes:

Plane-Plane	Angle	Plane-Plane	Angle
2-1	76.52	7-4	75.36
3-1	125.32	7-5	121.21
3-2	75.46	7-6	65.27
4-1	14.22	8-1	86.64
4-2	90.79	8-2	98.46
4-3	126.10	8-3	52.96
5-1	50.98	8-4	79.13
5-2	27.97	8-5	105.04
5-3	100.80	8-6	43.00
5-4	66.09	8-7	22.34
6-1	83.07	9-1	88.40
6-2	55.88	9-2	140.10
6-3	42.45	9-3	84.29
6-4	86.64	9-4	73.83
6-5	69.70	9-5	133.64
7-1	87.36	9-6	86.08
7-2	120.17	9-7	20.86
7-3	68.37	9-8	43.20

APPENDIX 5

Structural Analysis of $(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$.

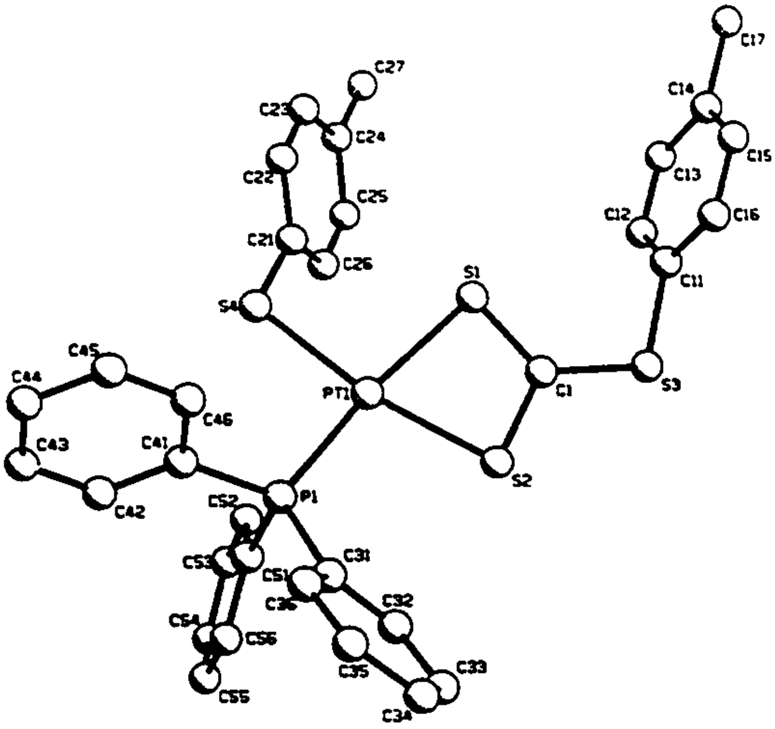

Table A5.1: Crystal data for $(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$.

Space Group: monoclinic $P\bar{1}$ (#2)

Cell Dimensions:

a = 10.205(2) Å	b = 11.206(2) Å	c = 15.235(2) Å
α = 93.14(2)°	β = 91.06(2)°	γ= 144.14(1)°

Volume = 1583.2(5) $Å^3$

Empirical formula: $C_{33}H_{29}PPtS_4$

Cell dimensions were obtained from 25 reflections with 2θ angle in the range 55.0-60.0°

Crystal dimensions: 0.480 x 0.350 x 0.170 mm

FW = 779.90   Z = 2   F(000) = 768

$D_{calc} = 1.636$ $g.cm^{-3}$, μ =114.54 mm^{-1}, λ = 1.54178 Å, $2\theta_{(max)}$ = 120.6°

The intensity data were collected on a Rigaku AFC5R diffractometer, using the $\omega/2\theta$ scan mode.
T = 20 °C.

No. of reflections measured	9462
No. of unique reflections	4731
No.of reflections with $I_{net} > 3.0\sigma(I_{net})$	4177

A psi correction was made for absorption.

Data set was solved by direct methods.
The last least squares cycle was calculated with 353 variable parameters and 4177 out of 9462 reflections.
Weights based on counting-statistics were used.

The residuals are as follows:-
For significant reflections, R = 0.038   Rw = 0.050
GoF = 1.77

where
$$R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$$
$$Rw = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/\Sigma(wFo^2)]}$$
$$GoF = \sqrt{[\Sigma(w(|Fo|-|Fc|)^2)/(\text{No.of obsvn.} - \text{No.of params.})]}$$

The maximum shift/σ ratio was 0.02.

In the last D-map, the deepset hole was -2.40 $e^-/Å^3$, and the highest peak 1.88 $e^-/Å^3$.

Table A5.2: Atom coordinates, x, y, z and B_{iso} for $(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Pt(1)	0.19211(03)	0.08143(02)	0.21658(02)	2.46(1)
S(1)	0.0700(02)	-0.1153(02)	0.28634(12)	3.16(5)
S(2)	0.3532(02)	-0.0160(02)	0.23170(13)	3.56(6)
S(3)	0.2517(02)	-0.2754(02)	0.3013(02)	5.44(9)
S(4)	0.0024(02)	0.1414(02)	0.2062(01)	4.34(7)
P(1)	0.3298(02)	0.2564(01)	0.14752(12)	2.67(5)
C(1)	0.2205(08)	-0.1405(07)	0.2749(05)	3.2(2)
C(11)	0.0836(08)	-0.3890(07)	0.3334(06)	4.0(3)
C(12)	0.0238(10)	-0.3621(07)	0.4066(06)	4.7(3)
C(13)	-0.1039(10)	-0.4547(08)	0.4309(06)	4.6(3)
C(14)	-0.1707(09)	-0.5762(08)	0.3841(06)	4.6(3)
C(15)	-0.1057(10)	-0.6007(07)	0.3133(07)	4.9(3)
C(16)	0.0194(09)	-0.5095(07)	0.2856(06)	4.5(3)
C(17)	-0.3120(11)	-0.6791(10)	0.4118(08)	6.7(4)
C(21)	-0.1001(07)	0.0740(07)	0.2958(05)	3.4(3)
C(22)	-0.2465(08)	0.0005(08)	0.2811(06)	4.4(3)
C(23)	-0.3312(08)	-0.0468(09)	0.3498(06)	4.7(3)
C(24)	-0.2740(09)	-0.0270(08)	0.4365(06)	4.2(3)
C(25)	-0.1271(08)	0.0485(08)	0.4503(05)	3.9(3)
C(26)	-0.0430(08)	0.0975(08)	0.3820(06)	4.0(3)
C(27)	-0.3652(12)	-0.0852(12)	0.5103(07)	6.6(4)
C(31)	0.4641(07)	0.2279(06)	0.0851(05)	3.0(2)
C(32)	0.5767(08)	0.2154(08)	0.1299(06)	4.2(3)
C(33)	0.6773(09)	0.1854(09)	0.0850(07)	4.9(3)
C(34)	0.6609(10)	0.1658(09)	-0.0053(08)	5.4(4)
C(35)	0.5496(10)	0.1814(11)	-0.0514(07)	5.7(4)
C(36)	0.4528(09)	0.2114(09)	-0.0066(06)	4.6(3)
C(41)	0.2289(07)	0.3048(07)	0.0669(05)	3.0(2)
C(42)	0.2528(08)	0.4348(07)	0.0588(06)	4.1(3)
C(43)	0.1744(12)	0.4632(10)	-0.0069(07)	6.1(4)
C(44)	0.0735(12)	0.3674(13)	-0.0626(07)	6.4(5)
C(45)	0.0496(10)	0.2389(11)	-0.0547(06)	5.3(4)
C(46)	0.1266(08)	0.2060(08)	0.0099(05)	3.8(3)
C(51)	0.4325(07)	0.4013(06)	0.2225(05)	3.2(2)
C(52)	0.3801(10)	0.4146(08)	0.3008(07)	4.9(3)
C(53)	0.458(02)	0.5219(11)	0.3595(08)	6.8(5)
C(54)	0.586(02)	0.6131(11)	0.3397(10)	8.0(6)
C(55)	0.6370(12)	0.6026(09)	0.2607(10)	7.2(5)
C(56)	0.5613(10)	0.4939(08)	0.1990(07)	5.5(4)

B_{iso} is the Mean of Principal Axes of the Thermal Ellipsoid.

Table A5.3: Anisotropic thermal factors for $(PPh_3)Pt(S\text{-}4\text{-}C_6H_4Me)(S_2CS\text{-}4\text{-}C_6H_4Me)$. U(i,j) values × 100. E.S.Ds. refer to the last digit printed.

atom	U11	U22	U33	U12	U13	U23
Pt(1)	3.42(02)	2.17(02)	3.89(02)	1.16(14)	0.50(13)	1.01(12)
S(1)	4.04(09)	3.08(07)	5.05(11)	1.37(08)	1.10(08)	1.94(08)
S(2)	4.28(09)	3.34(08)	6.54(12)	1.90(08)	1.73(09)	2.01(09)
S(3)	5.38(11)	3.84(09)	12.5(02)	2.46(10)	1.75(12)	3.70(13)
S(4)	4.98(10)	6.09(11)	7.09(14)	3.39(10)	2.00(10)	3.88(12)
P(1)	3.63(09)	2.24(07)	4.12(10)	0.97(07)	0.42(07)	0.92(07)
C(1)	4.7(04)	3.2(03)	3.9(04)	1.2(03)	0.5(03)	0.3(03)
C(11)	5.8(05)	3.2(04)	7.0(06)	2.4(04)	0.6(04)	2.3(04)
C(12)	8.0(06)	2.7(03)	6.6(06)	1.9(04)	-0.2(05)	1.3(04)
C(13)	7.9(06)	4.1(04)	6.1(06)	2.7(05)	1.6(05)	1.6(04)
C(14)	6.3(05)	4.1(04)	7.2(06)	2.1(04)	-0.2(05)	2.0(04)
C(15)	6.8(05)	3.0(04)	0.86(07)	1.9(04)	-0.0(05)	0.8(04)
C(16)	6.5(05)	3.5(04)	7.7(06)	2.6(04)	1.3(05)	0.8(04)
C(17)	7.0(06)	5.5(05)	12.4(10)	1.4(05)	1.2(06)	3.9(07)
C(21)	4.4(04)	3.8(03)	5.4(05)	2.1(04)	0.9(03)	1.7(04)
C(22)	4.7(04)	5.3(04)	5.7(05)	1.1(04)	-1.1(04)	1.4(04)
C(23)	3.7(04)	5.5(05)	7.8(06)	0.6(04)	1.1(04)	2.9(05)
C(24)	5.9(05)	5.1(04)	5.7(05)	3.1(05)	1.1(04)	0.9(04)
C(25)	5.1(04)	4.5(04)	5.2(05)	2.2(04)	0.1(04)	-0.2(04)
C(26)	3.6(04)	5.3(04)	5.9(05)	1.4(04)	0.7(04)	1.4(04)
C(27)	8.5(07)	8.8(07)	7.8(07)	2.9(07)	3.1(06)	2.9(07)
C(31)	3.6(04)	2.1(03)	5.4(05)	1.0(03)	0.6(03)	0.9(03)
C(32)	4.5(04)	5.1(04)	6.8(06)	2.3(04)	1.2(04)	2.2(04)
C(33)	4.6(04)	5.4(05)	9.1(07)	2.3(04)	1.5(05)	3.0(05)
C(34)	5.2(05)	5.4(05)	10.1(08)	2.0(05)	2.5(05)	0.7(06)
C(35)	6.5(06)	8.3(07)	6.9(07)	3.3(06)	1.8(05)	-0.1(06)
C(36)	4.9(05)	5.9(05)	6.7(06)	2.4(04)	0.5(04)	0.2(05)
C(41)	3.9(04)	3.5(03)	4.2(04)	1.5(03)	0.5(03)	1.2(03)
C(42)	5.7(05)	3.1(03)	6.6(06)	1.4(04)	0.2(04)	1.5(04)
C(43)	9.5(07)	5.7(05)	9.1(08)	3.8(06)	0.9(06)	4.8(06)
C(44)	8.3(07)	10.1(08)	7.1(07)	4.7(08)	-0.9(06)	3.6(07)
C(45)	6.2(05)	8.3(07)	5.2(06)	2.6(06)	-0.9(04)	1.3(05)
C(46)	5.0(04)	4.3(04)	4.4(05)	1.4(04)	-0.5(04)	0.8(04)
C(51)	4.2(04)	2.1(03)	5.1(05)	0.7(03)	-0.2(03)	0.3(03)
C(52)	7.5(06)	3.8(04)	7.6(07)	2.7(05)	-0.6(05)	-0.4(04)
C(53)	11.9(10)	6.5(06)	7.6(08)	4.3(08)	0.5(07)	-2.0(06)
C(54)	13.2(12)	5.7(07)	11.7(11)	4.9(08)	-4.7(09)	-3.6(07)
C(55)	6.7(07)	4.2(05)	13.7(11)	0.1(05)	-2.8(07)	-2.2(06)
C(56)	6.1(05)	4.1(04)	9.1(08)	0.6(04)	-1.1(05)	-0.9(05)

Table A5.4: Selected bond lengths (Å) and angles (deg) for (PPh$_3$)Pt(S-4-C$_6$H$_4$Me)-(S$_2$CS-4-C$_6$H$_4$Me).

Pt(1)-S(1)	2.381(2)	C(23)-C(24)	1.39(1)
Pt(1)-S(2)	2.326(2)	C(24)-C(25)	1.39(1)
Pt(1)-S(4)	2.296(2)	C(24)-C(27)	1.49(1)
Pt(1)-P(1)	2.243(2)	C(25)-C(26)	1.37(1)
S(1)-C(1)	1.685(7)	C(31)-C(32)	1.37(1)
S(2)-C(1)	1.688(7)	C(31)-C(36)	1.39(1)
S(3)-C(1)	1.732(7)	C(32)-C(33)	1.40(1)
S(3)-C(11)	1.777(8)	C(33)-C(34)	1.37(1)
S(4)-C(21)	1.767(7)	C(34)-C(35)	1.39(1)
P(1)-C(31)	1.822(7)	C(35)-C(36)	1.36(1)
P(1)-C(41)	1.812(6)	C(41)-C(42)	1.39(1)
P(1)-C(51)	1.827(7)	C(41)-C(46)	1.39(1)
C(11)-C(12)	1.37(1)	C(42)-C(43)	1.38(1)
C(11)-C(16)	1.38(1)	C(43)-C(44)	1.36(2)
C(12)-C(13)	1.38(1)	C(44)-C(45)	1.37(2)
C(13)-C(14)	1.39(1)	C(45)-C(46)	1.39(1)
C(14)-C(15)	1.36(1)	C(51)-C(52)	1.35(1)
C(14)-C(17)	1.53(1)	C(51)-C(56)	1.38(1)
C(15)-C(16)	1.37(1)	C(52)-C(53)	1.38(1)
C(21)-C(22)	1.38(1)	C(53)-C(54)	1.35(2)
C(21)-C(26)	1.38(1)	C(54)-C(55)	1.35(2)
C(22)-C(23)	1.37(1)	C(55)-C(56)	1.42(1)

S(1)-Pt(1)-S(2)	73.67(6)	C(21)-C(22)-C(23)	121.1(8)
S(1)-Pt(1)-S(4)	96.48(6)	C(22)-C(23)-C(24)	122.1(7)
S(1)-Pt(1)-P(1)	172.24(6)	C(23)-C(24)-C(25)	116.0(7)
S(2)-Pt(1)-S(4)	169.74(6)	C(23)-C(24)-C(27)	121.9(8)
S(2)-Pt(1)-P(1)	98.71(6)	C(25)-C(24)-C(27)	122.0(8)
S(4)-Pt(1)-P(1)	91.06(6)	C(24)-C(25)-C(26)	121.8(8)
Pt(1)-S(1)-C(1)	85.4(2)	C(21)-C(26)-C(25)	121.7(7)
Pt(1)-S(2)-C(1)	87.1(2)	P(1)-C(31)-C(32)	119.0(6)
C(1)-S(3)-C(11)	104.5(3)	P(1)-C(31)-C(36)	122.5(5)
Pt(1)-S(4)-C(21)	104.9(2)	C(32)-C(31)-C(36)	118.4(7)
Pt(1)-P(1)-C(31)	112.9(2)	C(31)-C(32)-C(33)	121.0(8)
Pt(1)-P(1)-C(41)	113.4(2)	C(32)-C(33)-C(34)	119.3(8)
Pt(1)-P(1)-C(51)	113.4(2)	C(33)-C(34)-C(35)	120.2(9)
C(31)-P(1)-C(41)	104.3(3)	C(34)-C(35)-C(36)	120.2(9)
C(31)-P(1)-C(51)	105.0(3)	C(31)-C(36)-C(35)	120(1)
C(41)-P(1)-C(51)	107.0(3)	P(1)-C(41)-C(42)	122.7(6)
S(1)-C(1)-S(2)	113.6(4)	P(1)-C(41)-C(46)	117.4(5)
S(1)-C(1)-S(3)	128.1(4)	C(42)-C(41)-C(46)	119.8(6)
S(2)-C(1)-S(3)	118.3(4)	C(41)-C(42)-C(43)	118.8(8)
S(3)-C(11)-C(12)	121.4(7)	C(42)-C(43)-C(44)	121.9(8)
S(3)-C(11)-C(16)	117.7(8)	C(43)-C(44)-C(45)	119.4(7)
C(12)-C(11) -C(16)	120.7(8)	C(44)-C(45)-C(46)	121(1)
C(11)-C(12)-C(13)	119.5(8)	C(41)-C(46)- C(45)	119.4(8)
C(12)-C(13)-C(14)	120.9(9)	P(1)-C(51)-C(52)	118.8(6)
C(13)-C(14)-C(15)	117.8(8)	P(1)-C(51)-C(56)	119.9(7)
C(13)-C(14)-C(17)	121(1)	C(52)-C(51)-C(56)	121.4(8)
C(14)-C(15)-C(16)	122.9(8)	C(51)-C(52)-C(53)	120(1)
C(15)-C(14)-C(17)	121.5(9)	C(52)-C(53)-C(54)	121(1)

C(11)-C(16)-C(15)	118.0(9)	C(53)-C(54)-C(55)	120(1)
S(4)-C(21)-C(22)	119.4(6)	C(54)-C(55)-C(56)	121(1)
S(4)-C(21)-C(26)	123.3(6)	C(51)-C(56)-C(55)	117(1)
C(22)-C(21)-C(26)	117.2(7)		