Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author’s right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.
http://researchspace.auckland.ac.nz/feedback

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.
THIOCARBONYL COMPLEXES OF

RUTHENIUM AND OSMIUM

A thesis presented to the
University of Auckland
for the degree of
Doctor of Philosophy in Chemistry

Terence James Collins
December 1977
This thesis deals with thiocarbonyl complexes of ruthenium and osmium $[L_n M-CS]$. In chapter 1 a comprehensive review of all transition metal thiocarbonyl complexes is presented. Unlike carbon monoxide, carbon monosulphide is a highly reactive molecule which does not exist under normal laboratory conditions. However, transition metal complexes of this reactive intermediate are typically stable compounds of which there are now approximately two hundred reported examples. This small number has made a complete review possible. Slow spasmodic growth has accompanied transition metal thiocarbonyl chemistry since the prototype complex was discovered in 1966 and chapter 1 discusses the synthetic reasons for this, describes critically the current bonding models, and presents the reactions of thiocarbonyl complexes. The very new field of the chemistry of selenocarbonyl complexes $[L_n M-CSe]$ is included and comparison with this and with the well-documented chemistry of carbonyl complexes allows for an analysis of periodic changes.

The review indicates that CS ligand reactions had received little attention at the outset of this project. Interligand reactions involving CS were unknown primarily because thiocarbonyl complexes containing ligands suitable for investigating reactions of this type had not been synthesised. In particular, transfer of hydrido or aryl ligand to CS had not been observed. Such
reactions are the subjects of chapters 3 and 6. The investigation of these transfer reactions necessitated the prior preparation of complexes containing hydrido or aryl ligands cis to the thio-carbonyl ligand. Suitable complexes were synthesised from the very versatile synthetic intermediate \( \text{OsCl}_2(\text{CS})(\text{PPh}_3)_3 \) [Chapter 3], which was discovered after considerable effort had been devoted to finding high yield routes for introducing the CS ligand into the coordination sphere of ruthenium and osmium [Chapter 2].

Chapter 3 is concerned with hydride transfer to the CS ligand. The thioformyl ligand \([\text{Os-C}^-\text{S}] \) results from the transfer of one hydrido ligand to CS and subsequent reactions, which are also probably hydride transfers, produce the thioformaldehyde
\[
\text{[Os-C=S]}^-\text{H}
\] and methylthiolato \([\text{Os-SCH}_3^-] \) ligands. The possible relevance of these ligands as models for postulated intermediates in the Fischer-Tropsch synthesis is noted. The thioformyl and thioformaldehyde ligands were hitherto unknown and the formulations have been additionally verified by investigating the reactivity of these novel ligands and characterising the derivatives obtained. A synthetic route to secondary carbene complexes and to nitrogen and oxygen equivalents of the thioformyl ligand \([\text{Os-CP}^-\text{NMe}_3] \) and \([\text{Os-CP}^-\text{O}] \) is demonstrated.

The review in Chapter 1 also recounts how observation has shown that strong \( \sigma \)-donor and strong \( \pi \)-acceptor properties of the CS ligand exert a profound effect upon the reactivity of CS complexes. In particular, strong \( \pi \)-acceptor properties mark the CS ligand as an ideal candidate for stabilising very electron-rich metal centres
such as $d^8$ ruthenium(0) or osmium(0). In chapter 4 high yield routes to zerovalent osmium thiocarbonyl complexes are detailed and the reactivity of these complexes is exploited to afford the first high yield syntheses of dithiocarbonyl complexes.

The thiocarbonyl ligand is also viewed, from the collected information in chapter 1, as being more responsive to the coordinative environment than the better-known carbonyl ligand. Thus, while CS can remove more electron-density from basic metal centres than CO, CS can also donate more electron-density than CO when coordinated to very electron-poor metal centres. Consequently, it is not surprising that reactions which have been regarded in a classical sense as electrophilic or nucleophilic attack at CO are also found for CS. In chapter 5 several novel reactions which can be described as nucleophilic attack at the CS carbon atom are reported for both neutral and cationic complexes. One such reaction is an interligand reaction of cis thiocarboxamido and thiocarbonyl ligands which affords a four-membered osmium metallocycle.

Chapter 6 describes how coordinatively unsaturated aryl-thiocarbonyl-containing complexes react with potentially bidentate anionic ligands to produce coordinatively saturated complexes. Coordinative saturation also occurs with carbon monoxide or isocyanide and these latter compounds undergo a rearrangement reaction which involves the thiocarbonyl ligand. Available evidence, which includes the results of an incomplete X-ray crystal structure determination, suggests that a bidentate thioacyl ligand $[\text{Os} - \text{CS} - \text{R}]$ is produced by transfer of the aryl ligand to CS with ring-closure. Some further reactions of this novel ligand are also discussed.
In conclusion, the work reported here extends this research group's interest in the chemistry of low valent transition metal compounds and the ligands which stabilise such compounds to thiocarbonyl complexes of ruthenium and osmium. The present status of the chemistry of transition metal thiocarbonyl complexes has been examined and the work presented in the experimental chapters contributes to this small area of chemistry by examining, for the first time, interligand reactions which involve CS, by providing synthetic routes to CS complexes of osmium(0), and by beginning to examine the synthetic potential of the novel compounds and ligands obtained.
TABLE OF CONTENTS

ABSTRACT
List of Tables
List of Important Figures
List of Abbreviations

CHAPTER 1: INTRODUCTION
THIOCARBONYL AND SELENOCARBONYL COMPLEXES OF
TRANSITION METALS

(I) SYNTHESIS:
   (i) Coordination of Molecular Carbon Monosulphide; 3
   (ii) Interaction Between Carbon Disulphide and Carbon Diselenide and a Suitable Metal Substrate, Usually in the Presence of Triphenylphosphine; 6
   (iii) Reductive Fragmentation of Thiophosgene; 15
   (iv) Modification of Thioester and Selenoester Ligands; 17
   (v) Reductive Elimination of Methyl Thiol. 20

(II) STRUCTURE AND BONDING:
   (i) X-Ray Crystallography; 22
   (ii) Infrared and Raman Spectroscopy; 26
   (iii) Theoretical Studies and Photoelectron Spectroscopy; 38
   (iv) $^{13}$C N.M.R. Spectroscopy; 38
   (v) Mass Spectrometry; 38
   (vi) Mössbauer Spectroscopy. 39

(III) CHEMICAL REACTIVITY

   A. Reactions at the Metal Centre.
   (i) Substitution Reactions; 40
   (ii) Oxidative Addition and Redox Reactions. 53
B. Ligand Reactions.

(i) Nucleophilic Attack at the CS Carbon Atom; 57
(ii) Electrophilic Attack at the CS Sulphur Atom; 62
(iii) Migratory Insertion Reactions; 64
(iv) Intramolecular Isomerisation Reactions Involving Bridged CS Ligands; 67
(v) Miscellaneous Reactions of Other Than The CS Ligand. 69

CONCLUSION 69

CHAPTER 2

THIOCARBONYL COMPLEXES FROM CARBON DISULPHIDE

ADDITIONS 70

2.1 Early Preparative Routes To Ruthenium and Osmium Thiocarbonyl Complexes; 70
2.2 Attempts To Find New Routes to Ruthenium and Osmium CS complexes; 73
2.3 Improvement of Synthetic Routes to CS Complexes; 75
2.4 A Novel Synthetic Route to Zerovalent Ruthenium and Osmium Complexes; 83
2.5 Coordinated Tetrafluoroborate and Perchlorate Complexes. 89

GENERAL EXPERIMENTAL 92

EXPERIMENTAL 95

CHAPTER 3

REDUCTION OF THE THIOCARBONYL LIGAND 116

3.1 OsCl₂(CS)(PPh₃)₃; 120
3.2 Hydridio-Thiocarbonyl Complexes; 122
3.3 Hydride Transfer Reactions; 128
3.4 Reactions of Thioformyl Complexes.
   (i) Carbene Formation and Derived Products; 132
   (ii) Further Reduction of the Thioformyl Ligand. 137

EXPERIMENTAL 143

CHAPTER 4

ZEROVALENT THIOCARBONYL COMPLEXES OF OSMIUM 168

4.1 Synthesis and Reactions of Zerovalent Complexes; 169
4.2 Synthesis of Dithiocarbonyl Complexes. 174

EXPERIMENTAL 179
CHAPTER 5

NUCLEOPHILIC ATTACK AT THE THIOCARBONYL LIGAND

EXPERIMENTAL

CHAPTER 6

ARYL—THIOCARBONYL COMPLEXES AND REARRANGEMENT

REACTIONS

6.1 Production of Aryl-Thiocarbonyl Complexes; 212
6.2 Rearrangement Reactions of Aryl-Thiocarbonyl Complexes. 215

EXPERIMENTAL 222

REFERENCES 237

ACKNOWLEDGEMENTS 253
# LIST OF TABLES

## CHAPTER 1

1. Representations of Cs and CSe Complex Structures  
2. I.R. Data for CSe Complexes and CS Analogues  
3. $^{13}$C N.M.R. Data for Thiocarbonyl Complexes

## CHAPTER 2

2.1 I.R. Data for Thiocarbonyl Complexes  
2.2 I.R. Data for Thioester and Related Complexes  
2.3 I.R. Data for Other Complexes  
2.4 $^1$H N.M.R. Data

## CHAPTER 3

3.1 I.R. Data for Hydrido-Thiocarbonyl Complexes  
3.2 $^1$H N.M.R. Data for Hydrido-Thiocarbonyl Complexes  
3.3 I.R. Data for Thioformyl and Derived Complexes  
3.4 $^1$H N.M.R. Data for Thioformyl and Derived Complexes  
3.5 I.R. and $^1$H N.M.R. Data for Related Adducts of Os(CO)$_2$(PPh$_3$)$_2$

## CHAPTER 4

4.1 I.R. Data for Thiocarbonyl Complexes  
4.2 $^1$H N.M.R. Data for Thiocarbonyl Complexes

## CHAPTER 5

5.1 I.R. Data for New Complexes  
5.2 $^1$H N.M.R. Data for New Complexes

## CHAPTER 6

6.1 I.R. Data for New Compounds  
6.2 $^1$H N.M.R. Data for New Complexes
LIST OF IMPORTANT FIGURES

CHAPTER 2

2.2 Structure of [Ru(η²-CS₂Me)(CO)₂(PPh₃)₂]⁺. 80

2.3 (a) The Inner Coordination Sphere of OsH(η¹-CS₂Me)(CO)₂(PPh₃)₂ with some distances presented. 86

(b) A stereoview of OsH(η¹-CS₂Me)(CO)₂(PPh₃)₂. 86

2.5 Structure of [RuH₂O(CO)₂(PPh₃)₂]BF₄⁻. 91

CHAPTER 5

5.1 Structure of Os(η¹-CS₂CNMeR)H(CO)(PPh₃)₂. 198

CHAPTER 6

6.1 Preliminary Results of X-Ray Crystal Structure Analysis of OsBr(η²-CS₅)(CO)(PPh₃)₂. 217
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>phen</td>
<td>o-phenanthroline</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>dmf</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>diphos</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>triphos</td>
<td>bis(2-diphenylphosphinoethyl)phenylphosphine</td>
</tr>
<tr>
<td>Cp</td>
<td>pentahapto-cyclopentadienyl</td>
</tr>
<tr>
<td>diars</td>
<td>o-phenylenebis(dimethylarsine)</td>
</tr>
<tr>
<td>TCNE</td>
<td>tetracyanoethylene</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>acac</td>
<td>acetylacetonoato</td>
</tr>
<tr>
<td>OH</td>
<td>benzene</td>
</tr>
<tr>
<td>COD</td>
<td>cyclo-octa-1,5-diene</td>
</tr>
<tr>
<td>triflate</td>
<td>trifluoromethanesulphonate</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulphoxide (perdeutero- in $^1$H N.M.R. tables)</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>$^\eta$Pr</td>
<td>$n$-propyl</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl</td>
</tr>
<tr>
<td>$^\eta$Bu or Bu</td>
<td>$n$-butyl</td>
</tr>
<tr>
<td>$t$Bu</td>
<td>$t$-butyl</td>
</tr>
<tr>
<td>CNR</td>
<td>p-tolylisocyanide (unless otherwise specified)</td>
</tr>
<tr>
<td>conc.</td>
<td>concentrated</td>
</tr>
</tbody>
</table>
INTRODUCTION

Perhaps no other single entity has been more closely linked with organo-transition metal chemistry than the carbonyl ligand. The knowledge accumulated in studies of carbonyl complexes forms an indispensable part of the present understanding of organometallic chemistry and represents a major contribution to chemistry. In contrast, work on thiocarbonyl (CS) complexes has been limited, on selenocarbonyl (CSe) complexes meagre and the tellurocarbonyl ligand is unknown. The study of complexes containing CS and CSe ligands has been hindered by the lack of uncomplicated synthetic routes of general applicability. The research published has prompted one review, concerned in part with thiocarbonyl complexes, which covers the literature to March 1973. In that review the information was organised according to the metal in each complex. However, it is considered that enough is now understood about the CS ligand to lend coherence to a more general treatment. Accordingly, in this treatise it is intended to review the current literature under the separate subtitles of (I) Synthesis; (II) Structure and Bonding and; (III) Chemical Reactivity. The formally similar CSe ligand will be treated in context with the CS ligand.

(I) SYNTHESIS

The several hundred CS complexes which have been reported include complexes of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Rh, Ir, Ni and Pt. However, fewer than 50 examples can be cited where the course of a
reaction eventuates in a CS ligand being formed. The majority of CS complexes have been obtained from precursors already containing a CS ligand by such processes as ligand substitution and oxidative addition. Seven CSe complexes have been isolated and some investigations of the reactivity of several of these Cr, Mn and Ru compounds have been communicated. Reactions which afford CS or CSe ligands will be discussed in this section and reactions of CS and CSe complexes which do not generate additional CS or CSe ligands will be reviewed in section III.

The various methods of synthesising CS and CSe complexes that have been developed can be loosely grouped into the following categories -

(i) Coordination of molecular carbon monosulphide;

(ii) Interaction between carbon disulphide or carbon diselenide and a suitable metal substrate, usually in the presence of triphenylphosphine;

(iii) Reductive fragmentation of thiophosgene;

(iv) Modification of thioester and selenoester ligands;

(v) Reductive elimination of methyl thiol from hydrido-\(\eta^1\)-dithioester complexes.

Except for the first, these processes are all closely related in that each involves the modification of a coordinated ligand which contains a C-S linkage of bond order greater than one. In each case metal complexes with very specific characteristics are required as precursors, so that the circumstances in which a CS or CSe ligand can be introduced into the coordination sphere of a transition metal atom are still quite restricted.
(i) Coordination of Molecular Carbon Monosulphide

While carbon monoxide gas is used extensively to prepare carbonyl complexes, the inaccessibility and reactivity of monomeric carbon monosulphide and carbon monoselenide has prevented the use of these compounds in similarly facile syntheses. Carbon monosulphide has been detected in the upper atmosphere\(^2\) and in interstellar space\(^3\) and the observation has been made that the gas phase monomer apparently shows the chemical stability of a normal molecule.\(^4\) However, Steudel, who has reviewed the earlier attempts to investigate carbon monosulphide,\(^5\) has shown that CS\(_2\), produced by decomposition of gaseous CS\(_2\) in an electric discharge and isolated in a CS\(_2\) matrix, rapidly polymerises according to equation 1.

\[
3\text{(CS)} \rightarrow \text{(CS)\_3} \rightarrow \text{C-S polymer}
\]

This polymerisation can be explosive so that CS is not produced in large quantities. The presence of the intermediate (CS)\(_3\), which is thought to contain a cyclopropane ring, was deduced by I.R. spectroscopy. The polymerisation reaction is slow in the matrix at \(-190^\circ\text{C}\) (0.2-1% min\(^{-1}\)), but at higher temperatures (ca. \(-180^\circ\text{C}\)) rapid diffusion of CS is possible and, if the temperature is allowed to slowly increase from \(-190^\circ\text{C}\) (4-5\(^\circ\text{C}\) min\(^{-1}\)), the CS monomer has essentially disappeared at \(-160^\circ\text{C}\).

Of the many procedures which have been used in attempted syntheses of carbon monosulphide, electric discharge through CS\(_2\) has been the
most successful.\textsuperscript{5,6} This method has been coupled with a vacuum flow system where CS is produced and then either codeposited with other substrates, or passed into a solution containing a suitable substrate at low temperatures to yield several gram quantities of the products of CS reactions.\textsuperscript{6} The reactions of CS with non-metallic substrates which have been reported in the recent literature are summarised in Scheme 1.

![Chemical diagram](image)

**Scheme 1:** The Reactions of CS with Non-Metallic Substrates.

Ref. 6 unless otherwise noted; (i) $X = Cl, Br$;\textsuperscript{5} (ii) $Y = S, Se, Te$;\textsuperscript{5} (iii) warm in CS$_2$ matrix; (iv) $X = Cl, Br, I$, reaction time 0.1 s.\textsuperscript{7}

At low temperatures CS will not displace ligands such as CO or triphenylphosphine in the compounds Ni(CO)$_4$, Fe(CO)$_5$ or RhCl(PPh$_3$)$_3$.
Thiocarbonyl-containing complexes have been detected spectroscopically after the codeposition of nickel atoms and CS in argon matrices. I.R. and mass spectroscopic evidence suggests that Ni(CS)₄ is produced either directly in the matrix, or by pyrolysis of a Ni-CS polymer in the mass spectrometer. Other workers have detected the four nickel thiocarbonyl complexes Ni(CS)ₙ [n = 1-4] using I.R. techniques in similar experiments.

While CSe can also be produced by the decomposition of gaseous CSe₂ in an electric discharge, attempts to isolate this monomer, employing trapping techniques similar to those used to isolate CS, have not proved successful. Instead, the existence of CSe as a reactive intermediate has been verified by reactions with sulphur and tellurium according to equation 2.  

\[
CSe + S \rightarrow SCS\text{e} \\
CSe + Te \rightarrow TeCS\text{e}
\]

No reactions of CSe with transition metals or transition metal complexes have been described. A number of spectroscopic studies of CS and CSe have been reported.

The chemistry of CS and CSe that has been documented leaves little doubt that synthetic pathways to thiocarbonyl or selenocarbonyl complexes directly involving the reactive intermediates carbon monosulphide or carbon monoselenide are not practicable. Consequently, CS and CSe complexes have usually been produced either by the modification of suitable ligands, or by the reaction of a CS or CSe source molecule with a suitable metal substrate where stable intermediate complexes, if any actually exist, have not been isolated.
(ii) Interaction between Carbon Disulphide or Carbon Diselenide and a Suitable Metal Substrate, Usually in the Presence of Triphenylphosphine.

The first metal thiocarbonyl complexes, trans-RhX(CS)(PPh₃)₂ [X = Cl, Br], reported in 1966, were produced from the reactions of RhX(PPh₃)₃ with carbon disulphide. Following this initial discovery, Wilkinson and his coworkers investigated the reactions of CS₂ with a number of transition metal complexes and successfully isolated CS complexes of Rh, Ir and Ru. The yield of trans-RhCl(CS)(PPh₃)₂ was improved from 50% to virtually 100% by adding methanol and excess triphenylphosphine (equation 3).

\[
\begin{align*}
\text{RhCl(PPh}_3\text{)}_3 & \xrightarrow{(i) \text{CS}_2, \text{CHCl}_3} \text{trans-RhCl(CS)(PPh}_3\text{)}_2 \quad 50\% \\
\text{CS}_2, \text{MeOH} & \quad \text{(i)} \\
\text{RhCl(PPh}_3\text{)}_3 & \xrightarrow{(i) \text{MeOH}} \text{trans-RhCl(CS)(PPh}_3\text{)}_2 \quad 100\% \\
\text{PPh}_3 & \quad \text{(ii)} \\
\end{align*}
\]

Similar treatment of IrCl(PPh₃)₃ with CS₂ and then CHCl₃, or heating of the cyclo-octa-1,5-diene complex [IrCl(COD)]₂ under reflux in CHCl₃ and CS₂ in the presence of PPh₃, gave low yields (20-30%) of trans-IrCl(CS)(PPh₃)₂. The interaction of RuCl₂(PPh₃)₃ with CS₂ supposedly lead to the dimeric complex [RuCl₂(CS)(PPh₃)₂]₂ in 70% yield.

It has been suggested that the thiocarbonyl ligand is generated in these systems from an intermediate "π-bonded" CS₂ (η²-CS₂) ligand of the type found in the complex Pt(η²-CS₂)(PPh₃)₂ (figure 1). Thus, in this proposed mechanism, RhCl(PPh₃)₃ reacts with CS₂ to give a red complex, formulated as RhCl(η¹-CS₂)(η²-CS₂)(PPh₃)₂. In the presence
of polar solvents, e.g. methanol, a cationic species containing the \( \eta^2\)-CS\(_2\) group is formed and this is then attacked by triphenylphosphine to form the CS complex \( \text{trans-RhCl(CS)(PPh}_3\text{_3)}_2 \) and triphenylphosphine sulphide, which can be isolated quantitatively as a by-product (equation 4).

\[
\begin{align*}
\text{(Ph}_3\text{P)}_2\text{Rh} & \quad \text{+ PPh}_3 \rightarrow \text{SPPh}_3 + [(\text{Ph}_3\text{P})_2\text{Rh(CS)}]^- \\
\text{trans-RhCl(CS)(PPh}_3\text{_3)}_2 & \\
\end{align*}
\]

The validity of this mechanism has not been demonstrated. The highly coloured cationic complexes of composition \([\text{Ir(CS}_2\text{(CO)(PPh}_3\text{_3)}_3]^{1+}\), \([\text{Ir(CS}_2\text{(PPh}_3\text{_3)}_2]^{1+}\), \([\text{Ir(CS}_2\text{(CO)(PPh}_3\text{_3)}_3]^{1+}\), \([\text{Rh(CS}_2\text{(CO)(PPh}_3\text{_3)}_3]^{1+}\), \([\text{Rh(CS}_2\text{(PPh}_3\text{_3)}_2]^{1+}\) and \([\text{Rh(CS}_2\text{(PPh}_3\text{_3)}_3]^{1+}\),\(^{14}\) and the red complex of composition \(\text{RuCl}_2\text{(CS}\_2\text{(PPh}_3\text{_3)}_1\) were also produced in these studies and formulated as containing \(\eta^2\)-CS\(_2\) ligands. However, a reinvestigation of \([\text{Ir(CS}_2\text{(CO)(PPh}_3\text{_3)}_3]^{1+}\) indicated that the physical and chemical properties of this violet cation are not consistent with such a formulation. An X-ray crystal structure determination showed \([\text{Ir(CS}_2\text{(CO)(PPh}_3\text{_3)}_3]BF_4\) to be a five-coordinate complex of Ir(I) containing the bidentate sulphur-bound triphenylphosphine-carbon disulphide zwitterion, Ph\(_3\text{P}^+\text{-CS}_2^-\), as a ligand (figure 2), and it is probable that all these clearly related complexes should be reformulated as containing Ph\(_3\text{P}^+\text{-CS}_2^-\) ligands.\(^{18}\)

It has been established that \(\text{IrCl(CO)(PPh}_3\text{_3)}_2\) forms a weak CS\(_2\) adduct of the \(\pi\)-bonded type when dissolved in CS\(_2\).\(^{19,20}\) The zwitterion-containing complex \([\text{Ir(\eta}_2\text{-S}_2\text{CPPh}_3\text{(CO)(PPh}_3\text{_3)}_2]^{1+}\) is formed when \(\text{IrCl(CO)(PPh}_3\text{_3)}_2\) is dissolved in CS\(_2\) and methanol containing excess triphenylphosphine.\(^{14}\)
Fig. 1 - Arrangement of $\text{CS}_2$ in $\text{Pt}(\eta^2-\text{CS}_2)(\text{PPh}_3)_2$.

Fig. 2 - Arrangement of the $\text{Ph}_3\text{P}^{+}-\text{CS}_2^{-}$ ligand in $[\text{Ir}(\eta^2-\text{S}_2\text{CPPh}_3)(\text{CO})(\text{PPh}_3)_2]^+$.  

With the evidence available it is not possible to distinguish between an $\eta^2-\text{CS}_2$-containing complex, a zwitterion-containing complex, or some other as yet unidentified $\text{CS}_2$-containing complex as being the key intermediate which leads to the thiocarbonyl ligand in these systems. It is also not possible to specify whether the mechanism of thiocarbonyl formation involves an intermolecular or an intramolecular process. Resolution of these mechanistic details must await further studies. The stable $\eta^2-\text{CS}_2$-containing complexes $\text{MCl}(\eta^2-\text{CS}_2)(\text{PCy}_3)_2$ [M=Rh, Ir], decompose spontaneously in the presence of excess $\text{PCy}_3$ to give, in high yields, the CS complexes $\text{MCl(CS)(PCy}_3)_2$, but the mechanism has not been elucidated.

The addition of carbon disulphide to IrCl($\text{N}_2$)(PPh$_3$)$_2$ leads to the quantitative evolution of nitrogen and formation of black crystals with empirical formula IrCl($\text{C}_2\text{S}_5$)(PPh$_3$)$_2$. The further reactions of this black material were exploited to obtain a number of novel complexes and to provide an improved synthetic route to trans-IrCl(CS)(PPh$_3$)$_2$. The tentatively proposed structures for these compounds are shown in Scheme 2.  

\[ \text{Scheme 2.} \]
The reaction between RuCl₂(PPh₃)₃ and CS₂ has been re-examined in detail and found to be more complex than originally reported. The mechanism depicted in Scheme 3 was proposed to explain the multiplicity of products. As already noted the complex 2, formulated as [RuCl(η²-CS₂)(PPh₃)₃]Cl in this study, is probably correctly formulated as the zwitterion-containing complex represented in the scheme. The coordinatively unsaturated intermediate 3, which could not be isolated, is formed from a CS₂-containing complex of unknown identity (possibly 1 or 2) by the loss of triphenylphosphine sulphide. Three competing reactions then determine the nature of the products, namely: (a) coupling with unchanged RuCl₂(PPh₃)₃ (or 1) to give 4; (b) self-dimerisation without phosphine loss to generate the six-coordinate doubly-chloro-bridged dimer 5; (c) isomerisation to form an intermediate complex such as 6.
(probably solvated) with the sterically more stable trans-RuL₂ arrangement, which can then dimerise with concomitant phosphine loss to give the dinuclear species 7, or dimerise with concomitant Cl⁻ loss to give the dinuclear species 8. Both 7 and 8 contain the triply-chloro-bridged unit RuCl₃Ru. Data derived from far I.R. and ³¹P N.M.R. techniques,²³,²⁶ an X-ray crystal structure of the triply-chloro-bridged dinuclear 4,²⁴ and a close comparison with the related carbonyl system²⁵,²⁶ were important in
the deduction of this mechanism. A relationship between the stereo-
chemistries of the reactants and the product distribution was discerned.26

Thiocarbonyl complexes of ruthenium(III) were claimed to be the
products formed when RuBr₃(MeOH)(EPh₃)₂ [E = P, As] were heated under
reflux in CS₂ for 30 minutes, the process affording RuBr₃(CS)(EPh₃)₂ in
good yields (ca. 70%). However, the evidence which supports these
formulations is not definitive. The chloro-containing analogues
RuCl₃(MeOH)(EPh₃)₂ did not give CS complexes when similarly treated.27
The dithiocarbonyl complexes RuCl₂(CS)₂(EPh₃)₂ [E = P, As], for which
good elemental analysis data exists, were produced when RuCl₂(EPh₃)₂
was reacted with CS₂.28 The I.R. spectroscopic data (only one ν_CS
band at 1295 cm⁻¹ for both complexes) must imply a trans disposition
of the thiocarbonyl ligands, but the position of these bands is
extremely surprising since the ν_CS bands of the cis-dithiocarbonyl complex,
OsCl₂(CS)₂(PPh₃)₂, are found at 1370 cm⁻¹ and 1260 cm⁻¹. The ν_CS bands
in thiocarbonyl complexes behave in a similar fashion to the ν_CO bands in
carbonyl complexes [see section II(ii)]. Such behaviour would suggest
that RuCl₂(CS)₂(EPh₃)₂, containing two mutually trans CS ligands, would
exhibit a higher ν_CS value than a similar complex containing two mutually
cis CS ligands.

In marked contrast with the ruthenium system the reaction between
OsCl₂(PPh₃)₃, excess PPh₃ and CS₂, which occurs when these components
are heated in benzene under reflux, affords the single product, white
monomeric OsCl₂(CS)(PPh₃)₃, in quantitative yield.29

Manganese thiocarbonyl complexes have been produced from the thermal
reactions of non-phosphine-containing complexes with CS₂.30,31 When a
solution of CpMn(CO)₂(cis-cyclo-octene) [Cp = η⁵-C₅H₅] in CS₂ is heated
at reflux temperature, a complex reaction ensues from which
\[ \text{CpMn}(\text{CO})_2(\text{CS}) \] can be isolated in low yield (<10%). A black insoluble
deposit, two other unidentified compounds and \( \text{CpMn}(\text{CO})_3 \) (ca. 5%) are
also formed.\(^{31}\) It is thought that the olefin acts as a sulphur
acceptor in this reaction, thus being converted to an episulphide
(equation 5). The episulphide
\[ \text{CpMn}(\text{CO})_2(\text{C}_8\text{H}_{14}) + \text{CS}_2 \rightarrow \text{CpMn}(\text{CO})_2(\text{CS}) + \text{C}_8\text{H}_{14}^{+} \] (5)
has not been detected. The substituted cyclopentadienyl complex
\( (\eta^5-\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{C}_8\text{H}_{14}) \) reacts with \( \text{CS}_2 \) in a similar manner.\(^{31}\)

When the same reaction is repeated in the presence of triphenylphosphine
\[ \text{CpMn}(\text{CO})_2(\text{CS}) \] is produced in very good yields.\(^{31,32}\) Kinetic studies of
this latter reaction lead to the postulated mechanism shown in equation 6.\(^{31}\)
\[ \text{CpMn}(\text{CO})_2(\text{olefin}) \quad \text{olefin [slow]} \rightarrow \text{CpMn}(\text{CO})_2 + \text{CS}_2 \quad \text{[fast]} \] (6)
\[ \begin{array}{c}
\text{Cp}(\text{CO})_2 \text{Mn} \quad \text{S} \\
\text{S} \quad \text{C=S} \quad \text{Ph}_3\text{P} \\
\rightarrow \quad \text{CpMn}(\text{CO})_2(\text{CS}) + \text{Ph}_3\text{PS}
\end{array} \]

The π-bonded \( \text{CS}_2 \) adduct was not isolated and characterised in this study.
A principal intuitive objection to this mechanism is that the process
involves attack of the nucleophilic triphenylphosphine molecule at a
sulphur atom where no substantial localisation of positive charge is
anticipated. Well-defined \( \eta^2-\text{CS}_2 \)-containing complexes of the type
\( \text{M}(\eta^2-\text{CS}_2)(\text{CO})_2 \text{L}(\text{PPh}_3) \) \( [\text{M} = \text{Ru, Os}; \text{L} = \text{CO, CN-p-tolyl}] \) do not react with
triphenylphosphine to give thiocarbonyl complexes.\(^{33}\) Furthermore, the
marked acceptor strength of the \( \text{CS}_2 \) ligand in \( \text{g} \) and other related
$\eta^2$-CS$_2$-containing complexes has been carefully described.\cite{footnote34} When the labile tetrahydrofuran complex CpMn(CO)$_2$(THF) is treated with CS$_2$ two well-characterised complexes containing the $\eta^2$-CS$_2$ ligand, 9 and 10, are produced (figure 3).\cite{footnote35} Complex 9 is the $\pi$-bonded CS$_2$ adduct which was suggested to be the key intermediate to CS ligand formation in the mechanism shown in equation 6.

![Complexes 9 and 10](image)

**Figure 3**

Complex 10 represents a situation in which the exocyclic sulphur atom of the CS$_2$ moiety could be activated towards nucleophilic attack by triphenylphosphine. However, both 9 and 10 are not stereochemically rigid. H and C N.M.R. studies showed that, at room temperature, an intramolecular motion is clearly taking place in complex 10 in which the two [CpMn(CO)$_2$] fragments rapidly exchange sites and functions.\cite{footnote35} Thus, if complex 10 is an intermediate to thiocarbonyl formation, the exact nature of the transition state would probably be very difficult to depict. The complexity of the reaction between CpMn(CO)$_2$(THF),
CS$_2$ and PPh$_3$ has been further assessed in a detailed study of the various species which can be isolated during the course of the reaction. In this paper the existence of 10 as an intermediate to thiocarbonyl formation was suggested. Other intermediates were also proposed and a mechanism involving several pathways was put forward.

The analogous reaction of CpRe(CO)$_2$(THF) with CS$_2$ and PPh$_3$ leads to CpRe(CO)$_2$(CS)$_2$ [34%] and the dithiocarbonyl complex CpRe(CO)(CS)$_2$ is obtained in spectroscopic quantities as a by-product. The preparation of CpMn(CO)$_2$(CS) from CpMn(CO)$_2$(C$_8$H$_{14}$) has been published in Inorganic Synthesis.

The first complexes containing more than one CS ligand, CpMn(CO)(CS)$_2$ and CpMn(CS)$_3$, were also synthesised in these studies. Thus CpMn(CO)(CS)(C$_8$H$_{14}$) and CpMn(CS)$_2$(C$_8$H$_{14}$), produced respectively by U.V. irradiation of n-hexane solutions of CpMn(CO)$_2$(CS) and CpMn(CO)(CS)$_2$ containing cis-cyclo-octene, react thermally with CS$_2$ in the presence of PPh$_3$ to give the di- and tri-thiocarbonyl complexes. Unfortunately, the irradiation experiments were accompanied by considerable decomposition resulting in poor yields of CpMn(CO)(CS)$_2$, which was fully characterised, and CpMn(CS)$_3$, which was identified solely by I.R. spectroscopy.

Chromium thiocarbonyl complexes have been similarly obtained. The very reactive olefin complexes ($\eta^6$-C$_6$H$_5$CO$_2$Me)Cr(CO)$_2$(cis-cyclo-octene) and [($\eta^6$-C$_6$H$_4$(Me)CO$_2$Me]Cr(CO)$_2$(cis-cyclo-octene), when dissolved in a CS$_2$ solution containing triphenylphosphine, give, respectively, the thiocarbonyl complexes ($\eta^6$-C$_6$H$_5$CO$_2$Me)Cr(CO)$_2$(CS) (60%) and [($\eta^6$-C$_6$H$_4$(Me)CO$_2$Me]Cr(CO)$_2$(CS). Similar reactions of ($\eta^6$-C$_6$H$_5$R)Cr(CO)$_2$(THF) [R = H, Me] afford the thiocarbonyl complexes
$(\eta^5-\text{C}_6\text{H}_5\text{R})\text{Cr(CO)}_2(\text{CS})$, but the yields are lower (ca. 20\%) than when the labile alkene complexes are used as precursors. 36

The synthetic procedure under discussion here presumably involves the formation of a \text{CS}_2-containing intermediate which interacts with triphenylphosphine to form a thiocarbonyl ligand and triphenylphosphine sulphide. In 1975 it was reported that the procedure had been successfully extended to produce the first selenocarbonyl complexes. 39 Reaction of the complex $\text{CpMn(CO)}_2(\text{THF})$ with an equimolar quantity of $\text{CSe}_2$ gives a green solution from which can be obtained, after addition of triphenylphosphine (1 mole equivalent), yellow air stable crystals of $\text{CpMn(CO)}_2(\text{CSe})$ \text{\textsuperscript{11}} (40\%). Triphenylphosphine selenide was isolated as a side-product of the reaction. By analogy with the proposed mechanism of thiocarbonyl ligand formation it was suggested that \text{\textsuperscript{11}} is formed as in equation 7.

\[
\text{CpMn(CO)}_2(\text{THF}) \xrightarrow{\text{CSe}_2} \text{CpMn(CO)}_2(\text{CSe}_2) \xrightarrow{\text{Ph}_3\text{P}} \text{CpMn(CO)}_2(\text{CSe}) + \text{Ph}_3\text{PSe} \text{ \textsuperscript{7}}
\]

The same uncertainty as to the nature of the interaction represented in the second step also pertains to this system. Similar treatment of $\text{CpMn(CO)}_2(\text{C}_8\text{H}_{14})$ or of $(\eta^5-\text{C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr(CO)}_2(\text{THF})$ gave, respectively, \text{\textsuperscript{11}} in 10\% yield, or the red complex $(\eta^5-\text{C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr(CO)}_2(\text{CSe})$ in 20\% yield.

(iii) Reductive Fragmentation of Thiophosgene

Thiophosgene, $\text{Cl}_2\text{CS}$, has been successfully used as a source of the thiocarbonyl ligand. The Group VI thiocarbonyl complexes $\text{M(CO)}_5(\text{CS})$ [$\text{M} = \text{Cr}, \text{Mo}, \text{W}$] can be synthesised by treating solutions of reduced metal carbonyl complexes (apparently containing mainly the dianions $[\text{M}_2(\text{CO})_6]^{2-}$)
with excess thiophosgene (equation 8). 40, 41

\[
\text{M(CO)}_6 \xrightarrow{(i) \text{Na/Hg, THF}} \text{M(CO)}_5(\text{CS}) \xrightarrow{(ii) \text{Cl}_2\text{CS}} \text{M(CO)}_5(\text{CS})
\] (8)

After sublimation of the evaporated reaction mixture the thiocarbonyl complexes could be obtained in low but reproducible yields (2-15%), but were always contaminated by the hexacarbonyl complexes M(CO)_6. Repeated recrystallisation or gas-liquid chromatography were effective methods for separating small quantities of these mixtures, but a more convenient chemical method was used to purify the tungsten thiocarbonyl complex (equation 9).

\[
[\text{Bu}_4\text{N}]^+ [\text{W(CO)}_5(\text{CS})] \xrightarrow{\text{Ag}^+} \text{W(CO)}_5(\text{CS}) + \text{AgI}
\] (9)

Under the mild conditions employed W(CO)_6 does not react with [Bu_4N]I and the significance of this difference will be discussed in section III. The mechanism of the reductive fragmentation of thiophosgene in these systems is not clear, but, in a phenomenological sense, the results are appropriately described as such.

The facile oxidative-addition of the three fragments of thiophosgene to the complexes IrCl(\text{N}_2)(\text{PPh}_3)_2, [Ir(\text{MeCN})(\text{CO})(\text{PPh}_3)_2]^+ and RhCl(\text{PPh}_3)_3 affords, respectively, IrCl(\text{CS})(\text{PPh}_3)_2, [IrCl(\text{CS})(\text{CS})(\text{PPh}_3)_2]^+ and RhCl(\text{CS})(\text{PPh}_3)_2 in relatively high yields. The reaction of thiophosgene with Pt(\text{PPh}_3)_3 or Pt(\text{C}_2\text{H}_4)(\text{PPh}_3)_2 in the presence of the halide acceptor BCl_3 generates a thiocarbonyl complex of suggested formulation trans-[PtCl(\text{CS})(\text{PPh}_3)_2]^+. The reactivity of this complex with respect to hydrolysis precluded complete characterisation. 42

This same complex has been produced elsewhere and shown to be highly reactive towards nucleophilic attack at the thiocarbonyl carbon atom 43 [see sections I(iv), III B(i)]. The reaction of Ru_3(\text{CO})_12 with thiophosgene in heptane solution affords RuCl_2(\text{CO})(\text{CS}) in high yield. 44
(iv) Modification of Coordinated Thioester and Selenoester Ligands

The treatment of some thioester-, dithioester- and diselenoester-containing complexes with acids has proven to be a viable procedure for the synthesis of CS or CSe complexes. The first complex produced in this way, \([\text{CpFe(CO)}_2\text{(CS)}]^{+}\), was prepared by treatment of the thioester-containing complex \(\text{CpFe(CO)}_2\text{[C(S)OEt]}\) with anhydrous HCl in benzene, and was isolated as the PF$_6^-$ salt (equation 10).\(^{45}\)

\[
\begin{align*}
\text{(i) HCl/benzene} & \quad \text{CpFe(CO)}_2\text{[C(S)OEt]} \\
\text{(ii) NH}_4\text{PF}_6/\text{acetone} & \rightarrow \quad \text{[CpFe(CO)}_2\text{(CS)}]\text{PF}_6^{10\%} + \text{EtOH + NH}_4\text{Cl}
\end{align*}
\]

The yield was subsequently improved (45%) by using the analogous methyl-thioester-containing complex \(\text{CpFe(CO)}_2\text{[C(S)OMe]}\).\(^{46}\) The thioester complexes are produced by reacting the anion \([\text{CpFe(CO)}_2]^-$ with the appropriate chlorothioformate, ClC(S)OR. This same thiocarbonyl cation can be produced from a methylthioester complex which is formed by methylation of an intermediate metalloethiocarboxylate anion (equation 11).\(^{46}\)

\[
\begin{align*}
\text{[CpFe(CO)}_2\text{]^- + CS}_2 & \rightarrow \quad \text{[CpFe(CO)}_2\text{(CS)}_2\text{]^- \rightarrow MeI} \quad \text{CpFe(CO)}_2\text{[C(S)SMe]} \\
\text{HCl} & \rightarrow \quad \text{[CpFe(CO)}_2\text{(CS)}\text{]}^{+} + \text{MeSH}
\end{align*}
\]

While attempts to isolate the CS$_2$-containing anion and the dithioester complex were unsuccessful, the metalloethiocarboxylate anion was characterised spectroscopically and the related dithioester complex \(\eta^5\text{-Me}_5\text{C}_5\text{Fe(CO)}_2\text{[C(S)SMe]}\) was fully characterised in a later study concerned with the interaction of CS$_2$ with metal carbonyl anions.\(^{47}\)

Complexes containing bidentate dithiomethylester or bidentate diselenomethylester ligands were produced as suitable precursors to
CS and CSe complexes by methylation of the π-bonded carbon disulphide or carbon diselenide ligands in the complexes

\[ M(\eta^2-CS_2)(CO)_2(PPh_3)_2 \quad [M = Ru, Os] \quad ^{48} \quad \text{and} \quad Ru(\eta^2-CSe_2)(CO)_2(PPh_3)_2 \quad ^{49} \]

equation 12.

\begin{align*}
L = & \ PPh_3; \ M = Ru; \ Y = S, Se; \ X = I, CF_3SO_3 \ \text{or} \\
& M = Os; \ Y = S; \ X = I, CF_3SO_3.
\end{align*}

That the exocyclic sulphur atom in the dithioester complexes is attached to the methyl group was shown by an X-ray crystal structure determination of the cationic complex \( [Ru(\eta^2-C[S]SMe)(CO)_2(PPh_3)_2]ClO_4 \). The ruthenium cations are labile with respect to displacement of CO by halide ions, but the osmium cation can be isolated in the presence of halide ion. The ester complexes are slowly converted to CS or CSe complexes by reaction with aqueous acids (equation 13).

\[ M[\eta^2-C(Y)YMe]X(CO)(PPh_3)_2 \xrightarrow{HX} M(CY)(PPh_3)_2 \xrightarrow{HX} MX_2(CO)(CY)(PPh_3)_2 \]

equation 13.

The mechanism of thiocarbonyl ligand formation in these systems has not been elucidated, but among the plausible reaction pathways are:

(i) the 1,2-elimination of MeYH from an intermediate carbene complex (equation 14)

\begin{align*}
& L = PPh_3
\end{align*}
and; (ii) proton attack at the methylated Y-atom followed by MeYH elimination and halide coordination. The possible mechanism (i) is supported by the observation that, whereas the bidentate dithioester and diselenoester complexes react only slowly with aqueous acids and are not alkylated by methyl iodide, the monodentate dithioester-containing complex, Ru(n²-S₂CNET₂)[η¹-C(S)SMe](CO)(PPh₃)₂, reacts very rapidly with HBF₄ to give a CS complex, or with methyl iodide to give a stable dithiocarbene complex.⁵⁰

The complex Os(n²-CS₂)(CO)(PPh₃)₂ also reacts directly with aqueous HCl evolving H₂S and forming OsCl₂(CO)(CS)(PPh₃)₂, but Ru(n²-CS₂)(CO)(PPh₃)₂ affords a mixture of RuCl₂(CO)(CS)(PPh₃)₂ and RuCl₂(CO)(PPh₃)₂ when similarly treated.⁵¹ The monodentate dithioester complex IrCl₂[C(S)SMe](CO)(PPh₃)₂ reacts with iodine to yield [IrCl₂(CO)(CS)(PPh₃)₂]I₃.¹⁰²

This synthetic procedure has been extended to obtain dithiocarbonyl complexes in high yields. By oxidative addition of carbon disulphide to Os(CO)(CS)(PPh₃)₃ (see section III) Os(n²-CS₂)(CO)(CS)(PPh₃)₂ can be produced and this complex is rapidly methylated by methyl trifluoromethanesulphonate (or methyl iodide) to give the dithioester cation [Os(n²-C[S]SMe)(CO)(CS)(PPh₃)₂]⁺. Both the π-bonded CS₂ complex and the dithioester cation react with aqueous acids HX [X = Cl, Br] to give the dithiocarbonyl complexes OsX₂(CS₂)₂(PPh₃)₂ in high yields. The monodentate dithioester complex Os(n²-S₂CNET₂)[C(S)SMe]-(CS)(PPh₃)₂ is rapidly cleaved by acids to afford the dithiocarbonyl cation [Os(n²-S₂CNET₂)(CS)₂(PPh₃)₂]⁺.⁵²

The thioester complexes PtCl[C(S)OMe](PPh₃)₂ and
PtCl[C(S)SEt](PPh₃)₂, which react readily with alkylating agents to give cationic S-alkylated carbene complexes, form methanol or ethyl thiol and a complex believed to be [PtCl(CS)(PPh₃)₂]Cl when reacted with dry HCl in CH₂Cl₂ solution. The complex trans-PtCl[C(S)OME](PPh₃)₂ also reacts with BF₃ to produce trans-[PtCl(CS)(PPh₃)₂]^+ which was characterised by further reactions [section III B(i)].

An extensive chemistry of the n²-CS₂-containing complexes Fe(n²-CS₂)(CO)₂L L′ [L = L′ = P(OMe)₃, P(OEt)₃, PPh₃, PBu₃, PMe₂Ph, PMe₃; L = PPh₃, L′ = PMe₃, PMe₂Ph], including the formation of thiocarbonyl complexes, has been noted but not described.

(v) Reductive Elimination of Methyl Thiol

The production of a CS ligand, accompanied by a reduction of the metal oxidation state by two units, has been achieved for osmium and iridium. The bidentate dithiomethylester cations [Os(n²-C[S]SMe)(CO)₂(PPh₃)₂]^+ and [Ir(n²-C[S]SMe)Cl(CO)(PPh₃)₂]^+ react with NaBH₄ to afford the neutral complexes OsH[n¹-C[S]SMe](CO)₂(PPh₃)₂ and IrH[n¹-C(S)SMe]Cl(CO)(PPh₃)₂. These compounds, which contain the mutually cis hydrido and n¹-dithiomethylester ligands, undergo 1,2-elimination of MeSH on heating to produce Os(CO)₂(CS)(PPh₃)₂ and trans-IrCl(CS)(PPh₃)₂ in high yields (equation 15).

\[
\begin{align*}
\text{H} & \quad \text{SMe} \\
\text{L} & \quad \text{M-C=S} \\
\text{MeSH} & \\
\end{align*}
\]

An X-ray crystal structure determination of OsH[n¹-C(S)SMe](CO)₂(PPh₃)₂ has shown that, in the solid state, the dithiomethylester is orientated so that the metal, the hydrido ligand and the CS₂ grouping lie in a plane. The SMe entity and the hydrido ligand are mutually cis with
the dithioester ligand tilted towards the hydrido ligand suggesting an interaction even in the solid state, and alluding to the known course of the elimination reaction (figure 4).\(^\text{56}\)

![Figure 4](image_url)

This preparation of trans-IrCl(CS)(PPh\(_3\))\(_2\) is the most attractive synthetic route to this complex so far reported.

(II) **STRUCTURE AND BONDING**

From the first discovery of CS complexes it was apparent that the M–CS bond is exceptionally strong. Thus I.R. data concerning trans-RhX(CS)(PPh\(_3\))\(_2\) \([X = \text{Cl, Br}]\) indicated that considerable metal-to-ligand \(\pi\)-backbonding existed in the Rh-CS bond. The failure of trans-RhCl(CS)(PPh\(_3\))\(_2\) to add HCl, where the carbonyl analogue does so react, and the inertness of the CS complexes to replacement of CS by CO further supported the existence of such \(\pi\)-backbonding.\(^\text{12}\) An early M.O. treatment of the CS molecule showed that the carbonyl and the thio-carbonyl ligands ought to display similar bonding behaviour but concluded that, because of orbital energy considerations, both the \(\sigma\)- and \(\pi\)-components should be stronger in the thio-carbonyl case.\(^\text{57}\)

Many of the physical techniques that are available for probing electronic and structural properties have now been applied in studies
of CS complexes. However, various researchers have arrived at
different conclusions concerning the bonding capacity of the CS ligand
based on their individual experimental findings. Thus, while recognition
of a very strong M-CS bond has been unanimous, discussions concerning
the relative importance of σ-donor, π-acceptor and, more recently,
π-donor properties have been controversial. Because of the obvious
relationship between the thiocarbonyl and carbonyl ligands, analyses
have tended to converge on those experimental findings which define
the bonding properties of the former in terms of those known for the
latter. Such deliberations have served to highlight the differences
in the bonding capacity of the two ligands and the present understanding
is focussed on the greater sensitivity of the CS ligand to the
electronic environment of the transition metal complex; i.e. CS is a
softer ligand than CO. It is still too soon to discuss the nature of
the bonding in selenocarbonyl complexes in any detail, other than to
note that early results point to a strong interaction between the metal
and the CSe ligand. In the following summary the contributions of the
various physical techniques towards discerning the nature of the
bonding in CS and CSe complexes will be presented and, where appropriate,
interpretations based on these studies will be assessed.

(i) X-Ray Crystallography

The CS ligand has been found in terminal and bridging environments.
The CSe ligand has, to date, been isolated only in the terminal
environment (figure 5). Thiocarbonyl compounds
of the end-to-end bridging type, for which structural characterisation
does not yet exist, are otherwise well characterised. A further type
of bridging CS group, involving the bridging of three metal centres, has
been postulated for the complex of empirical formula Co$_3$(CO)$_6$CS$_2$,
but the evidence is not conclusive. Carbonyl analogues of each of
the above coordination types are known.

X-ray crystallographic studies of six CS complexes and one CSe
complex and preliminary mention of the CS bond length for a seventh
CS complex have been published. The reliability of the information
reported is variable and in the case of the triply-chloro-bridged
dinuclear complex (Ph$_3$P)$_2$ClRuCl$_3$Ru(CS)(PPh$_3$)$_2$ the parameters associated
with the CS moiety [e.g. C-S bond length 1.14(10)Å] are presented as
a "rough indication" of the true structure and do not contribute to
any meaningful discussion.

Fortunately most of the other complexes contain CO so that
comparison of those structural parameters which contrast the bonding
capacity of the CO ligand with that of the CS or CSe ligand is possible.
Representations of the structurally studied complexes with some of the
more important parameters are shown in Table 1. For the terminal
CS complexes $^{14 \text{59a}}$ and $^{15 \text{60}}$ the M-CS bond lengths are, on average,
0.051(5)Å and 0.120(43)Å shorter than the M-CO bond lengths in the
same complex, the best comparison being afforded by 14 where the trans environments of the CS and CO ligands are similar. The M-CS bonds are also apparently shorter than the M-CO bonds in the two crystallographically independent cations 13. For 12, which does not contain a carbonyl ligand, the Rh-CS bond length \( [1.787(10)\text{Å}] \) has been compared with the one reported parameter for the CO analogue RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}; viz. Rh-CO 1.86\text{Å} (without standard deviation).\textsuperscript{59c,61} The M-C-S entity is effectively linear in all cases so that the available structural data supports the contention that the M-CS bond in terminal CS complexes is stronger than the M-CO bond in the same, or parent carbonyl complex. This observation can be taken to imply that CS will have a greater trans-influence relative to CO, but there is a noticeable lack of structures from which such details would be evident.

The terminal C-S bond distance varies from 1.501(4)\text{Å} in 18\textsuperscript{60} to 1.570(2)\text{Å} in 14\textsuperscript{59a}, both shorter and longer than in free CS [1.5349(2)\text{Å}].\textsuperscript{62} The shorter C-S bonds are found in cationic complexes (13, 18) favouring a σ-donor/π-acceptor model which emphasises the importance of the π-acceptor character of CS and supports the theoretical finding that the σ-donor electrons of CS are antibonding with respect to the C-S bond.\textsuperscript{57} The C-S bond lengths in the bridging CS complex 16, 1.587(7)\text{Å} and 1.592(8)\text{Å}, are longer than terminal bond lengths, reflecting the expected lower multiplicity of the bridging C-S bonds.\textsuperscript{63}

In the one reported structure of a selenocarbonyl complex, 17, the M-CSe and M-CO bonds are of similar length. However, the marked trans-influence of the CSe ligand is evident from the trans Ru-Cl
TABLE 1. REPRESENTATIONS OF CS AND CSe COMPLEX STR.

(a) ref. 59(c), (b) ref. 59(b); (c) ref. 59(a); (d) ref. 60, 1104 < C-O < 1155(26); (e) ref. 63,
(f) ref. 64; (g) ref. 60; (h) all bond lengths quoted in Å, all bond angles in degrees.
bond distance, $2.477(7)\,\AA$, which is significantly longer than the Ru-Cl (trans to CO) distance of $2.428(6)\,\AA$.\textsuperscript{49,64} A considerable donor component in the M-CSe bond is implied by this structure.

Structural information which might resolve the relative importance of $\pi$-donation in suitable complexes to either the M-CS or M-CSe bonds is not available. The $\pi$-donation phenomenon, if this is real, is expected to be strongest in weakly basic cationic complexes where the metal has less than 6 d-electrons. An unusual lengthening of the C-S bond in such a complex would be evidence for the authenticity of a $\pi$-donor component.

(ii) Infrared and Raman Spectroscopy

Infrared spectroscopy is a technically facile method which is very applicable to the study of CS or CSe complexes. The dipole moment derivative of CS is large\textsuperscript{57,65} and for both uncomplexed and terminally complexed CS, the CS stretching vibration registers as a very intense absorption band, bounded so far by the limits $1409\,\text{cm}^{-1}$\textsuperscript{42} and $1161\,\text{cm}^{-1}$.\textsuperscript{41} This is both greater and less than $v_{\text{CS}}$ for CS isolated in a $\text{CS}_2$ matrix, $1274\,\text{cm}^{-1}$.\textsuperscript{66} The greater $v_{\text{CS}}$ values have been attributed to the coupling of the C-S vibration with other vibrations (below $700\,\text{cm}^{-1}$),\textsuperscript{1} or to the antibonding nature of the CS $\sigma$-donor lone pair with respect to the C-S bond.\textsuperscript{60} While coupling could preclude the existence of a reliable group frequency for CS compounds,\textsuperscript{67} thus invalidating correlations of the bonding properties of the CS ligand with the position of $v_{\text{CS}}$, the latter has, to a surprising extent, shifted according to the expected basicity of the
metal centre. Electron-rich complexes exhibit a low $\nu_{CS}$ band and electron-poor complexes a high $\nu_{CS}$ band.

All but very recent literature discussions concerning the significance of $\nu_{CS}$ to the bonding capacity of the CS ligand have centred on how $\nu_{CS}$ reflects the relative importance of $\sigma$-donor and $\pi$-acceptor properties. However, the results of studies concerning infrared and other techniques have led to contentious interpretations. The existence of a near linear correlation of $\nu_{CS}$ with the CS bond length in five complexes is consistent with a $\sigma$-donor/$\pi$-acceptor model; short C-S bond lengths corresponding to high $\nu_{CS}$ values and long C-S bond lengths to low $\nu_{CS}$ values. The lowering of $\nu_{CS}$ in a series of compounds by replacing one or more ligands with ligands of greater basicity can be observed to be a general phenomenon, attesting to the importance of $\pi$-acid character.

Considerable attention has also been directed to interpretations of $\nu_{CO}$ or $\nu_{NO}$ which shed light on the bonding properties of CS ligands in complexes also containing carbonyl or nitrosyl ligands. Thus, for instance, consider the series $[\text{CpFe(CO)}_2L]^+$ [L = CS, C$_2$H$_4$, PPh$_3$, CNMe, py], $^{45}$ $[\text{CpFe(CO)}L_1L_2]^+$ [L$_1$ = CS, CNMe; L$_2$ = PCy$_3$, P(CH$_2$H$_4$F)$_3$ (substituted arenes are para-substituted unless otherwise stated) and $L_1$ = CS, CNMe, CNCy; $L_2$ = PPh$_3$]$^{68}$ and $\text{M(CO)}_3L$ [M = Cr, Mo, W; L = CS, CNMe and M = W; L = CNCH$_2$CO$_2$Me]. $^{40}$ The $\nu_{CO}$ bands occur at the highest frequency in the thiocarbonyl complexes suggesting that the CS ligand is a remarkably good $\pi$-acceptor, comparing favourably in this respect with PF$_3$. $^{40}$ Also for the series $[\text{CpMn(NO})(\text{CX})L]^+$ [X = S, O; L = PPh$_3$, AsPh$_3$, SbPh$_3$] $\nu_{NO}$ is slightly greater for the
thiocarbonyl complexes implying that CS is a slightly stronger π-acceptor than CO. However, for the complexes
\[(\eta^5-RC_{5}H_{4})Mn(NO)(CO)(CX)]^{+} \quad [R = H, Me; \quad X = S, O] \] the ν\textsubscript{NO} values are lower for the thiocarbonyl complexes, perhaps indicating the relative π-acidity order is CO > CS. For these latter complexes and for the related series [CpFe(CO)\textsubscript{2}(CX)]^{+} \quad [X = S, O] and CpMn(CO)(CX)L \quad [X = S, O; L = phosphines, phosphites and related ligands] the ν\textsubscript{CO} (max) of each CS complex is invariably lower than that of the CO analogue and this has been taken to reflect that CO is a stronger π-acceptor than CS. However, the direct interpretation of bonding properties from a comparison of I.R. bands which derive from vibrations involving different numbers of carbonyl ligands is not meaningful. Indeed, a comparison of the carbonyl force constants for the same complexes for which the ν\textsubscript{CO} (max) correlation was made shows, in some instances, the reverse of the above predicted acceptor trend to be true.

Absolute integrated I.R. intensities of the carbonyl and thiocarbonyl stretching modes have been used to calculate the dipole moment derivatives, μ', for the MCO and MCS entities in CpMn(CO)\textsubscript{2}(CS). That the μ'(MnCS) value was greater than the μ'(MnCO) values was taken as direct evidence for the greater π-acceptor ability of CS compared to CO.

Detailed vibrational spectroscopic studies concerning the complexes (\eta^6-C\textsubscript{6}H\textsubscript{5}CO\textsubscript{2}Me)Cr(CO)\textsubscript{2}(CS), CpMn(CO)\textsubscript{2}(CS) and CpMn(CO)(CS)\textsubscript{2} and M(CO)\textsubscript{5} (CS) \quad [M = Cr, W] and trans-W(CO)\textsubscript{4}(\textsuperscript{13}CO)(CS) have been reported. Calculated Cotton-Kraihanzel CO force constants gradually increase for the series CpMn(CO)\textsubscript{3} < CpMn(CO)\textsubscript{2}(CS) < CpMn(CO)(CS)\textsubscript{2}
indicating that CS is a stronger π-acceptor than CO. The CS force constants in this same series appeared insensitive to the environmental change. 73 On replacing CO with CS in M(CO)₆ [M = Cr, W] the axial (trans to CS) CO force constant increases appreciably and the axial M–C force constant decreases appreciably, while the equatorial force constants are little changed, further implying the greater π-acid strength of CS relative to CO. The M–CS force constants are also significantly larger than any of the M–CO force constants. 74 For the series (η⁵-arene)Cr(CO)₂L [L = PPh₃, P(OEt)₃, P(OME)₃, P(OPh)₃, CO, CS; arene unspecified] the average CO force constant is greatest for the thiocarbonyl complex. 75

While the above summary tends strongly to favour the contention that CS is a stronger π-acceptor than CO, some studies employing other techniques, which will be detailed below, figure conclusively to the contrary. It will become apparent that these seemingly incompatible results highlight the deficiencies of arguments which presuppose that the electronic properties of the CS ligand can be divorced from those of the complex environment to which the ligand is coordinated. Present discussions are consolidating around a more complex model in which the relative bonding parameters of the CS ligand are determined for every particular complex instead of generalising the parameters to all CS complexes. The first and the most informative and unifying study of this kind concerns detailed correlations involving the vibrational stretching frequencies of the CS ligand in a large series of mixed carbonyl–thiocarbonyl complexes, M(CO)ₙ(CS), and the Cotton-Kraihanzel CO force constants, k, for M(CO)ₙ(CS) and M(CO)ₙ₊₁. For details of the procedure the interested reader is referred to Andrew's paper. 71
This study has indicated that a crossover in the relative electronic properties of CS and CO exists which can be correlated semiquantitatively with the carbonyl force constant of the parent carbonyl complex. Thus, for complexes where $k_{\text{CO}}[\text{M(CO)}_{n+1}] < 17.1$ mdyn Å$^{-1}$ the $\pi$-acceptor to $(\sigma + \pi)$-donor ratio in $\text{M(CO)}_n$ (CS) is greater for CS than for CO, and for $k_{\text{CO}}[\text{M(CO)}_{n+1}] > 17.1$ mdyn Å$^{-1}$ this ratio is lower for CS than for CO. Furthermore, a correlation of $v_{\text{CS}}$ with $k_{\text{CO}}[\text{M(CO)}_{n+1}]$ appears to be sensitive to the electronic effects of other ligands in the coordination sphere. The crossover is consistent with those specific properties of various CS complexes which have not been explained by invoking the simple model that CS is a better $\pi$-acceptor than CO. Further mention of this study will be made where the crossover phenomenon can or has been used to clarify apparent incongruities.

I.R. spectroscopy has proven invaluable for diagnosing the presence of thiocarbonyl complexes where other methods are not practicable. Thus for the multithiocarbonyl complexes Ni(CS)$_n$ [n = 1–4], which were obtained in matrix isolation experiments, and CpMn(CS)$_3$, which could not be obtained in sufficient quantity for more detailed characterisation, the formulations were defined on the basis of the I.R. spectra. The value of $v_{\text{CS}}$ reproduces expected lowerings of the C-S bond multiplicity. When the CS ligand is found in the normal bridging environment (figure 5) $v_{\text{CS}}$ occurs in the range 1118 cm$^{-1}$ to 1178 cm$^{-1}$, and in the end-to-end bridging environment (figure 5) in the vicinity of 1100 cm$^{-1}$. Estimates of the relative trans-influence of the CS ligand compared to the CO ligand have been obtained by considering $v_{\text{Rh-X}}$ in trans-RhXL(PPH$_3$)$_2$ [X = Cl, Br; L = CO, CS]; $v_{\text{Rh-X}}$ is lower in the thiocarbonyl complexes
suggestion that CS has the greater trans-influence. A method for comparing the changes in \( \nu_{\text{CO}} \) and \( \nu_{\text{CS}} \) upon adduct formation with Lewis acids in the complexes trans-IrClL(PPh\(_3\))\(_2\) [L = CO, CS] has been advanced and discussed.

The six published I.R. \( \nu_{\text{CSe}} \) values lie in the range 1071 cm\(^{-1}\) to 1137 cm\(^{-1}\). Each \( \nu_{\text{CSe}} \) value is approximately 175 cm\(^{-1}\) less than the \( \nu_{\text{CS}} \) value in the corresponding thiocarbonyl complex (the media in which the corresponding values are measured are not always identical). With only minor deviations \( \nu_{\text{CSe}} \) follows the same trend as \( \nu_{\text{CS}} \) in the series of analogous complexes (Table 2) (these deviations may be the result of the different media in which the spectra are measured). The seven known selenocarbonyl complexes also contain CO and it is apparent from the \( \nu_{\text{CO}} \) data in Table 2 that the CS and CSe ligands have quite similar bonding properties. While correlations or comparisons based on \( \nu_{\text{CO}} \) would probably be premature, I.R. data resolving the relative importance of \( \pi \)-acceptor and \( (\sigma^* \pi) \)-donor properties and the possible existence of crossovers in relative electron properties between CO and CSe, and CS and CSe are anticipated.

Studies of the laser Raman spectra of thiocarbonyl complexes have shown that the CS stretching vibration is not particularly Raman active. This band could not be identified in the Ra spectra of CpMn(CO)(CS)\(_2\), [CpFe(CO)\(_2\)(CS)] BPh\(_4\) or W(CO)\(_4\)(CS)(PPh\(_3\)) but was found as a very weak band for CpMn(CO)\(_2\)(CS), M(CO)\(_5\)(CS) [M = Cr, W] and trans-W(CO)\(_4\)(CO)(CS), and as a medium intense band for \((\pi^5-C_6H_5)CO_2Me)Cr(CO)\(_2\)(CS). This was initially interpreted as being a surprising feature because of the large polarisability change expected
<table>
<thead>
<tr>
<th>Compound</th>
<th>X = Se</th>
<th>Medium</th>
<th>Ref.</th>
<th>X = S</th>
<th>Medium</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{Me})\text{Cr(CO)}_2\text{(CX)})</td>
<td>1990, 1947</td>
<td>1071</td>
<td>-</td>
<td>1992, 1939</td>
<td>1225</td>
<td>CCl₄</td>
</tr>
<tr>
<td>Cr(CO)_5(CX)</td>
<td>2093, 2031, 2000</td>
<td>1077</td>
<td>n-hexane</td>
<td>2091, 2023</td>
<td>1253a</td>
<td>n-hexane a) CS₂</td>
</tr>
<tr>
<td>CpMn(CO)_2(CX)</td>
<td>2015, 1963</td>
<td>1105</td>
<td>-</td>
<td>2010, 1959</td>
<td>1271</td>
<td>nujol mull</td>
</tr>
<tr>
<td>RuCl₂(CO)(CX)(PPh₃)₂</td>
<td>2030</td>
<td>1125</td>
<td>nujol mull</td>
<td>2050, 2040</td>
<td>1302</td>
<td>nujol mull</td>
</tr>
<tr>
<td>RuBr₂(CO)(CX)(PPh₃)₂</td>
<td>2030</td>
<td>1125</td>
<td>nujol mull</td>
<td>2040, 2030</td>
<td>1300</td>
<td>nujol mull</td>
</tr>
<tr>
<td>RuI(OH)(CO)(CX)(PPh₃)₂</td>
<td>2070</td>
<td>1137</td>
<td>nujol mull</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
for the CS vibration. Butler and his associates suggested that the low Raman activity could be explained by assuming that the CS bond in metal thiocarbonyls is more ionic \((C^+S^-)\) than the CO bond in metal carbonyls. However, an alternative explanation has emerged from a study involving a combination of photoelectron spectroscopy and approximate molecular orbital calculations [section II(iii)]\(^{61}\). Deductions from this study maintain that "the C-S stretch lowers the CS \(\pi^*\)-orbitals and increases their carbon character, thus increasing their interaction with the metal. The CS \(\pi\)-levels are destabilised with stretching and their interaction with the metal levels is diminished. These two competing influences will tend to reduce the change in polarisability along a stretching mode and hence weaken the Raman activity, as is observed". This explanation has been accepted by Butler et al. as being "more quantitative" than their ionic description.\(^{74}\) The laser Raman spectrum of \(\text{Cr(CO)}_5\)(CSe) exhibits a broad medium intense peak at 1093 cm\(^{-1}\) attributed to \(\nu_{\text{CSe}}\).\(^{94}\)

(iii) Theoretical Studies and Photoelectron Spectroscopy

Richard's early theoretical treatment of the ground state CS molecule\(^{57}\) has been used extensively to explain and unify experimental results. Subject to the qualifications already noted experimental results substantiate the prediction that CS can behave as a stronger \(\sigma\)-donor and a stronger \(\pi\)-acceptor than CO.

Photoelectron spectroscopic studies of \(\text{Cr(CO)}_5\)(CS), \(\text{W(CO)}_5\)(CS) and \(\text{CpMn(CO)}_2\)(CS) produced ionisation spectra in which certain features were surprising in the light of the known greater \(\pi\)-acidity of CS in comparison to CO.\(^{61}\) It was found that the degeneracy of the \(t_{2g}\)
ionisations of Cr(CO)$_6$ did not appear to be lifted in the spectrum of Cr(CO)$_5$(CS), despite the fact that the electronic structure of CS was known to be much different to CO. Also the metal ionisations from the d-levels of the thiocarbonyl complexes consistently occurred at lower binding energy than the metal ionisations of the carbonyl complexes, which seemed to be a contradiction to the expected better $\pi$-acceptor ability of the CS ligand. Approximate M.O. calculations for CO, CS, Cr(CO)$_5$L and CpMn(CO)$_2$L [L = CO, CS] were then discussed with a view to assessing the meaning of these ionisation experiments. The limitations and approximations inherent in the calculations, and the discrepancies between the approximate and ab initio$^{57}$ calculations for CO and CS were first reviewed and the validity of the discussion, including the extension to the transition metal complexes, was taken to be based on the fact that the shift in eigenvalues from CO to CS was in quite close agreement for both the approximate and ab initio calculations. The M.O. calculations for Cr(CO)$_5$L and CpMn(CO)$_2$L [L = CO, CS] accurately reproduced the experimental trends in ionisation potentials and were interpreted to indicate that the primary factor producing the unusual ordering of metal levels is an increased metal interaction with the CS $\pi$-bond. The tendency to stabilise the metal e levels through increased interaction with the CS $\pi^*$-orbitals was thus proposed to be offset by a greater interaction with the CS $\pi$-orbitals. These interactions were expected to produce a stronger metal-carbon bond and a correspondingly weaker carbon-sulphur bond. Thus, supposedly, the e levels are destabilised by being in the proximity of the electron-rich CS carbon centre and hence the expected loss of degeneracy for the t$_{2g}$ levels is not observed and ionisations from the metal d-levels are at the lower energies observed. Furthermore, it was stated that the
σ-donor orbital can only partially reduce the electron density that accumulates at the C centre. This result was said to have important consequences concerning CS ligand reactions of the type shown in equation 16 which had previously been described as nucleophilic attack at the carbon centre of CS. Since this behaviour appeared to be contrary to the expected increase in electron density at the carbon

\[
(CO)_{5}W(CS) + \text{RNH}_{2} \rightarrow (CO)_{5}W-C-C-NH
\]

\[
\text{SH} \rightarrow H_{2}S \rightarrow (CO)_{5}W(CNR)
\]  

(16)

centre, the suggestion was made that such reactions might be better described as "lumophilic", in which the HOMO of the amine (the lone pair) interacts with the LUMO of the complex (π* \text{CS}). Ligand reactions of this type are reviewed in section IIIA(i).

In this study Lichtenberger and Fenske have emphasised the importance of an interaction between the CS filled π-orbital and the d π e levels on the metal. In the context of this paper it is difficult to define what is meant by the term "interaction", but π-donation is implied (a coulombic interaction between the metal and ligand filled π-orbitals might also explain the P.E. results) and, subsequently, other workers have used the term π-donation openly. However, if π-donation is an important component in the M-CS bond, then such a component ought to be more significant in \([\text{CpFe(CO)}_{2}(\text{CS})]^+\), which contains a considerably less basic metal centre than the complexes studied by P.E. and M.O. techniques; \(\text{CpMn(CO)}_{2}(\text{CS})\) and \(\text{M(CO)}_{5}(\text{CS})\) \([\text{M} = \text{Cr, W}]\). However, the C-S bond length of 1.501(4) Å is the shortest found to date and does not reflect the presence of a
bond-weakening π-donor component. Consequently, it is probably not valid to suggest that π-donation is important in the M-CS bond in order to explain the results of other experimental determinations. Several P.E. spectroscopic studies of the uncomplexed CS molecule have also been reported.\textsuperscript{82}

(iv) $^{13}\text{C}$ N.M.R. Spectroscopy

There have been two approaches to the problem of applying $^{13}\text{C}$ N.M.R. data towards acquiring an insight into the nature of the M-CS bond. One has been to correlate the observed $^{13}\text{C}$ carbonyl chemical shift data for a series of compounds, $L_n M(\text{CO}) L'$, [$L' = \text{series of ligands including CS}$] with the known electronic properties of the other $L'$ ligands. The other approach has attempted to interpret the $^{13}\text{C}$ thiocarbonyl chemical shift data.

In the first method the $^{13}\text{C}$ CO resonance has been demonstrated to be subject to increased deshielding with increased transition metal to carbonyl π-back donation (which is monitored by the change in the I.R. force constant of the carbonyl ligand).\textsuperscript{83,84} Thus the position of the $^{13}\text{C}$ CO resonance for each member of the series $L_n M(\text{CO}) L'$ is considered to be a direct measure of the overall basicity (total donation - total acceptance) of $L'$. For the series $\text{CpMn(}CO\text{)}_2 L'$ [$L' = \text{CS, CO, } P(\text{OPh})_3, \text{C}_8\text{H}_{14}, P(\text{OMe})_3, \text{PPh}_3, \text{PBu}_3, \text{C}_5\text{H}_{10}\text{NH}$] the CS complex exhibits the most shielded $^{13}\text{C}$ carbonyl resonance implying that the σ-donor/π-acceptor [or (σ + π)-donor/π-acceptor] ratio of $L'$ is the smallest for the CS ligand. (The thiocarbonyl chemical shift of $\text{CpMn(}CO\text{)}_2(\text{CS})$ exhibits the most intensely deshielded $^{13}\text{C}$ resonance yet reported.)\textsuperscript{83} However, for the series $[\text{CpFe(}CO\text{)}_2 L' ]^{PF_6}$ [$L' = \text{CO, CS, PPh}_3, \text{NH}_3$] the $^{13}\text{C}$ carbonyl
chemical shift implies that the $(\sigma + \pi)$-donor/$\pi$-acceptor ratio is slightly smaller for CO than for CS. This apparent anomaly is consistent with the crossover in relative electronic properties for CS and CO which was discussed in section II(ii).\textsuperscript{71}

The $^{13}$C thiocarbonyl chemical shifts in the series $[\text{CpFe(CS)L}_1\text{L}_2]^+$ ($L_1 = \text{CO}; \ L_2 = \text{CO}, \ P(C_6H_4F)_3, \ PPh_3, \ PCy_3$ and $L_1 = L_2 = \text{CNPh}$) were also found to be proportional to the electron density on the transition metal (as measured by the I.R. force constant of the CS ligand). The $^{13}$C CS chemical shifts follow the same trend as the $^{13}$C CO chemical shifts suggesting that the former is also a good measure of the relative $(\sigma + \pi)$-donor/$\pi$-acceptor properties of other ligands in the coordination sphere.\textsuperscript{68} The reported thiocarbonyl chemical shift data are recorded in Table 3. All the resonances occur at very low field values. The suggestion has been made that this would appear to indicate that a substantial positive charge is localised on the CS carbon atom.\textsuperscript{83} However, such a positive charge localisation would contradict the interpretations of the combined P.E. and M.O. study discussed in section II(iii).\textsuperscript{61} The authors of this later study have stated that it is unlikely that the CS chemical shift is due to any reasonable changes in charge at the carbon centre, but that instead, the shift can be accounted for by the mutual interactions of the CS $\pi$- and $\pi^*$-levels with the metal $\pi$-levels.

(v) **Mass Spectrometry**

Thiocarbonyl and selenocarbonyl complexes are usually compounds of low volatility which are not particularly suitable for mass
Table 3

$^{13}$C N.M.R. DATA FOR THIOCARBONYL COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{13}$C $^a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Bu}_4\text{N} \text{[trans-WI(CO)}_4 \text{(CS)}]$</td>
<td>-285.7 $^b, c$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{[Bu}_4\text{N} \text{[trans-WCl(CO)}_4 \text{(CS)}]$</td>
<td>-287.3 $^b, c$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{[Bu}_4\text{N} \text{[trans-WBr(CO)}_4 \text{(CS)}]$</td>
<td>-287.4 $^b, c$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{W(CO)}_5 \text{(CS)}$</td>
<td>-298.7 $^b, c$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{W(CO)}_3 \text{(CS) (diars)}$</td>
<td>-306.9 $^b, c$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{Cr(CO)}_5 \text{(CS)}$</td>
<td>-331.1 $^b, c$</td>
<td>41</td>
</tr>
<tr>
<td>$\text{[CpFe(CO)}_2 \text{(μ-CS)}]_2$</td>
<td>-287.6 $^b, c$</td>
<td>63</td>
</tr>
<tr>
<td>$\text{[CpFe(CO)}_2 \text{(CS)} \text{][PF}_6$</td>
<td>-307.9 $^d$</td>
<td>83</td>
</tr>
<tr>
<td>$\text{[CpFe(CO)} \text{(CS) (P[CH}_3\text{H}_4\text{F)}_3 \text{)][PF}_6$</td>
<td>-316.4 $^c, d$</td>
<td>68</td>
</tr>
<tr>
<td>$\text{[CpFe(CO)} \text{(CS) (PPH}_3 \text{)][PF}_6$</td>
<td>-317.4 $^c, d$</td>
<td>68</td>
</tr>
<tr>
<td>$\text{[CpFe(CO)} \text{(CS) (PCY}_3 \text{)][PF}_6$</td>
<td>-320.0 $^c, e$</td>
<td>68</td>
</tr>
<tr>
<td>$\text{[CpFe(CO)} \text{(CNPh)}_2 \text{][PF}_6$</td>
<td>-320.1 $^b, c$</td>
<td>68</td>
</tr>
<tr>
<td>$\text{CpMn(CO)}_2 \text{(CS)}$</td>
<td>-442.6 $^b, -442.9$ $^d$</td>
<td>83</td>
</tr>
</tbody>
</table>

$^a$ relative to TMS; $^b$ CDCl$_3$; $^c$ Cr(acac)$_3$ added;

$^d$ (CD$_3$)$_2$CO; $^e$ CD$_3$CN/CH$_2$Cl$_2$. 
spectroscopic studies. However, a considerable quantity of mass spectroscopic data has been accumulated, for the purposes of molecular weight determination and complex formulation, \(^8,31,36,41,77,78,85\) and mass spectral interpretation. These latter studies all support the existence of very strong M-CS and M-CSe bonds. For instance, the absence of the ions \([\text{CpMn(CO)}_2]^+\) and \([\text{CpMn(CO)}]^+\) from the mass spectrum of \(\text{CpMn(CO)}_2\) (CS) was taken to indicate that the dissociation of the CS ligand occurs after, rather than simultaneously with or before the dissociation of the CO ligands, and hence to imply that the Mn-CS bond is considerably stronger than the Mn-CO bond.\(^{70,81}\) The major mass spectral fragmentation pathways were assigned for \((\eta^5-\text{RC}_{5}H_4)\text{Mn(CO)}_2\) (CX) \([R = H, \text{Me}; \; X = S, 0]\) and an analysis of the dissociation energies of the various steps appeared to show that the M-CO bond is strengthened in the presence of the CS ligand. This observation was considered to conflict with interpretations of other data concerning \(\text{CpMn(CO)}_2\) (CS) which indicated the relative \(\pi\)-acidity order CS > CO. The suggestion was made that the reverse order might actually be correct.\(^{70}\) These apparently conflicting data have been reconciled by the crossover phenomenon \([\text{section II(ii)}]\). The mass spectral data actually apply to the cationic complex \([\text{CpMn(CO)}_2\) (CS)]\(^+\) for which the \(\pi\)-acceptor to \((\sigma + \pi)\)-donor ratio is presumably less for CS than for CO whereas the reverse is known to be correct for \(\text{CpMn(CO)}_2\) (CS).\(^{71}\)

(vi) Mössbauer Spectroscopy

The Mössbauer isomer shift values of the complexes \([\text{CpFe(CO)}_2L]^+\) were measured and the electron density on the iron atom was found to decrease with L in the order CS > CO > CN\(^-\) > PC\(_3\) > NO\(^-\) > NCS\(^-\) > Br\(^-\).\(^{86}\)
The increase of the donor strength and the increase of the \( \pi \)-acceptor ability of \( L \) both increase the electron density at the place of the iron nucleus, the former by increasing the \( s \) electron density, the latter by decreasing the \( d \) electron density, and through this, the shielding effect of the \( d \) electrons of iron. The higher electron densities at the iron nucleus in the complexes containing the stronger \( \pi \)-acceptor ligands were taken to indicate that, in these systems, the different \( \pi \)-acceptor ability of \( L \) seems to be the dominant factor which causes the changes in isomer shift values, and thus that the CS ligand is the most effective \( \pi \)-acid in the series. Andrews found that the \( \pi \)-acceptor to \((\sigma + \pi)\)-donor ratio is lower for CS than for CO in \([\text{CpFe(CO)}_2(\text{CS})]\)\(^+\) [section II(ii)] so that, in this complex, if CS is a stronger \( \pi \)-acid than CO, CS must also be a better donor than CO on an absolute scale.\(^7\) The Mössbauer evidence further suggests that \( \sigma \)-donation is much more important than \( \pi \)-donation for this complex, since \( \pi \)-donation would reverse the effect of \( \pi \)-acceptance on the isomer shift value.

In conclusion, physical data obtained on thiocarbonyl complexes supports a \( \sigma \)-donor/\( \pi \)-acceptor model for the bonding of the CS ligand to the metal centre. It might also be valid to assume that the filled \( \pi \)-orbitals of the CS ligand exert a more profound effect on the M-CS bond than do the corresponding carbonyl \( \pi \)-levels on the M-CO bond. Interpretations of physical data which attempt to assess the bonding properties of the CS ligand should deal with individual or at least closely related complexes. It is also worth stating the obvious fact that correlations of the bonding capacity of the CS ligand with those of the CO ligand are only valid in an absolute sense when the total
bonding capacity of the CO ligand is also considered. Thus to state that the $\pi$-acceptor to $(\sigma + \pi)$-donor ratio for CO is greater than for CS is not to imply that the CS ligand is not primarily a strong $\sigma$-donor and a strong $\pi$-acceptor. Early results indicate that the selenocarboxyl ligand interacts strongly with the metal and that this interaction is probably also derived from $\sigma$-donor and $\pi$-acceptor components.

(III) CHEMICAL REACTIVITY

There are several aspects of chemical reactivity which are worthy of detailed consideration in a review of this nature. On the one hand a reaction at the metal centre might generate a novel CS-or CSe-containing complex. Alternatively a ligand reaction at the CS or CSe group might form a new ligand entity or produce some ligand in a previously unrecognised manner. On the other hand some feature of chemical reactivity might disclose a property of the electronic distribution which can be attributed to the presence of the CS or CSe ligand. These aspects are better treated jointly rather than separately. The material in this section has been grouped according to the different types of reactions which occur at the metal centre or at the ligand.

A REACTIONS AT THE METAL CENTRE

(i) Substitution Reactions

The first communication in thiocarbonyl chemistry noted that $\text{trans-RhCl(CS)(PPh}_3\text{)_2}$ appeared to be inert towards displacement of CS by CO.$^{12}$ This initial observation has been found to be a general phenomenon
HYDRIDO-THIOCARBONYL COMPLEXES AS PRECURSORS OF LOW-VALENT THIOCARBONYL COMPLEXES

T.J. COLLINS and W.R. ROPER*
Department of Chemistry, University of Auckland, Auckland (New Zealand)

(Received July 27th, 1977)

Summary

The hydrido-thiocarbonyl osmium(II) complexes
\[ \text{OsH}_2(\text{CS})(\text{PPH}_3)_3^+, \text{OsHCl(CS)}(\text{PPH}_3)_3^+, \text{OsH(OClO}_3)(\text{CS})(\text{PPH}_3)_3^+, \]
\[ \text{OsHCl(CS)(CN)}(\text{PPH}_3)_2^+ \text{ and } [\text{OsH(CS)(CO)}(\text{PPH}_3)_3]^+, (R = p\text{-tolyl}), \]
have been derived from \[ \text{OsCl}_2(\text{CS})(\text{PPH}_3)_3 \text{ and } [\text{OsH(CS)(CO)}(\text{PPH}_3)_3]^+, \]
the latter can be deprotonated to give the zerovalent complex, \[ \text{Os(CS)(CO)}(\text{PPH}_3)_3. \]

The limited number of synthetic routes available for the preparation of thiocarbonyl complexes has restricted development of this area of chemistry and in particular compounds in which thiocarbonyl ligands occur in combination with hydrido-, alkyl-, or \(\sigma\)-bound aryl- ligands are rare or unknown. Exceptions are provided by [WH(CS)(CO)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+ which results from protonation of \[ \text{W(CS)(CO)}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2 \] and the iridium compounds \[ \text{IrH}_2(\text{CS})(\text{PPH}_3)_3 \text{ and } [\text{IrH}_2(\text{CS})(\text{CO})(\text{P(c-hexyl)}_3)_2]^+. \]
In order to explore the possibility of hydride migration to the thiocarbonyl ligand and also to develop synthetic routes to low-valent thiocarbonyl complexes, we have prepared and characterised various hydrido-thiocarbonyl complexes of osmium(II) and we describe these here.

Treatment of \[ \text{OsCl}_2(\text{PPH}_3)_3 \] with \[ \text{CS}_2 \] and excess \[ \text{PPH}_3 \]
in benzene under reflux affords \[ \text{OsCl}_2(\text{CS})(\text{PPH}_3)_3 \] in high yield (see Scheme). This reacts with \[ \text{NaOH} \] and 2-methoxyethanol under reflux to produce \[ \text{OsH}_2(\text{CS})(\text{PPH}_3)_3 \] which has the same stereochemistry as the well-known \[ \text{CO} \] analogue \[ \text{OsH}_2(\text{CO})(\text{PPH}_3)_3 \]
(see Table for I.R. and N.M.R. data). Reaction of this dihydride with strong acids results in cleavage of one hydride ligand and formation of \[ \text{OsHX(CS)}(\text{PPH}_3)_3 \]. One phosphine ligand in \[ \text{OsHX(CS)}(\text{PPH}_3)_3 \] is labile and readily displaced by other
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{\text{CO}}$(cm$^{-1}$)</th>
<th>$\nu_{\text{CS}}$(cm$^{-1}$)</th>
<th>$\nu_{\text{CN}}$(cm$^{-1}$)</th>
<th>$\nu_{\text{OsH}}$(cm$^{-1}$)</th>
<th>Chemical Shift ($\tau$)$_{\text{Os-H}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsCl$_2$(CS)(PPh$_3$)$_3$</td>
<td>1290</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsH$_2$(CS)(PPh$_3$)$_3$</td>
<td>1233</td>
<td></td>
<td></td>
<td>2070, 1895</td>
<td>d</td>
</tr>
<tr>
<td>OsHCl(CS)(PPh$_3$)$_3$</td>
<td>1280</td>
<td></td>
<td></td>
<td>2100</td>
<td>15.5, $^2J$(H-P $\text{trans}$), 93Hz; $^2J$(H-P $\text{cis}$), 24.5Hz.</td>
</tr>
<tr>
<td>OsH(OClO$_3$)(CS)(PPh$_3$)$_3$</td>
<td>1295</td>
<td></td>
<td></td>
<td>2070</td>
<td>15.2, $^2J$(H-P $\text{trans}$), 82Hz; $^2J$(H-P $\text{cis}$), 24.5Hz.</td>
</tr>
<tr>
<td>OsHCl(CS)(CN)(PPh$_3$)$_2$</td>
<td>1280</td>
<td></td>
<td></td>
<td>2150, 1955</td>
<td>12.75, $^2J$(H-P), 19Hz.</td>
</tr>
<tr>
<td>[OsH(CS)(CO)(PPh$_3$)$_3$]$^+$</td>
<td>2045</td>
<td></td>
<td></td>
<td>1310</td>
<td>17.9, $^2J$(H-P $\text{trans}$), 38Hz; $^2J$(H-P $\text{cis}$), 22Hz.</td>
</tr>
<tr>
<td>Os(CS)(CO)(PPh$_3$)$_3$</td>
<td>1890, 1870</td>
<td></td>
<td></td>
<td>1230</td>
<td></td>
</tr>
</tbody>
</table>

a) Satisfactory elemental analyses obtained for all compounds.  b) Measured as nujol mulls.  c) In CDCl$_3$ solution.  
d) $^1$H NMR spectrum typical of MH$_2$X(PPh$_3$)$_3$ with meridional phosphine ligands and $\text{cis}$ hydride ligands.
neutral ligands, e.g. CNR to give OSHX(CS)(CNR)(PPh₃)₂.

For X = ClO₄⁻, OSHX(CS)(PPh₃)₃ reacts with CO to provide a cationic hydrido-complex, [OSH(CS)(CO)(PPh₃)₃]ClO₄. This cation is an ideal precursor of a tris-phosphine-substituted zеровалент complex and is readily deprotonated to Os(CS)(CO)(PPh₃)₃ which is formed as red-brown crystals. This complex, with three bulky phosphine ligands can provide, through phosphine dissociation, the reactive, co-ordinatively unsaturated entity, Os(CS)(CO)(PPh₃)²⁺, and indeed reaction with C₂H₄ or PhC≡CPh leads to the adducts Os(C₂H₄)(CS)(CO)(PPh₃)₂ and Os(PhC≡CPh)(CS)(CO)(PPh₃)₂, respectively. The further chemistry of these and other zerовалent complexes and adducts is being studied.

References
and it has never been clearly demonstrated that any of the few reactions which appear to be CS substitution reactions proceed by simple associative or dissociative mechanisms. Thus the discussion of ligand substitution reactions for CS (and CSe) complexes largely concerns the substitution of other groups at the metal centre. The complex trans-RhCl(CS)(PPh₃)₂ reacts by chloride substitution with SCN⁻ to give trans-Rh(SCN)(CS)(PPh₃)₂.¹³

An early paper claimed that the supposedly doubly-chloro-bridged dimeric complex [RuCl₂(CS)(PPh₃)₂]₂ was cleaved by a variety of neutral monodentate or bidentate ligands to give octahedral complexes in high yields.¹⁵ The resulting derivatives were assigned the formulations RuCl₂(py)(CS)(PPh₃)₂, RuCl₂(phen)(CS)(PPh₃)₂, RuCl₂(CO)(CS)(PPh₃)₂ [two isomers suggested] and RuCl₂(bipy)(CS)(PPh₃)₂. It has since been shown that "[RuCl₂(CS)(PPh₃)₂]₂" is actually a mixture of compounds containing only 16% of the dimer as formulated.²³ The first two derivatives in the above list were satisfactorily characterised, but the others were poorly characterised and are probably also mixtures.

However, the genuine dimer [RuCl₂(CS)(PPh₃)₂]₂ is cleaved by M⁺Cl⁻/HCl (M⁺ = [Ph₄As]⁺, [Ph₃(PhCH₂)P]⁺, [Et₄N]⁺) to give the anionic complexes M[RuCl₃(CS)(PPh₃)₂].²³ The dimer is also cleaved by dimethylformamide to give RuCl₂(dmf)(CS)(PPh₃)₂ which reacts with methanol to yield RuCl₂(MeOH)(CS)(PPh₃)₂.²⁶

The thiocarbonyl analogue of Vaska's compound, IrCl(CS)(PPh₃)₂,¹⁹ has been used as the starting material for a series of ligand substitution reactions which are summarised in Scheme 4.⁸⁷ Complex ¹⁹ undergoes phosphine substitutions with tricyclohexylphosphine to produce ²₀,
or phosphine and chloro substitution with 1,2-diphenylphosphinoethane or methyldiphenylphosphine to afford the coordinatively saturated cations 21 and 22. Treatment of 19 or 20 with CO in CHCl₃ affords the five-coordinate cationic complexes 23. The five-coordinate hydrido-containing complex 24 is produced by treating an ethanolic suspension of 19 with sodium borohydride in the presence of excess triphenylphosphine.¹⁴

The ligand substitution reactions of CpMn(CO)₂(CS) and the derivatives of this complex are described in Scheme 5. The photolytic reactions of 25 with a large number of monodentate and polydentate Group Vb donor ligands lead to the successive substitution of the carbonyl ligands forming the derivatives 26 to 31. The thermal reaction between
CpMn(CO)$_2$(CS) and NO$^+$SbF$_6^-$ in acetonitrile gives the cations 32, which react thermally with EPH$_3$ [E = As, Sb] to yield the cationic complexes 33a, 69 or with $I^-$ to form CpMn(CO)(CS)I. 76 If NO$_2^+$PF$_6^-$ is used as the nitrosylating reagent to produce 32 then some loss of CS is observed and this is postulated to occur via oxygen transfer to CS followed by elimination of OCS. 69 The yields for the reactions depicted vary from poor to good; the photolysis reactions are often accompanied by some decomposition.

Scheme 5

(i) $L = P$Cy$_3$, PMe$_2$Ph, PPh$_3$, AsPh$_3$, SbPh$_3$, P(OEt)$_3$, P(OMe)$_3$, P(OCH$_2$CH$_2$Cl)$_3$, P(OPh)$_3$; (ii) $L = PMe_2$Ph, PPh$_3$, P(OEt)$_3$, P(OMe)$_3$, P(OCH$_2$CH$_2$Cl)$_3$, P(OPh)$_3$; (iii) complex and derivatives formed as a mixture of diastereomers which were all separated except for the phosphine oxide complex; (iv) Methylcyclpentadienyl analogues also prepared 69; (v) thermally produced $\eta^5$-MeC$_5$H$_4$ analogues also prepared but not purified, $L = P$Ph$_3$, AsPh$_3$, SbPh$_3$; (vi) 31, 88; (vii) 31; (viii) 31, 89; (ix) 76.
It could be argued that the reactions in equation 17 might be more aptly described as oxidative addition and reductive elimination processes (or adduct formation and separation) rather than as ligand substitution reactions. While this descriptive inaccuracy is acknowledged the reactions are included in this section as the alkene complex is an intermediate in what is overall a ligand substitution process.

That CO is always lost preferentially to CS in these reactions has been generally accepted as evidence that the Mn-CS bond is stronger than the Mn-CO bond. Kinetic data were obtained for the replacement of cis-cyclo-octene in CpMn(CO)(CX)(C\textsubscript{8}H\textsubscript{14}) to form CpMn(CO)(CX)(PPh\textsubscript{3}) [X = O, S]. The observed reaction rates were found to be first order in substrate and independent of the concentration of PPh\textsubscript{3}, suggesting a mechanism in which the dissociation of the olefin is the rate-determining step. An increased lability of the olefin in the CS complex was reported as further evidence that CS is a better π-acceptor than CO. This rationalisation is now understood not to apply in a general sense to all thiocarbonyl complexes.

The photochemical reaction of CpRe(CO)\textsubscript{2}(CS) with PPh\textsubscript{3} affords CpRe(CO)(CS)(PPh\textsubscript{3}) in 12% yield.

The ligand substitution reactions which emanate from the complex W(CO)\textsubscript{5}(CS) are summarised in Scheme 6. Substitution reactions of this substrate, as well as generally adding weight to the contention
Scheme 6 (ref. 41 unless otherwise stated)

(i) $L = \text{PPh}_3^{13}CO, \text{CNCy}^{60}; \ X = \text{CF}_3\text{SO}_3, \text{BF}_4; \ (ii) \ L = \text{CO}^{91};$

(iii) dioxane/heat; $L = \text{P}(_6\text{H}_4\text{Cl})_3$; (iv) heat; (v) xylene/L/heat;

$L = \text{PPh}_3; \ (vi) \ X = \text{Cl,Br}; \ in \ \text{THF}; \ (vii) \ \text{xylene, 135}^\circ\text{C}; \ (viii) \ L-L=$ bipy, phen; thermal reaction; (ix) xylene, $110^\circ\text{C}; \ (x) \ extended \ heating;

(xi) xylene, $135^\circ\text{C}; \ (xii) \ 195^\circ\text{C}; \ (xiii) \ 91.$
that the M-CS bond is stronger than the M-CO bond, have provided further valuable information concerning the relative electronic properties of the CO and CS ligands. This additional information has been obtained from interpretations of product distributions and from kinetic studies. There are two separate environments for the carbonyl ligands in W(CO)$_5$(CS); trans or cis to the CS ligand. Preferential substitution in the trans position has been taken as evidence that the CS ligand is more strongly trans-labelling than the CO ligand. The importance of any observed preferential substitution in the one trans position is amplified as there are four equivalent cis positions, and analysis by $^{13}$C N.M.R. of equilibrium mixtures of W(CO)$_4$(CS)L [L = phosphine, phosphite, isocyanide] showed that the cis/trans ratio is always considerably less than 4. The speculation was made that the preference of these complexes for a trans geometry could originate from the greater π-acceptor capability of CS as compared to CO (in these complexes$^{71}$), or perhaps a steric difference between CS and CO.$^{40,41}$ The reaction of [trans-WI(CO)$_4$(CS)]$^-$ with silver salts and $^{13}$C labelled CO (or other ligands, see Scheme 6) to produce specifically labelled trans-W(CO)$_4$(CO)$_3$(CS) was discussed and compared with the analogous reactions of [cis-WX(CO)$_4$L]$^-$ [L = CNCy, X = Cl; L = P(C$_6$H$_4$Cl)$_3$, X = I] which give almost exclusively cis-W(CO)$_4$(CO)$_3$L. Detailed consideration was given to possible mechanisms which account for the retention of configuration.$^{91}$

Several detailed kinetic studies have highlighted the effect of the CS ligand on substitution reactions in this system. Comparative investigations of the reactions of W(CO)$_6$ and $^{34}$ with PPh$_3$ in decalin
solution showed that the CS ligand activates the complex towards carbonyl substitution. The rate equation contains both a dissociative and associative term, the former pathway being ca. 75 times faster and the latter ca. 250 times faster for 34. Similarly, CO substitution in 34 by $I^-$, which occurs only in the trans site at mild temperatures, is more than 1000 times faster than the analogous reaction for W(CO)$_6$, but is solely an associative process. Notably the labelled trans carbonyl is lost with high specificity in the reaction of trans-W(CO)$_4$(CO)(CS) with $I^-$. Speculative mechanisms, both of which emphasise the strong π-acid character of the CS ligand, were postulated to account for this specificity. One involves attack by the $I^-$ ion at the metal atom accompanied by simultaneous loss of the trans carbonyl. The second involves attack by the $I^-$ ion at the C-atom of the trans carbonyl followed by rearrangement and loss of the trans CO.

A high preference for trans dissociation over cis dissociation in 34 was observed by following ligand exchange reactions with labelled $^{13}$CO in the gas phase. The trans CO exchanges at least 20 times faster than the cis CO. This result shows that, in this complex, CS has a substantially greater trans-effect than CO. The isomerisation of trans-W(CO)$_4$(CO)(CS) was studied in decalin solution and the activation parameters $\Delta H^\dagger = 31.5 \pm 1.9$ kcal mol$^{-1}$ and $\Delta S^\dagger = 9.1 \pm 5$ cal K$^{-1}$ mol$^{-1}$ were calculated from the rate constants. These compare with the values $\Delta H^\dagger = 31.5 \pm 1$ kcal mol$^{-1}$ and $\Delta S^\dagger = 3.1 \pm 3$ cal K$^{-1}$ mol$^{-1}$ for the dissociative substitution process in the reaction involving PPh$_3$. The close agreement of these values suggested that the isomerisation and dissociation processes are closely linked. The possibility that
isomerisation might be fortuitously identical to dissociation (i.e. simple rate-determining dissociation followed by isomerisation and recoordination of the solvent trapped molecule) was considered. However, that the two processes are actually different was demonstrated by studying the gas phase isomerisation of trans-W(CO)$_4$(\textsuperscript{13}CO)(CS) (where no solvent is present). This investigation showed that the rate constants of the two reactions are in the order $k_f$ (isomerisation) > $k_{trans}$ (dissociation).\textsuperscript{91}

The photochemistry and photoisomerisation of M(CO)$_5$(CS) and M(CO)$_4$(CS) [M = Cr, W] were studied in low temperature matrices and found to mirror similar studies based on M(CO)$_6$. The five-coordinate complexes M(CO)$_4$(CS) are produced from M(CO)$_5$(CS) by U.V. irradiation. On the basis of I.R. evidence the five-coordinate complexes were assigned square pyramidal geometries, and two isomers, one with an apical CS ligand and one with a basal CS ligand, were detected. It was concluded that in many of the reactions studied the CS ligand behaves merely as a labelled CO group (a surprising result) allowing otherwise unobservable processes to be investigated.\textsuperscript{92} This "labelling" was then used to examine the photolysis of \textsuperscript{34} which was shown to proceed in two stages; loss of CO, followed by an excited state rearrangement of the photoproduct.\textsuperscript{93}

There are reactions depicted in scheme 6 where loss of CS is observed. Thus the reaction of \textsuperscript{34} with pyridine affords considerable quantities of W(CO)$_5$(py) and the reactions with 2,2'-bipyridine and o-phenanthroline yielded no thiocarbonyl-containing products.\textsuperscript{41} The mechanisms of these reactions have not been elucidated, but since \textsuperscript{34} has
been observed to undergo thiocarbonyl ligand reactions with nitrogen donors [section III B(i)] the implication is strong that the reactions do not follow simple associative or disassociative substitution pathways.

Several of the above reactions have also been investigated for the chromium analogue Cr(CO)$_5$(CS). These include the formation of a mixture of cis- and trans-Cr(CO)$_4$(CS)(PPh$_3$)$_2$, Cr(CO)$_3$(CS)(PPh$_3$)$_2$ (in spectroscopic quantities for both Cr and W complexes) and Cr(CO)$_3$(CS)(diphos) (but Cr(CO)(CS)(diphos)$_2$ could not be obtained). No ligand substitution reactions of Mo(CO)$_5$(CS) have been reported.

A number of photolytic ligand substitution reactions of the substrates $(n^6$-RR'C$_6$H$_4$)Cr(CO)$_2$(CS) and $(n^6$-RC$_6$H$_5$)Cr(CO)$_2$(CSe) have been described (equations 18, 19). The synthesis of Cr(CO)$_5$(CS) by the method of equation 19 gives substantially higher yields than does the reductive fragmentation

\[ \text{U.V. light} \]

\[
\begin{array}{ccc}
\text{R}_1 & \text{Cr} & \text{CS} \\
\text{R}_2 & \text{CO} & \text{CO} \\
\hline
\end{array}
\]

\[
\begin{array}{ccc}
\text{R}_1 & \text{Cr} & \text{L} \\
\text{R}_2 & \text{CO} & \text{CS} \\
\hline
\end{array}
\]

(18)

\[
\begin{align*}
R_1 &= \text{CO}_2\text{Me}, \quad R_2 = \text{H}; \quad L = \text{PMe}_2\text{Ph}, \quad \text{P(OEt)}_3^{38a,c}, \quad \text{PPh}_3^{36} \\
R_1 &= \text{CO}_2\text{Me}, \quad R_2 = \text{Me}; \quad L = \text{P(OEt)}_3^{38b,c}, \quad \text{P(OPh)}_3^{75}
\end{align*}
\]
of thiophosgene with reduced chromium carbonyl anions [section I(iii)]
(30-50% based on Cr(CO)$_6$, which is the starting material for both
syntheses, compared with ca. 5%). The first examples of resolved
enantiomeric chromium(0), the enantiomers of ($^6$-Me$_2$C$_6$H$_4$)Cr(CO)(CS)-
[(P(OPh)$_3$], where produced in a reaction sequence which was dependent
upon the finding that the Cr-CS bond is stronger than the Cr-CO
bond. 75

The complex mer-cis-RuCl$_2$(CO)$_3$(CS)$_35$ (figure 6) is reported to
react with PPh$_3$ to give RuCl$_2$(CO)$_2$(CS)(PPh$_3$)$_36$ (suggested geometry
depicted in figure 6), and with the bidentate ligands Ph$_2$ECH$_2$CH$_2$EP Ph$_2$

![Chemical structures](image-url)
[E = P, As] to give a mixture of at least two products from which only 
[RuCl(CO)$_2$(CS)(PH$_2$AsCH$_2$CH$_2$AsPH$_2$)]BPH$_4$ could be isolated in a pure form. 44 The CSe complex RuI$_2$(CO)(CSe)(PPh$_3$)$_2$ was observed to undergo iodide substitution when chromatographed on alumina to give RuI(OH)(CO)(CSe)(PPh$_3$)$_2$. 49

A number of ligand substitution reactions derived from the precursor complex OsCl$_2$(CS)(PPh$_3$)$_3$ have been communicated (Scheme 7). 29

Scheme 7 (L = PPh$_3$; R = p-tolyl; ref.29 unless otherwise stated.)

(i) NaOH in 2-methoxyethanol; (ii) 95.

These reactions all proceed in high yield and, notably, CS loss is not observed.

The cationic complex [CpFe(CO)$_2$(CS)]$^+$ reacts with Group VB donor ligands to give substitution products of the CO group according to equation 20, and with a tenfold excess of phenyl isocyanide

[CpFe(CO)$_2$(CS)]PF$_6$ + L → [CpFe(CO)(CS)L]PF$_6$ + CO  (20)

[L = PCY$_3$, PPh$_3$, P(C$_6$H$_4$F)$_3$, P(C$_6$H$_4$OCH$_3$)$_3$,AsPh$_3$, SbPh$_3$]

[CpFe(CO)$_2$(CS)]PF$_6$ + 2CNPh → [CpFe(CNPh)$_2$(CS)]PF$_6$ + 2CO  (21)

according to equation 21. 68
(ii) Oxidative Addition and Redox Reactions

Oxidative addition reactions provide for considerable synthetic versatility by enabling the incorporation of a large number of ligand entities into the coordination sphere. It is also well accepted that such reactions normally provide information concerning the basicity of the transition metal centre, which is derived from the nature of the metal centre and the coordinated ligands, and/or, information concerning steric effects in the complex. This latter facet is often very difficult to separate from electronic effects. Considering the importance of oxidative addition and the reverse process, reductive elimination, it is apparent that such reactions of low valent CS and CSe complexes form a most conspicuous area that remains to be further explored.

As already noted in section II trans-RhCl(CS)(PPh₃)₂ failed to add HCl. Because the carbonyl analogue does so react, it was suggested that π-backbonding to the CS ligand causes lowering of the non-bonded electron density more than does the CO ligand in this system.¹² The lower basicity of the low valent thiocarbonyl complexes, which typically undergo oxidative addition reactions, compared to the carbonyl analogues has been found to be a general phenomenon (see below) and adds credence to the crossover phenomenon⁷¹ [section II(ii)] which predicts a π-acceptor to (σ + π)-donor ratio which is greater for CS than for CO in very basic metal complexes. The complexes trans-RhX(CS)(PPh₃)₂ [X = Cl,Br] do, however, undergo oxidative addition reactions with X₂ to give RhX₃(CS)(PPh₃)₂¹³ and with tetracyanoethylene to give RhX(TCNE)(CS)(PPh₃)₂.⁹⁶
The cations \([\text{Ir(CO)}_3 L_2]^+\) \([L = \text{PPh}_3, \text{PCy}_3]\) easily and reversibly add dihydrogen but, of the CS analogues, only the more basic \([\text{Ir(CO)}_2 \text{(CS)} (\text{PCy}_3)_2]^+\) was found to react giving \([\text{IrH}_2 (\text{CO}) (\text{CS}) (\text{PCy}_3)_2]^+\). The dideuterido complex \([\text{IrD}_2 \text{(CO)} (\text{CS}) (\text{PCy}_3)_2]^+\) was also formed and deuterium exchange reactions with the dihydrido complex gave no evidence of mixed hydrido/deuterido complexes which, when compared with kinetic studies for the carbonyl analogue, suggested that reductive elimination from the substrate is the rate-determining step. Carbon monoxide also replaces dihydrogen in \([\text{IrH}_2 (\text{CO}) (\text{CS}) (\text{PCy}_3)_2]^+\) more readily than in any of the cations \([\text{IrH}_2 (\text{CO})_2 L_2]^+\) \([L = \text{tertiary phosphine or arsine}\)]. Furthermore, neither CS cation forms an adduct with dimethylacetylene dicarboxylate (A), though the tricarbonyl cations were found to give \([\text{Ir(A)(CO)}_2 L_2]^+\) at room temperature.\(^{87}\)

The complex \(\text{trans-IrCl(CS)(PPh}_3)_2\) \(^{19}\), which also does not add molecular hydrogen (at 25°C, 1 atm) reportedly forms 1:1 adducts with CO and SO\(_2\), the former being unstable in the solid state.\(^{14}\) Both \(^{19}\) and \(\text{trans-IrCl(CS)(PCy}_3)_2\) react with NO\(^+\)BF\(_4^-\) to give the five-coordinate cationic iridium(III) complexes \([\text{IrCl(NO)(CS)L}_2]^+\).\(^{87}\) The Lewis acidity of the olefins \((\text{NC})_2\text{C}==\text{C(}\text{CN})_2\), \((\text{NC})\text{HC}==\text{CH(CN)}\) and \((\text{NC})\text{HC}==\text{CH}_2\) decreases as the cyano groups are replaced by hydrogen. When reacted with \(^{19}\) stable adducts were formed only for the first two whereas all three react with \(\text{trans-IrCl(CO)(PPh}_3)_2\). Unstable adducts were formed between \(^{19}\) and BX\(_3\) \([X = \text{Cl, Br}\)] and oxidative addition was found to occur with anhydrous HCl in benzene to give \(\text{IrHCl}_2 (\text{CS})(\text{PPh}_3)_2\).\(^{79}\)

The tungsten complexes \(\text{W(CO)}_5 (\text{CS}), \text{W(CO)}_4 (\text{CS})(\text{PPh}_3)\) and \(\text{W(CO)}_3 (\text{CS})(\text{diphos})\) were found not to react with a variety of Lewis acids including some or all of BF\(_3\), B\(_2\)H\(_6\), HgCl\(_2\), \([\text{Et}_3\text{O}]\text{BF}_4\).
The complex \( W(CO)_{5}(CS) \) is, however, oxidised by \( Br_2 \) to give a complex presumed to have the formula \( WBr_2(CO)_3(CS) \), which was not isolated but which, on treatment with \( PPh_3 \), yielded the substituted complex \( WBr_2(CO)_2(CS)(PPh_3)_2 \). If \( WBr_2(CO)_3(CS) \) was treated instead with the very bulky phosphine \( P(\sigma-MeC_6H_4)_3 \), then the complex \( [(\sigma-MeC_6H_4)_3PH][WBr_3(CO)_3(CS)] \) was isolated in 45% yield.

The reaction of \( W(CO)_3(CS)(diphos) \) with iodine afforded a complex which was difficult to characterise, but which was tentatively formulated as \( WI_2(CO)_2(CS)(diphos) \). The reaction of \( W(CO)(CS)(diphos)_2 \) with \( I_2 \) also leads to the formation of \( WI_2(CO)(CS)(diphos)_2 \). It was suggested that this reaction occurs by decomposition of the intermediate complex \( [WI(CO)(CS)(diphos)_2]I_3 \), which was isolated and characterised. The action of strong protic acids on \( W(CO)(CS)(diphos)_2 \) leads to formation of a cationic tungsten hydrido complex (equation 22). For all these reactions the behaviour of \( W(CO)(CS)(diphos)_2 + CF_3SO_3H + [WH(CO)(CS)(diphos)_2]CP_3SO_3 \) the corresponding carbonyl complexes were described and peculiar differences in reactivity were noted. 97,98

The zerovalent osmium complex \( Os(CO)(CS)(PPh_3)_3 \) was found to react, through phosphine dissociation and generation of the reactive coordinatively unsaturated entity \( Os(CO)(CS)(PPh_3)_2 \), with the unsaturated molecules \( CS_2, C_2H_4 \) and \( PhC\equivCPh \), leading to the adducts \( Os(\eta^2-CS_2)(CO)(CS)(PPh_3)_2, Os(\eta^2-C_2H_4)(CO)(CS)(PPh_3)_2 \) and \( Os(\eta^2-PhC\equivCPh)(CO)(CS)(PPh_3)_2 \). The further reactions of \( Os(\eta^2-CS_2)(CO)-(CS)(PPh_3)_2 \) to give the dithiocarbonyl complexes \( OsX_2(CS)_2(PPh_3)_2 \) were described in section I(iv).

The thiocarbonyl-bridged dimeric complexes \( cis- \) and \( trans- \)
\[(\text{CpM(CO)(CS)})_2\quad [\text{M} = \text{Fe}^{63}, \text{Ru}^{77}]\) and the dinuclear thiocarbonyl-bridged complexes \textit{cis}- and \textit{trans}-Cp\textsubscript{2}Ru\textsubscript{2}(CO)\textsubscript{3}(CS)\textsuperscript{77} (figure 7) were produced by sodium hydride reduction of the cations \([\text{CpM(CO)}_2(\text{CS})]^+\). (The dinuclear bridging-CS complexes \textit{cis}- and \textit{trans}-Cp\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{3}(CS) have been reportedly formed from the reaction of \([\text{CpFe(CO)}_2]^-\) with \((\text{PhO})_2\text{CS}\textsuperscript{77}.\) The CS-bridged dimers \textit{cis}- and \textit{trans}-[\text{CpMn(NO)(CS)}]_2 were formed by the zinc reduction of CpMnI(NO)(CS) in diglyme but the isomers could not be separated\textsuperscript{76}. An unusual one electron oxidation occurs when the triply-chloro-bridged dinuclear complex \((\text{Ph}_3\text{P})_2\text{ClRuCl}_3\text{Ru(CS)(PPh}_3)_2\) is stirred in acetone containing HCl to yield the paramagnetic dinuclear \((\text{Ph}_3\text{P})\text{Cl}_2\text{RuCl}_3\text{Ru(CS)(PPh}_3)_2\) which contains both a ruthenium(II) and a ruthenium(III) centre\textsuperscript{23}.

\[\text{cis-isomer}\quad \text{trans-isomer}\]

Figure 7
B LIGAND REACTIONS

The examination of the different types of CS ligand reactivity provides considerable scope to observe, to test and to further attempt to explain some of the elementary paradigms of periodicity which guide the thinking of practical chemists. For instance, one can observe an increased propensity for the CS compared to the CO ligand to undergo reactions which decrease the multiplicity of the C-X [X = O, S] bond. This mirrors the decrease in the tendency to form multiple bonds down any group of the periodic table. The softness of the C-X ligand should increase with the atomic number of X and this trend can be discerned in some aspects of CS ligand reactivity. The synthetic flexibility of the CS ligand is consequently greater than that of the CO ligand. Mechanistic ideas concerning the charge (or frontier orbital) control of chemical reactions are closely related to these observed patterns and to bonding models.

The documented ligand reactions of thiocarbonyl complexes can be classified into the following groups:

(i) Nucleophilic attack at the CS carbon atom;
(ii) Electrophilic attack at the CS sulphur atom;
(iii) Migratory insertion reactions;
(iv) Intramolecular isomerisation reactions involving bridged CS ligands;
(v) Miscellaneous reactions of other than the CS ligand.

No ligand reactions of the CSe group have been reported.

(i) Nucleophilic Attack at the CS Carbon Atom

The first ligand reactions of the CS entity were reported for
Each reaction was postulated to occur via attack of the incoming nucleophile at the CS carbon atom to give an intermediate species, which then decomposes to give the observed product. If \( [\text{CpFe(CO)}_2\{\text{CS}\}]^+ \) is treated with methoxide in nondried methanol then a mixture of the thiocarboxylate complex \( [\text{CpFe(CO)}_2\{\text{CS}\}]^+ \) and the carboxylate complex \( \text{CpFe[COOMe]} \) (CO) (CS), formed by methoxide attack at the carbon atom of the carbonyl ligand, is produced. The reactions of some or all of the nucleophiles \( N_3^- \), \( \text{OR}^- \), or \( \text{NH}_2\text{NH}_2^- \) with the substituted cations \( [\text{CpFe(CO)}_2\{\text{CS}\}L]^+ \) \( [L = \text{PPPh}_3, \text{PCy}_3, \text{P(C}_6\text{H}_4\text{F}_3] \) were found to proceed in a similar manner, but reactions with primary amines afforded isocyanide complexes (equation 23). Isocyanide complexes were detected as further products of the reaction of primary amines with \( [\text{CpFe(CO)}_2\{\text{CS}\}]^+ \) in this latter work. Whereas attack occurs solely at the isocyanide carbon atom when \( [\text{CpFe(CNMe)}_2\{\text{CO}\}]^+ \) is treated with methylvamine, reaction of \( [\text{CpFe(CNPH)}_2\{\text{CS}\}]^+ \) with \( \text{C}_6\text{H}_{11}\text{NH}_2 \) also gives rise to attack at the CS carbon atom. Thus the CS ligand in these
systems is significantly more susceptible to attack at the carbon atom by electron-rich molecules than is the carbonyl ligand in the same or analogous carbonyl-containing complex. The ruthenium complex \([\text{CpRu(CO)}_2(\text{CS})]^{+}\) reacts with \(\text{N}_3^-\) and \(\text{N}_2\text{H}_4\) to give \(\text{CpRu(CO)}_2(\text{NCS})\) and with \(\text{NCO}^-\) to yield \(\text{CpRu(CO)}_2(\text{CN})\).\(^{77}\) However, when \([\text{Ir(CO)}_2(\text{CS})(\text{PPh}_3)_2]^{+}\) was treated with a stoichiometric quantity of \(\text{NaOMe}\) in methanol \(\text{Ir}[\text{C(O)OMe}](\text{CO})(\text{CS})(\text{PPh}_3)_2\) was the only isolated product \(\left(47\%ight)\).\(^{87}\)

The platinum(II) thiocarbonyl complex \([\text{PtCl(CS)(PPh}_3)_2]^{+}\)\(^{40}\) was found to be so reactive towards nucleophiles that a satisfactory elemental analysis could not be obtained.\(^{42,43}\) The complex was characterised by further reactions with electron-rich molecules (equations 24). If a solution of \(40\) was allowed to stand under an air atmosphere at 25°C for 1 to 2 days, then air stable yellow crystals could be isolated and an X-ray crystal structure showed these to be the metallo-dithiocarboxylate complex \(41\) (figure 8). The mechanism shown in

\[
\begin{align*}
\text{MeOH} & \rightarrow \text{PtCl[C(S)OMe](PPh}_3)_2 + \text{H}^+ \\
[\text{PtCl(CS)(PPh}_3)_2]^{+} \rightarrow \text{PtCl[C(S)NMe}_2](PPh}_3)_2 + \text{H}^+ \\
\text{H}_2\text{O} & \rightarrow [\text{PtCl(CO)(PPh}_3)_2]^{+} + \text{H}_2\text{S}
\end{align*}
\]

atmosphere at 25°C for 1 to 2 days, then air stable yellow crystals could be isolated and an X-ray crystal structure showed these to be the metallo-dithiocarboxylate complex \(41\) (figure 8). The mechanism shown in equation 25 was postulated to explain the formation of this unusual complex.\(^{43}\)
\[
\text{[PtCl} \text{(CS)}_2 \text{(PPh}_3 \text{)}_2 \text{]}^+ + \text{H}_2\text{S} \longrightarrow \text{(PPh}_3 \text{)}_2\text{ClPt(CS}_2 \text{)}^-
\]

\[
\text{(PPh}_3 \text{)}_2\text{ClPt(CS}_2 \text{)}^- + \text{[PtCl} \text{(CO)} \text{(PPh}_3 \text{)}_2 \text{]}^+ \longrightarrow \text{[PPh}_3 \text{)}_2\text{ClPt} \text{CS}_2 \text{Pt(PPh}_3 \text{)}_2 \text{]}^+ + \text{Cl}^- + \text{CO}
\]

(25)

The neutral thiocarbonyl complex W(CO)\textsubscript{5}(CS) \textsubscript{34} reacts with primary amines to afford the corresponding isocyanide complexes W(CO)\textsubscript{5}(CNR) \[R = \text{Me, } \text{C}_6\text{H}_{11}, \text{CH}_2\text{CO}_2\text{Me, } \text{nBu, } \text{tBu, } \text{CH}_2\text{Ph}\] in high yields. The chromium and molybdenum analogues behave similarly. The reaction of \textsubscript{34} with secondary amines gave complexes which were initially formulated as tertiary carbene complexes \textsuperscript{46} but which have since been shown to be thioformamidamido-containing complexes W(CO)\textsubscript{5}(SCHNR\textsubscript{2}) \[R = \text{Me; } R_2 = \text{CH}_2(\text{CH}_2\text{)}_2\text{CH}_2\]. \textsuperscript{101} Kinetic studies showed a second order dependence in amine concentration and it was suggested that the rate-determining step for isocyanide formation involves the addition of a hydrogen bonded amine to the CS carbon atom (Scheme 9). Complex \textsubscript{34} was found to react with two equivalents of a secondary amine producing unstable intermediates which then decompose slowly to give the thioformamidamido complexes. The process represented in equation 26 was suggested to explain the nature of the intermediate complexes. The phosphine substituted analogues of \textsubscript{34},
(CO)$_5$W + B → (CO)$_5$W + B → (CO)$_5$W + B → (CO)$_5$W C + B SH S^- HB^+ (26)

cis- and trans-W(CO)$_4$(CS)(PPh$_3$)$_2$, react much more slowly (the trans isomer much less rapidly than the cis isomer) and this was presumed to be due to an increased electron density at the CS ligand. As has been detailed in section II(iii) these reactions are now considered to be frontier orbital controlled. However, a number of weaker nucleophiles including H$_2$O, alcohols, N$_2$H$_4$, aniline, NH$_3$, CH$_3$SH and Ph$_3$PO do not react with 34 which suggests that the nucleophilic description is more informative than the "lumophilic" description [section II(iii)]. Stronger nucleophiles such as CH$_3$Li, R$_2$NLi and OR$^-$ appear to add to the CS ligand in 34 but the reactions are not straightforward. The addition of CH$_3$Li to 34 followed by [(CH$_3$)$_3$O]PF$_6$ gave several products in low yields of which W(CO)$_5$[S(CH$_3$)$_2$] was isolated and characterised. Azide ion reacts rapidly with 34 leading to the clean formation of [W(CO)$_5$(NCS)]$^-$ 101 The neutral complexes RuCl$_2$(CO)$_2$(CS)L [L = CO, PPh$_3$] also react with primary amines RNH$_2$ [R = C$_6$H$_5$, C$_6$H$_4$Me, C$_6$H$_4$OMe, C$_6$H$_5$] to afford isocyanide complexes, RuCl$_2$(CO)$_2$(CNR)L 144

The iridium CS cation [IrCl$_2$(CO)(CS)(PPh$_3$)$_2$]$^+$ and the osmium dithiocarbonyl cation [Os($^2$S$_2$CNEt$_2$)(CS)$_2$(PPh$_3$)$_2$]$^+$ react with borohydride to give the thioformyl complexes IrCl$_2$(CHS)(CO)(PPh$_3$)$_2$ and Os($^2$S$_2$CNEt$_2$)(CHS)(PPh$_3$)$_2$ (equation 27). Upon reaction with borohydride the bidentate thiocarboxamido-containing complex 42 forms, by an
interligand reaction, the novel four-membered metalloccyclic complex 43 (equations 28). This latter complex has been the subject of an X-ray crystal structure analysis. The nucleophilicity of the sulphur atom of a monohapto-thiocarboxamido complex is well documented so that this reaction can be described as nucleophilic condensation at the CS carbon atom. It is interesting that the analogous monohapto-dithioester complex \( \text{Os}[\eta^1-\text{C(S)SMe}]\text{H(CO)}(\text{CS})(\text{PPh}_3)_2 \) does not undergo this reaction, further reflecting the lower nucleophilicity of the unmethylated sulphur atom in \(-\text{C(S)SR}\) as compared with \(-\text{C(S)NR}_2\).  

(ii) Electrophilic Attack at the CS Sulphur Atom

The CS ligand has been found to be capable of developing a more substantial negative charge on the sulphur atom than can the CO ligand develop on the oxygen atom in some strongly basic mixed carbonyl–thiocarbonyl tungsten complexes. Thus the complex \( \text{W(CO)}(\text{CS})(\text{diphos})_2 \), when treated with the Lewis acids \( \text{HgX}_2, \text{AgBF}_4, \text{W(CO)}_5(\text{acetone}), \text{CH}_3\text{OSO}_2\text{F} \) or \([\text{CH}_3\text{CH}_2]_3\text{BF}_4\), reacts by electrophilic attack at the thiocarbonyl sulphur atom to give,
respectively, the end-to-end bridging thiocarbonyl complexes
W(CO)(diphos)$_2$(CSHgX)$_2$, [{W(CO)(diphos)$_2$(CS)}$_2$Ag]BF$_4$ and
(diphos)$_2$(CO)WCSW(CO)$_5$, and the thiocarbonyl complexes

Sulphur dioxide is also absorbed reversibly by W(CO)(CS)(diphos)$_2$
and I.R. evidence suggests that this Lewis acid also coordinates to
the CS sulphur atom, although attempts to trap the SO$_2$ adduct with
CH$_3$OSO$_2$F failed. The anionic CS complex [Bu$_4$N][WI(CO)$_4$(CS)] is
alkylated at sulphur by CH$_3$OSO$_2$F and [(CH$_3$CH$_2$)$_3$O]BF$_4$ to afford
WI(CO)$_4$(CSR) products, and is acylated by carboxylic acid anhydrides
to give WI(CO)$_4$[CSC(O)R] [R = CH$_3$, CF$_3$]. Formation of the end-to-end
bridging and acylated CS complexes is reversible. By contrast the
corresponding metal carbonyl complexes do not react at the oxygen
atoms of the carbonyl ligands with these substrates. This increased
nucleophilicity at the sulphur atom is in keeping with the marked
π-acceptor capacity of the CS ligand in these complexes. The
formation of the end-to-end bridged CS complexes reflects the softer
character of the CS sulphur atom in relation to the CO oxygen atom.
Stable oxygen-bonded adducts of carbonyl complexes characteristically
occur with hard acids containing trivalent aluminium, gallium and
lanthanides, or divalent magnesium (although an adduct of divalent
cobalt has also been proposed). The importance of π-back-donation,
which increases the electron density on the sulphur atom, is evidenced
by the fact that, in this system, only complexes with a ν$_{CS}$ value
below 1200 cm$^{-1}$ undergo electrophilic reactions at the sulphur atom.
An end-to-end bridging thiocarbonyl complex Cp(CO)$_2$MnCSMn(CO)$_2$Cp has
been proposed to form in the extended reaction of CpMn(CO)$_2$(THF) with
CS$_2$ (but has the anomalously low $v_{CS}$ value of 1048 cm$^{-1}$). This complex evidently decomposes to afford CpMn(CO)$_2$(CS) ($v_{CS}$ 1271 cm$^{-1}$) and CpMn(CO)$_2$.  

Bridging thiocarbonyl ligands also appear to be substantially more reactive than bridging carbonyl ligands. The bridging CS complex cis-[CpFe(CO)(CS)]$_2$ reacts with excess CH$_3$OSO$_2$F at room temperature to give the black, air stable, methylated bridging CS compound [Cp$_2$Fe$_2$(CSCH$_3$)(CS)(CO)]$_2$.  

(iii) Migratory Insertion Reactions

Transition metal complexes containing mutually cis hydrido and CS ligands were prepared with a view to inducing hydride transfer from the metal to CS, to produce a thioformyl ligand. The complex OsHCl(CO)(PPh$_3$)$_2$ is a suitable precursor to such migration reactions and to further ligand reactions of the thioformyl group (Scheme 10). The product of hydrogen addition to IrH(CS)(PPh$_3$)$_3$ was, surprisingly, not IrH$_3$(CS)(PPh$_3$)$_2$, but instead the compound IrH$_2$(SMe)(PPh$_3$)$_3$. It was postulated that this product resulted from a series of hydride transfers from the metal to the CS moiety (Scheme 11). Although none of the intermediates could be isolated, that a thioformyl complex is not an unreasonable intermediate was demonstrated by the subsequent preparation of IrCl$_2$(CHS)(CO)(PPh$_3$)$_2$. Proof that the thioformaldehyde complex is also not an unreasonable intermediate was then obtained by the production of a complex containing this reactive intermediate, viz. Os($\eta^2$-CH$_2$S)(CO)$_2$(PPh$_3$)$_2$ 44, which reacted with HCl to first form
Scheme 11 (L = PPh₃, bracketed compounds not isolated)

OsCl(SMe)(CO)₂(PPh₃)₂ and then, by subsequent acid cleavage of the SMe ligand, OsCl₂(CO)₂(PPh₃)₂ (Scheme 10). The thioformaldehyde adduct 44 could also be produced by transfer of the two hydrido ligands of OsH₂(CS)(PPh₃)₃ to the CS moiety. The forcing conditions required to induce these reactions lead also to the formation of an insoluble byproduct which, it was suggested, might contain thioformaldehyde as a bridging ligand. An analogue of each intermediate in the stepwise reduction of CS to the CH₃SH adduct IrH₂(SMe)(PPh₃)₃ was thus isolated and characterised. The formal similarity of this reduction with the reduction of carbon monoxide by hydrogen to methanol over heterogeneous transition metal catalysts, for which analogous
intermediates have been postulated, was noted. Hydride transfer from the metal to the CO ligand has never been observed.

(iv) Intramolecular Isomerisation Reactions Involving Bridged CS Ligands

The production of dimeric $[\text{CpRu(CO)(CS)}]_2$ and dinuclear $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ was reviewed in section III A(ii). In both complexes the CS groups are in the bridging positions and no evidence was found for nonbridged structures such as occur for $[\text{CpRu(CO)}]_2$. I.R. and $^1$H N.M.R. studies indicated that both $[\text{CpRu(CO)(CS)}]_2$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ exist in cis and trans forms, but these isomers have eluded separation because of rapid interconversion. This behaviour was also found for cis- and trans-$[\text{CpMn(NO)(CS)}]_2$, but the geometrical isomers of $[\text{CpFe(CO)(CS)}]_2$ were sufficiently stable to allow for separation. The presence of the CS group does, however, slow the rate of isomerisation, and qualitative studies showed that these rates decrease in the order $[\text{CpRu(CO)}]_2 > \text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS}) > [\text{CpRu(CO)(CS)}]_2$. The mechanism of isomerisation of $\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{CS})$ was proposed to be similar to that accepted for $[\text{CpFe(CO)}]_2$, and the possible alternative mechanisms shown in Scheme 13, for which the available evidence does not allow distinction, were postulated. The preference of CS for a bridging over a terminal position in these molecules was rationalised in terms of the weakness of the C=S $\pi$-bonds which lose little $\pi$-bond stabilisation in moving from a terminal (C=S) to a bridging (C=S) position. These arguments were also taken to imply
Scheme 12

Scheme 13
that CO should have a lesser preference for a bridging position than CS. 77

(v) Miscellaneous Reactions of Other Than the CS Ligand

Reactions at the arene ligands of the chromium complexes

\[(\eta^6{-}\text{MeC}_6\text{H}_4\text{CO}_2\text{Me})\text{Cr(CO)(CS)L} \quad [L = \text{P(OEt)}_3, \text{P(OPh)}_3\] 75 have been used
to generate new CS complexes (equation 29). The triphenylphosphite

\[
(\eta^6{-}\text{MeC}_6\text{H}_4\text{CO}_2\text{Me})\text{Cr(CO)(CS)L} \xrightarrow{\text{LiAlH}_4, \text{AlCl}_3} (\eta^6{-}\text{Me}_2\text{C}_6\text{H}_4)\text{Cr(CO)(CS)L}
\]

(29)
derivatives represent the first resolved enantiomers of chromium(0). 75

CONCLUSION

The chemistry of CS and CSe complexes is a relatively new feature
of organo-transition metal chemistry which has undergone slow growth.
While no general routes to such complexes have been devised synthetic
procedures exist for introducing the CS or CSe ligand into the
coordination sphere of some substrates. Both ligands form very strong
bonds to transition metal centres. The CS ligand is both a \(\sigma\)-donor
and a \(\pi\)-acceptor and the relative importance of these components depends
on the coordination environment to which the CS ligand is more
responsive than the CO ligand. Consequently, the CS ligand exhibits a
more diverse chemistry than the CO ligand. From early results it is
apparent that the CSe ligand has similar properties to the CS ligand.
CHAPTER 2

THIOCARBONYL COMPLEXES FROM CARBON DISULPHIDE ADDUCTS

This research group has been primarily concerned with the synthesis and reactivity of low valent complexes of Group VIII transition metals; especially ruthenium, osmium and iridium. The work reported in this thesis was begun in 1975 with a view to extending this interest to thio carbonyl complexes of ruthenium and osmium. At that time the two available synthetic procedures for forming ruthenium and osmium CS complexes were not considered adequate to sustain a long term project. The action of carbon disulphide on RuCl₂(PPh₃)₃ leads to a complex mixture of multinuclear thio carbonyl products²⁶ [Chapter 1 I(ii)].

The limitations of the acid cleavage of the dithioester complexes [M(η²-CS₂Me)(CO)₂(PPh₃)₂]⁺⁴⁸ [M = Ru, Os] [Chapter 1 I(iii)] are discussed below. Thus the first objective of this work was to develop improved synthetic procedures for introducing a CS ligand into the coordination sphere of ruthenium and osmium. This chapter deals with the efforts to develop such routes.

2.1 Early Preparative Routes to Ruthenium and Osmium

Thiocarbonyl Complexes

Pure thio carbonyl complexes MX₂L(CS)(PPh₃)₂ [M = Ru, Os; L = CO, CN-p-tolyl] are produced, in high yields, by the action of hydrohalic acids, HX, on the dithioester complexes [M(η²-CS₂Me)(CO)L(PPh₃)₂]⁺⁴⁸ or the osmium π-bonded CS₂ adducts Os(η²-CS₂)(CO)L(PPh₃)₂.¹¹⁰ Such
CS$_2$ adducts belong to a well documented class of compounds$^1$ and structurally characterised examples include Pt($\eta^2$-CS$_2$)(PPh$_3$)$_2$,$^{17}$ Pd($\eta^2$-CS$_2$)(PPh$_3$)$_2$,$^{111}$ Cp$_2$Nb($\eta^2$-CS$_2$)(\eta$^1$-CH$_2$=CH$_2$)$^{112}$ and Fe($\eta^2$-CS$_2$)(CO)$_2$(PMe$_3$)(PPh$_3$).$^{54}$ The limitations of this synthesis lie not in this final acid cleavage reaction, but in the earlier steps from which the $\pi$-bonded CS$_2$ adducts are derived.

The *dihapto*-carbon disulphide adducts were produced by the reaction sequences described in Scheme 2.1 and react with methyl iodide

\[ \text{Scheme 2.1 (L = PPh}_3\text{; M = Ru, Os; R = p-tolyl)} \]

(i) M = Ru,$^{109}$ Os $^{110}$ ; (ii) M = Ru,$^{108,125}$ Os $^{110}$ ; (iii) $^{48}$ ;

(iv) Photolytic reaction, sunlight; (v) M = Ru.$^{113}$

to produce [M($\eta^2$-CS$_2$Me)(CO)L(PPh$_3$)$_2$]I in high yields. It proved impossible to isolate [Ru($\eta^2$-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$]I free from the neutral complex RuI($\eta^2$-CS$_2$Me)(CO)(PPh$_3$)$_2$, which forms by iodide
displacement of a labile carbonyl ligand in the cationic complex. However, the strong methylating agent methyl triflate, CF₃SO₂CH₃, which contains the weakly coordinating ligand CF₃SO₃⁻ as a leaving group, reacts cleanly with M(n²-CS₂)(CO)L(PPh₃)₂ to give cationic dithioester complexes as the only products.

There are several intrinsic faults which mar the synthetic pathways described in Scheme 2.1. The use of silver ion to remove chloride from MHCl(CO)(PPh₃)₃ or MHCl(CO)(CNR)(PPh₃)₂ often leads to the incorporation of trace quantities of silver impurities in the product complexes. These initially inconspicuous impurities promote darkening and decomposition of the subsequent intermediates and lead ultimately to considerably diminished yields of the zerovalent complexes M(CO)L(PPh₃)₃. The substitution of acetonitrile by triphenylphosphine in the cations [MH(CO)₂(MeCN)(PPh₃)₂]⁺ is a prerequisite to reductive deprotonation. However, for the osmium cation this reaction requires very forcing conditions (heating under reflux in 2-methoxyethanol for 20 hours with a large excess of triphenylphosphine) and [OsH(CO)₂(PPh₃)₃]ClO₄ cannot be isolated in a pure form. Reductive deprotonation of this trisphosphine cation proceeds to afford Os(CO)₂(PPh₃)₃ in 70% yield. The mediocre yield is probably a consequence of impurities which are formed in the non-ideal substitution process. These problems, together with the further yield and time limitations imposed by the large number of steps in each sequence, prompted an investigation of alternative plausible routes to thiocarbonyl complexes.
2.2 Attempts to Find New Routes to Ruthenium and Osmium CS Complexes

It was anticipated that easily accessible thiocarboxamido complexes, \(110,115,116\) which are very similar to the dithioester complexes, might also react with hydrohalic acids to produce CS complexes.

\[
\begin{align*}
&\text{PPh}_3 \quad \text{N} \quad \text{R} \\
&\text{OC} \quad \text{M} \quad \text{S} \quad \text{OC} \\
&\text{PPh}_3
\end{align*}
\]

\[
\begin{align*}
&\xrightarrow{\text{HX, heat}} \\
&\text{PPh}_3 \quad \text{CS} \quad \text{X} \quad \text{X}
\end{align*}
\]

\(M = \text{Ru}, \text{Os}\)

However, the extended heating of \([\text{Ru}(\eta^2-\text{SCNPh})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4\) in 2-methoxyethanol containing HCl resulted in the loss of H\(_2\)S and the formation of \(\text{RuCl}_2(\text{CO})(\text{CNPh})(\text{PPh}_3)_2\). Similar treatment of a variety of \(N\)-alkyl and \(N\)-aryl substituted thiocarboxamido complexes did not yield a thiocarbonyl complex and so this route was abandoned. It was subsequently shown that the thiocarboxamido complex \([\text{Ru}(\eta^2-\text{SCN[CO}_2\text{Et}-p\text{-tolyl]})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4\), containing the strongly electron-withdrawing ester substituent on nitrogen, reacts with HCl to afford a mixture of \(\text{RuCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2\) and \(\text{RuCl}_2(\text{CO})(\text{CN-p-toly1})(\text{PPh}_3)_2\). The composition of this mixture is dependent on the solvent and the acid concentration, but the yield of \(\text{RuCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2\) never exceeded 50\%. \(117\)

A further reaction which appeared to be a feasible method for obtaining thiocarbonyl complexes involved the action of acids on complexes containing cis hydrido and xanthato ligands. Such reactions lead only to hydride cleavage and formation of \(\text{RuX}(\eta^2-\text{S}_2\text{COR})(\text{CO})(\text{PPh}_3)_2\),
which proved to be remarkably inert towards further reaction with hydrohalic acids or methyl triflate. Extended heating of the xanthato complexes with hydrohalic acids in the high boiling point solvent diglyme did not afford tractable products. Similar treatment of dithiocarbamato complexes was also unproductive.

The conversion of a carbonyl ligand to a thiocarbonyl ligand by exchange of oxygen for sulphur with triphenylphosphine sulphide was attempted. However, no exchange was observed after heating both neutral and cationic carbonyl complexes with triphenylphosphine sulphide in high boiling point solvents for periods of up to one week. Attempts to obtain CSe complexes by the interaction of triphenylphosphine selenide with both CO and CS complexes were also unsuccessful.

Ethylene trithiocarbonate is known to oxidatively add to Pt(PPh₃)₄ by cleavage of a C-S bond to give a platinum(II) metallocyclic complex. It was hoped that an analogous oxidative addition reaction would occur with the substrate Ru(CO)₂(PPh₃)₃ to afford a
metalocyclic complex which, on treatment with HCl, would lead to RuCl$_2$(CO)(CS)(PPh$_3$)$_2$ by cleavage of the ethyl dithiol group and loss of CO. Unfortunately, while this synthetic procedure might still be useful in other systems, the reaction between Ru(CO)$_2$(PPh$_3$)$_3$ and SC(SCH$_2$)$_2$ yielded products which were difficult to handle and so the route was not pursued. Because of these disappointing results attention was turned towards attempting to circumvent some of the difficulties experienced in the original synthetic systems.

2.3 Improvement of Synthetic Routes to CS Complexes

An alternative synthetic route to the complexes MX$_2$(CO)(CS)(PPh$_3$)$_2$ has been developed which avoids the use of silver ion and which offers significant time and yield improvements. The complexes MH$_2$(CO)(PPh$_3$)$_3$, which result from the action of NaOH on MHCl(CO)(PPh$_3$)$_3$ [M = Ru, Os$^{110,111,112}$] in boiling 2-methoxyethanol, react with
HX \( [X = \text{ClO}_4, \text{BF}_4] \) in dichloromethane–ethanol \( [M = \text{Ru}] \) or dichloromethane–methanol \( [M = \text{Os}] \) solution to evolve hydrogen and form \( \text{MHX(CO)}(\text{PPh}_3)_3 \). Treatment of \( \text{MHX(CO)}(\text{PPh}_3)_3 \) with carbon monoxide \textit{in situ} affords the neutral ruthenium complexes \( \text{RuHX(CO)}_2(\text{PPh}_3)_2 \) and the cationic osmium complex \( [\text{OsH(CO)}_2(\text{PPh}_3)_3]^+ \). The variable behaviour is assumed to be kinetic in origin. Osmium phosphine complexes are considerably less labile with respect to phosphine dissociation than the analogous ruthenium complexes. Coordinated tetrafluoroborate and perchlorate complexes are further discussed in section 2.5.

The action of \( \text{NaBH}_4 \) on \( \text{RuHX(CO)}_2(\text{PPh}_3)_2 \) in ethanol solution affords \( \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) which contains \textit{cis} hydrido and \textit{trans} phosphine ligands. (The \textit{cis} phosphine geometry has not been observed for any of the divalent bisphosphine complexes reported in this thesis. The preference for the \textit{trans} arrangement of these bulky ligands probably derives from steric interactions.) This complex has previously been prepared by the high temperature and pressure hydrogenation of \( \text{Ru(CO)}_3(\text{PPh}_3)_2 \) \(^{123}\) or by the mild hydrogenation of \( \text{Ru(CO)}_2(\text{PPh}_3)_3 \) \(^{124}\). Hydrogen loss from \( \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) occurs in boiling methanol in the presence of triphenylphosphine to afford the zerovalent complex \( \text{Ru(CO)}_2(\text{PPh}_3)_3 \). A bimolecular mechanism for the elimination of hydrogen from \textit{cis}-\text{OsH}_2(\text{CO})_4 \) has recently been recognised. \(^{125}\)

Treatment of \( \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \) with carbon disulphide in benzene solution at ambient temperatures leads to the formation of \( \text{Ru(}\eta^2-\text{CS}_2)(\text{CO})_2(\text{PPh}_3)_2 \) in high yield [Scheme 2.2]. Carbon disulphide normally reacts with transition metal hydrido complexes to form dithioformato complexes. \(^1\)
The reductive elimination of hydrogen is a common but not general reaction of transition metal multihydrido complexes.\textsuperscript{110,127}

The osmium cationic complex $[\text{OsH} \,(\text{CO}) \,(\text{PPh}_3)_3]^{+}$ has been produced, as described above, without the use of silver salts or very forcing conditions [scheme 2.2]. Not unexpectedly, it was found that the cation so formed reacts with NaOH in boiling methanol under nitrogen to afford the zerovalent complex, $\text{Os} \,(\text{CO}) \,(\text{PPh}_3)_3$, cleanly and in high yield (90-95\%). Furthermore, the zerovalent complex can be prepared by this new procedure directly from $\text{OsH}_2 \,(\text{CO}) \,(\text{PPh}_3)_3$ without isolation of the intermediate complexes $\text{OsHX} \,(\text{CO}) \,(\text{PPh}_3)_3$ and $[\text{OsH} \,(\text{CO}) \,(\text{PPh}_3)_3]X$ and this sequence consequently involves much less handling than the earlier route. The total yield, based on $\text{OsHCl} \,(\text{CO}) \,(\text{PPh}_3)_3$ usually lies in the range 82\% to 88\% which represents an improvement on the previous values of 65\% to 70\%. Similar yields are obtained in both ruthenium systems. The geometries of the hydrido-containing complexes shown in Scheme 2.2 can be deduced from the splitting patterns of the hydride resonances in the $^1\text{H}$ N.M.R., which arise from coupling with the $^3\text{P}$ nuclei ($I = \frac{5}{2}$) [see Table 2.4].

The ethylene adduct $\text{Os} \,(\eta^2-\text{C}_2\text{H}_4) \,(\text{CO}) \,(\text{PPh}_3)_2$ forms in a benzene solution saturated with ethylene in the presence of pyrex filtered sunlight.\textsuperscript{110} A 500 watt quartz-halogen lamp was found to be an adequate substitute for bright sunlight, eliminating reliance upon the
capricious Auckland sunshine. If Os(η²-C₂H₄)(CO)₂(PPh₃)₂ is heated under reflux in a benzene solution containing 1–1.2 equivalents of carbon disulphide Os(η²-CS₂)(CO)₂(PPh₃)₂ forms in high yield (90%).

When M(η²-CS₂)(CO)L(PPh₃)₂ [M = Ru, Os; L = CO and M = Ru; L = CN-p-toly1] are treated in benzene solution with a slight excess of methyl triflate, crystals of the dihapto-dithioester complexes [M(η²-CS₂Me)(CO)L(PPh₃)₂]CF₃SO₃ begin to form and, after addition of n-hexane, can be collected in quantitative yield. The extreme ease with which this alkylation takes place is demonstrated by the fact that even methyl chloride and n-propyl bromide are effective
reagents,

e.g. \( \text{Ru}(\eta^2-\text{CS}_2)(\text{CO})_2(\text{PPh}_3)_2 \xrightarrow{\text{CH}_3\text{Cl}} \text{RuCl}(\eta^2-\text{CS}_2\text{Me})(\text{CO})(\text{PPh}_3)_2 + \text{CO.} \)

From the available evidence it was concluded that the dithiomethylester ligands were coordinated through both C and S, but it was not possible to distinguish between the two arrangements I and II (figure 2.1).

Figure 2.1

The I.R. spectra of all the \( \eta^2 \)-dithioester compounds made in this laboratory show bands near 1100 cm\(^{-1} \) (the same region as \( \nu_{\text{CS}} \) for the precursor \( \eta^2-\text{CS}_2 \) complexes [see Table 2.2]) which perhaps supports the intuitively less favourable arrangement II. To settle this question \([\text{Ru}(\eta^2-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4\) was selected for an X-ray crystal structure determination. The geometry of \([\text{Ru}(\eta^2-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]^+\) is depicted in figure 2.2 and arrangement I is confirmed for the dithioester group. The two C-S bond lengths are closely similar to one another and also to the formal C-S double bond in \( \text{OsH}(\eta^1-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2 \) [1.648(4)Å, section 2.4]\(^{56} \) and to the C-S bond length in the \( \eta^2 \)-thiocarboxamido Rh(III) complexes

\[ \text{RhCl}(\eta^2-\text{S}_2\text{CNMe}_2)(\eta^2-\text{SCNMe}_2)(\text{PPh}_3)\cdot\text{CHCl}_3 \] \( [1.64(2)\text{Å}]^{128} \)

\[ \text{RhCl}[\eta^2-\text{SC(NPh)NMe}_2](\eta^2-\text{SCNMe}_2)(\text{PPh}_3\cdot(\text{CHCl}_3)_0.8][1.66(2)\text{Å}]^{129} \]
Figure 2.2: Structure of \([\text{Ru}(\eta^2-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]^+\).

(Bond lengths in Å in all figures.)
Acid cleavage of the dithiomethylester ligands occurs in boiling benzene-ethanol or boiling toluene-ethanol solution over several hours. The mechanism of thiocarbonyl formation is not known but several plausible pathways are shown in Scheme 2.3.

.Scheme 2.3 (L = PPh₃; X⁻ = halide ion; L¹ = CO, CN-ᵢ-p-toly; M = Ru, Os)

The neutral complex RuCl(η²-CS₂Me)(CO)(PPh₃)₂ can be isolated as an intermediate product by analysing reaction mixtures where methyl thiol elimination is incomplete. This same complex is formed
quantitatively when \([\text{Ru}(\eta^2\text{-CS}_2\text{Me})\text{(CO)}_2\text{(PPh}_3\text{)}_2]\text{CF}_3\text{SO}_3\) is treated with lithium chloride. The other suggested intermediate complexes could not be observed, but the mechanism, which involves three separate pathways, is supported by the following results.

The cationic complex \([\text{Ru}(\eta^2\text{-CS}_2\text{Me})\text{(CO)}_2\text{(PPh}_3\text{)}_2]^+\) reacts with diethylthiocarbamate or acetate ion to open the metallocycle and lose carbon monoxide forming monodentate dithioester complexes.

(All the monodentate substituted thiocarboxy ligands isolated in this work exhibit a medium to strong I.R. band in the vicinity of 1000 cm\(^{-1}\).)

The acetato complex reacts with acids to loose acetate and regenerate bidentate dithiomethylene complexes, but the more strongly chelating dithiocarbamate ligand is not cleaved by acids and, instead, recrystallisation of \(\text{Ru}(\eta^2\text{-S}_2\text{CNET}_2\text{)}(\eta^1\text{-CS}_2\text{Me})\text{(CO)}(\text{PPh}_3\text{)}_2\) from dichloromethane-ethanol in the presence of a few drops of tetrafluoroboric acid produces the thiocarbonyl cation \([\text{Ru}(\eta^2\text{-S}_2\text{CNET}_2\text{)}\text{(CO)}(\text{CS})(\text{PPh}_3\text{)}_2]^+\) by a rapid cleavage reaction of the dithioester function. Likewise, reaction with methyl iodide is fast to give the dithiocarbene cation \([\text{Ru}(\eta^2\text{-S}_2\text{CNET}_2\text{)}(\text{C[SMe}_2\text{]}\text{)}(\text{PPh}_3\text{)}_2]^+\).

Cyanide ion also induces the formation of a monodentate dithioester
ligand in \([\text{Ru}(\eta^2\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]^+\) giving \(\text{Ru}(\text{CN})(\eta^1\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2\), but carbonyl loss and metalloccycle reformation occurs readily, even in the solid state. Consequently, acid cleavage of the dithiomethyl ester function is not observed to occur rapidly and the intermediate \(\eta^2\text{-dithioester complex } \text{Ru}(\text{CN})(\eta^2\text{-CS}_2\text{Me})(\text{CO})(\text{PPh}_3)_2\text{ forms first}. These observations suggest; (i) intermediate carbene complexes are implicated; (ii) ring-opening of the chelate dithioester metalloccycle is slower than acid cleavage of the \(\eta^1\text{-dithioester group}; (iii) the major, perhaps only, pathway proceeds through the neutral bidentate dithioester complex \(\text{RuX}(\eta^2\text{-CS}_2\text{Me})(\text{CO})(\text{PPh}_3)_2\) as rapid acid cleavage is not observed.

Iodine was also found to be an effective and useful reagent for cleaving the dithiomethyl ester ligand. Heating of \(\text{RuI}(\eta^2\text{-CS}_2\text{Me})(\text{CO})(\text{PPh}_3)_2\) with one equivalent of iodine leads to the quantitative formation of \(\text{RuI}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2\) and the evolution of a colourless gas with a revolting odour presumed to be \(\text{CH}_3\text{SI}\).

2.4 A Novel Synthetic Route to Zerovalent Ruthenium and Osmium Complexes

Considerable effort was directed towards generating a complex which contained both an hydrido and a dithiomethyl ester ligand. It was hoped that such a complex might be induced to undergo reductive elimination of methyl thiol. While basic ethanol, basic isopropanol or hydrazine in ethanol promote decomposition of ruthenium dithioester complexes leading to black deposits, borohydride reacts cleanly with \([\text{M}(\eta^2\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]\text{X } [\text{M} = \text{Ru, Os}; \text{ X = CF}_3\text{SO}_3^{-}, \text{ClO}_4^{-}]\) in ethanol solution to afford the monodentate dithioester complexes
(Possible Reductive Elimination Reactions)

MH(η^1-CS₂Me)(CO)₂(PPh₃)₂. These complexes show no tendency to evolve carbon monoxide, but hydride cleavage occurs with acids or with iodine to regenerate η^2-dithioester complexes. However, RuH(η^1-CS₂Me)(CO)₂(PPh₃)₂ evolves methyl thiol in solution or in the solid state (and has consequently eluded satisfactory elemental analysis). If OsH(η^1-CS₂Me)(CO)₂(PPh₃)₂ is heated in degassed 2-methoxyethanol methyl thiol elimination proceeds to completion and the zerovalent complex Os(CO)₂(CS)(PPh₃)₂ is obtained. However, the heating of RuH(η^1-CS₂Me)(CO)₂(PPh₃)₂ in a series of degassed alcoholic solvents leads usually to dark solutions which do not afford tractable products.
Methanol is the only solvent which is conducive to the formation of Ru(\(\text{CO})_2(\text{CS})_2(\text{PPH}_3)_2\) in a pure form but the yields obtained were poor (ca. 45%). Previously Ru(\(\text{CO})_2(\text{CS})_2(\text{PPH}_3)_2\) had been obtained in low yield by the following sequence of reactions: \(\text{RuCl}_2(\text{CO})_2(\text{CS})_2(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\) \(\text{OH}^-(\text{MeOH})\rightarrow\text{CO}\) → \(\text{RuCl}(\text{OCIO}_3)(\text{CO})(\text{CS})(\text{PPH}_3)_2\)

The osmium complex \(\text{OsH}_2(\text{CS}_2\text{Me})(\text{CO})_2(\text{PPH}_3)_2\) as the hemibenzene solvate has been the subject of an X-ray crystal structure analysis [figure 2.3]. Of particular interest is the arrangement and geometry of the dithiomethylene and hydrido ligands. The dithiomethylene group is essentially planar and is coplanar with the Os and H atoms, the dithiomethylene function being oriented along the H, Os, C(3) plane with the H atom being only 0.11Å out of plane of the ester. Some deviations are observed at atom C(3). The angle Os-C(3)-S(2) has increased to 126.1(3)° and the Os-C(3)-S(1) angle has decreased to 112.5(2)°, suggesting that the ligand has tilted slightly towards the hydrido ligand. The S(1)·····H distance is only 2.66(6)Å so that, in the solid state, the orientation of the hydrido and dithiomethylene ligands is ideally suited to a 1,2-elimination of methyl thiol across the Os-C(3) bond. The dithiomethylene C(3), S(1), S(2) plane is constrained to lie in the region of the H, Os, C(3) plane by the presence of a phenyl group from each phosphine which lie above and below the dithiomethylene plane [figure 2.3(b)]. However, the orientation of the dithioester group, where there are two alternatives, with the SMe moiety lying cis to the hydrido ligand is intriguing and it is tempting to attribute this feature, and the tilting effect, to an attraction between hydride and S(1). The tilting could also be explained by repulsion between the C(3)-S(2)
Figure 2.3(a): The inner coordination sphere of OsH(η^1-CS₂Me)(CO)₂(PPh₃)₂ with some distances presented. The 50% probability ellipsoids are shown.

Figure 2.3(b): A stereoview of OsH(η^1-CS₂Me)(CO)₂(PPh₃)₂. The hydride hydrogen atom is included but other hydrogen atoms have been omitted. The 50% probability ellipsoids are shown.
multiple bond and the electron density in the adjacent metal-ligand and C(1)-O(1) bonds.

Mechanistic studies of this elimination reaction to determine, for instance, the possible involvement of radical species have not been conducted, but in the light of the structural evidence the most attractive mechanism is a concerted 1,2-elimination of methyl thiol across the Os-C(3) bond. The 1,1-elimination of two ligands from a transition metal centre is a common reaction which is, of course, what is meant by the term reductive elimination. The 1,2-reductive elimination from a transition metal complex where one centre is the metal is a very rare reaction. Reactions which have been suggested to proceed by concerted 1,2-elimination processes include

\[
\begin{align*}
\text{TiMe}_4 & \rightarrow [\text{Me}_2\text{Ti} = \text{CH}_2] + \text{CH}_4 \quad \text{\cite{132}} \\
\text{Cp}_2\text{Ti(CH}_2\text{Ph)}_2 & \rightarrow [\text{Ti(C}_5\text{H}_4)_2] + 2\text{PhMe} \quad \text{\cite{133}}
\end{align*}
\]

In each case the mechanistic description is based on labelling studies which imply that the processes are predominantly intramolecular and do not involve hydrogen abstraction from the solvent. However, a number of pathways have been recognised for the decomposition of transition metal alkyl complexes in which the alkyl ligand contains only \(\alpha\)-hydrogen atoms\cite{134} and it is apparent that methane could equally well be formed from \(\text{TiMe}_4\) by \(\alpha\)-hydrogen abstraction,

\[
\text{TiMe}_4 \rightarrow [\text{Me}_3\text{TiH(CH}_2\text{)}] \rightarrow [\text{Me}_2\text{Ti} = \text{CH}_2] + \text{CH}_4.
\]
The difficulty of demonstrating that this type of reaction is not occurring has been discussed.\(^{135}\) (Spectroscopic evidence for the formation of odd electron species during the thermolysis of \(\text{Cp}_2\text{TiMe}_2\) has been obtained.\(^{136}\) Similarly, the decomposition of \(\text{Cp}_2\text{Ti(CH}_2\text{Ph)}_2\) might proceed by ligand hydrogen abstraction by titanium from the cyclopentadienyl ring prior to elimination of toluene. Hence these reactions, for which the 1,2-elimination mechanism has been considered, might also proceed by alternative pathways and the available evidence does not permit an unambiguous choice. If methyl thiol elimination from \(\text{OsH(}^{1}\text{-CS}_2\text{Me)(CO)}_2(\text{PPh}_3)_2\) does proceed by a 1,2-elimination mechanism then this reaction might represent the only example of such a process yet reported.

This procedure has been extended to produce \(\text{trans-IrCl(CS)(PPh}_3)_2\) in very high yield by a three-step sequence (Scheme 2.4) and this is undoubtedly the most useful application of the process. Alternative

\[
\text{IrCl(CO)(PPh}_3)_2 \xrightarrow{\text{CS}_2, \text{CH}_3\text{OSO}_2\text{CF}_3} \text{[IrCl}(^{2}\text{-CS}_2\text{Me)(CO)(PPh}_3)_2]^{+}\text{CF}_3\text{SO}_3
\]

\[
\downarrow \text{NaBH}_4
\]

\[
\text{IrHCl}(^{1}\text{-CS}_2\text{Me)(CO)(PPh}_3)_2
\]

\[
\downarrow \text{heat}/^t\text{BuOH}
\]

\[
\text{trans-IrCl(CS)(PPh}_3)_2 + \text{MeSH} + \text{CO}
\]

Scheme 2.4

routes to \(\text{trans-IrCl(CS)(PPh}_3)_2\) suffer from the same disadvantages as those to the osmium and ruthenium complexes \(\text{M(CO)}_2(\text{CS})(\text{PPh}_3)_2\) mentioned above; i.e. multistep processes with yield and time limitations [see Chapter 1 section I].
2.5 Coordinated Tetrafluoroborato and Perchlorato Complexes

Ionic tetrafluoroborates of $T_d$ symmetry exhibit two triply degenerate I.R. active modes which absorb in the 1000-1100 cm$^{-1}$ region and around 525 cm$^{-1}$. The latter band is obscured in triphenylphosphine complexes by a very strong phosphine band in the same region. The former very intense broad band contains a series of maxima due to isotopic doubling ($^{10}$B 19.78%, $^{11}$B 80.22%) and to loss of degeneracy arising from lower symmetry in the crystal field environment.$^{137}$

Ionic perchlorates show two I.R. bands which are much less structured by isotope multiplicity around 1100 cm$^{-1}$ and 620 cm$^{-1}$. Upon coordination in a monodentate fashion, the original $T_d$ symmetry is lowered to $C_{3v}$ and as a consequence the asymmetric stretch at 1000-1100 cm$^{-1}$ in tetrafluoroborato complexes and $\alpha\alpha$. 1100 cm$^{-1}$ in perchlorato complexes becomes split. The tetrafluoroborate band is broadened considerably and loses the most pronounced maximum at $\alpha\alpha$. 1050 cm$^{-1}$. The perchlorate band becomes split into two I.R. bands and the magnitude of this splitting (usually 30-90 cm$^{-1}$) is generally considered to be proportional to the degree of association of the perchlorato ligand with the metal.$^{110}$

Coordinated perchlorato and tetrafluoroborato complexes that have been obtained in this laboratory normally form crystals which contain one or more equivalents of donor solvents such as water or ethanol. Where these solvents are absent then anomalously large structuring or splitting is observed such as in $\text{RuCl(OClO}_3\text{(CO)(CS)(PPh}_3\text{)_2}}$ $^{115}$ or one form of $\text{MCl(OClO}_3\text{(CO)(CN-}p\text{-tolyl)(PPh}_3\text{)_2}}$ [$M = \text{Ru, }^{109}\text{ Os}^{110}$] where the splitting is as large as 140 cm$^{-1}$. This behaviour was thought to be a result of the different $M^1X_4^-$ [$M^1X_4^- = BF_4^-, ClO}_4\text{^-}$] complex environments shown
in figure 2.4. An X-ray crystal structure of the complex

![Ionic, H-bonded, Covalent Structures]

RuH(FBF\textsubscript{3})(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}.(H\textsubscript{2}O)\textsubscript{2} was undertaken to determine the mode of coordination of the tetrafluoroborate group to the metal. The $^1$H N.M.R. spectrum of this complex exhibits two separate resonances for the two water molecules [τ,6.87(2H),τ,8.30 (2H)] and the crystal structure confirms that the tetrafluoroborate group is in the H-bonded environment and that one water molecule is coordinated to the metal and the other is a solvent molecule (figure 2.5). The compound is consequently better formulated as the cationic complex

[RuH(H\textsubscript{2}O)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}]BF\textsubscript{4}.H\textsubscript{2}O. The I.R. and $^1$H N.M.R. spectra of RuH(FBF\textsubscript{3})(CO)(PPh\textsubscript{3})\textsubscript{3}.(H\textsubscript{2}O)\textsubscript{2} and OsH(FBF\textsubscript{3})(CO)(PPh\textsubscript{3})\textsubscript{3}.(H\textsubscript{2}O)(CH\textsubscript{3}CH\textsubscript{2}OH)\textsubscript{1.5} indicate that these compounds are also best formulated as cationic complexes containing coordinated water molecules to which the tetrafluoroborate group is connected by H-bonding.
Figure 2.5: Structure of $[\text{RuH(H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$.

Phosphine ligands are coordinated above and below plane shown.
The procedures outlined here relate to the experimental sections of all chapters. Solvents were degassed either by the freeze-thaw method using nitrogen (<6 v.p.m. oxygen) or by passing a stream of nitrogen through the boiling solvent for 10 minutes prior to use. Reactions involving heating under reflux were carried out in a nitrogen atmosphere, but unless stated otherwise subsequent workups were performed in open conditions. The removal of solvents was performed at reduced pressure using a rotary evaporator. Routine recrystallisations were normally achieved by one of the following methods:

(1) The sample was dissolved in a low boiling point solvent and a higher boiling point solvent, in which the compound was insoluble, was added. Evaporation at reduced pressure effected gradual crystallisation. This technique was found most suitable for the less soluble neutral and cationic complexes.

(2) The sample was dissolved in a solvent, commonly benzene or dichloromethane, and A.R. petroleum spirit (b.p. 40-60°C), was added to the point of precipitation. The solution was then seeded and left until crystallisation was complete. This technique found greatest application in the recrystallisation of the more soluble neutral complexes.

(3) Cationic complexes were generally recrystallised in the following manner. The sample was dissolved in a minimum of dichloromethane containing approximately 0.05-0.2 ml of absolute ethanol. Cyclohexane was then added to the point
of precipitation and the open vessel was placed in an atmosphere saturated with cyclohexane. Gradual diffusion of cyclohexane into the solution effected crystallisation of the complex. The inclusion of solvent molecules in the crystalline samples was often observed with this technique.

Some room temperature reactions involving cationic complexes called for dissolution in absolute ethanol. Where the cationic complex was too insoluble in pure absolute ethanol to allow for complete dissolution it was found that dissolution was best achieved by dissolving the complex in the minimum quantity of dichloromethane, adding the requisite quantity of absolute ethanol and then removing the dichloromethane under reduced pressure at a slightly elevated temperature. The solution was then used immediately before the crystallisation process could begin.

Purification of compounds prior to crystallisation was sometimes achieved using column chromatography. Alumina for columns was Spence type H, 100-200 mesh, deactivated by shaking 100 g with 5-10 ml of 10% acetic acid solution. Other solid phases were silica gel (Riedel de Haen Kiesel-gel S) and Florisil (B.D.H. 100-200 mesh).

Characterisation of new compounds was achieved by means of elemental analysis, I.R. and $^1$H N.M.R. spectroscopy. Analytical data were obtained from the Microanalytical Laboratory, University of Otago, and these services of Professor A.D. Campbell are gratefully acknowledged. I.R. spectra (4000-400 cm$^{-1}$) were measured on a Shimadzu IR-27g spectrometer or a Perkin Elmer 397 spectrometer, either as nujol or Kel-F mulls or dichloromethane solution between KBr plates. $^1$H N.M.R. spectra were recorded on a Varian Associates T60 spectrometer using
tetramethyilsilane (t,10) as internal calibrant. Melting points (uncorrected) were measured on a Reichert hot stage microscope.

Osmium tetroxide and ruthenium trichloride were obtained commercially from Johnson Matthey Chemicals Limited. \((\text{NH}_4)_2\text[OsCl}_6\) was prepared by the method of Dwyer and Hogarth\(^{139}\) and \text{OsHCl(CO)(PPh}_3)_3\) by a modification\(^{110}\) of the method of Vaska.\(^{119}\) \text{OsCl}_2(P\text{PPh}_3)_3\) was synthesised on a larger scale by the method of Hoffman and Caulton.\(^{140}\) \text{RuHCl(CO)(PPh}_3)_3\) was produced by the method of Vaska.\(^{120(b)}\)
EXPERIMENTAL

$\pi$-CS$_2$ COMPLEXES

RuHCl(CO)(PPh$_3$)$_3$: Chlorohydridocarbonylris(triphenylphosphine)-ruthenium(II).

RuCl$_3$$\cdot$3H$_2$O (3.0 g) and triphenylphosphine (23.0 g) in 2-methoxyethanol (methyl glycol) (35 ml) were heated under reflux for 48 h. If crystals did not form after 6 h seed crystals were added. The mixture was allowed to cool to room temperature and the cream to pale pink crystalline solid was filtered, washed with ethanol and hexane and dried at room temperature (10.3 g).

RuH$_2$(CO)(PPh$_3$)$_3$: Dihydridocarbonylris(triphenylphosphine)ruthenium(II).

RuHCl(CO)(PPh$_3$)$_3$ (2.0 g), triphenylphosphine (0.2 g) and sodium hydroxide (0.5 g) were heated under reflux in 2-methoxyethanol (50 ml) for 20 min. The mixture was cooled in an ice-bath and the white crystalline solid was collected and washed with ethanol, water and then ethanol again. The solid was dissolved in dichloromethane with triphenylphosphine (0.1 g) (and filtered through a celite pad if any undissolved NaCl was apparent) and ethanol was added. Removal of dichloromethane afforded white crystals (1.81 g, 94%).

RuH₂(CO)(PPh₃)₃ (1.81 g) was stirred in a degassed solution comprised of dichloromethane (70 ml), ethanol (10 ml) and tetrafluoroboric acid (ca. 40%) (1 ml) until dissolution had been effected. The slow evolution of hydrogen was evident. The dichloromethane was removed and water was added slowly until crystallisation was complete. (Diethyl ether was also found to be effective for inducing crystallisation.) Recrystallisation from dichloromethane-ethanol-water yielded large white crystals of the solvate [RuH(H₂O)(CO)(PPh₃)₃]BF₄•H₂O (1.90 g, 93%).

¹H N.M.R. (CDCl₃) shows τ, 7.97[s(broad), 2H, H₂O]. M.p. 126-128°C.

Anal. Found: C, 63.73; H, 4.69; P, 9.30%.

C₅₅H₄₈BF₄O₄P₃Ru.H₂O requires C, 63.53; H, 4.85; P, 8.94%.

[RuH(H₂O)(CO)₂(PPh₃)₂]BF₄. Hydriodoaquodicarbonylrbis(triphenylphosphine)-ruthenium(II)tetrafluoroborate.

a) [RuH(H₂O)(CO)(PPh₃)₃]BF₄•H₂O (1.0 g) was dissolved in dichloromethane-ethanol (50 ml, 1:1) and stirred under an atmosphere of carbon monoxide (60 p.s.i.) for 1 h. The solvent was evaporated to 10 ml and the slow addition of water to the warm solution effected crystallisation. (Diethyl ether was also found to be effective for inducing crystallisation.) Recrystallisation from dichloromethane-ethanol-water gave the product as large colourless crystals of the water solvate [RuH(H₂O)(CO)₂(PPh₃)₂]BF₄•H₂O (0.71 g, 91.6%). ¹H N.M.R. (CDCl₃) shows τ, 8.30[s(broad), 2H, H₂O]. M.p. 122-125°C. Product was further characterised by an X-ray crystal structure. Anal. Found: C, 56.85; H, 4.86; P, 6.72%.

C₃₈H₃₃BF₄O₄P₂Ru.H₂O requires C, 56.66; H, 4.38; P, 7.69%.
b) This compound could be synthesised directly from
\[ \text{RuH}_2(\text{CO})(\text{PPh}_3)_3 \] by following the instructions for the immediate above
two compounds without isolating [RuH(H\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_3] \text{BF}_4\cdot\text{H}_2\text{O}. No
triphenylphosphine was added to the solution.

\[ \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \quad \text{Dihydridodicarbonylbis(triphenylphosphine)-}
\text{ruthenium(II).} \]

[\text{RuH(H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2] \text{BF}_4\cdot\text{H}_2\text{O} \quad (0.7 \text{ g}) \text{ was suspended in ethanol (30 ml)}
and a filtered solution of sodium borohydride (0.1 g) in ethanol (10 ml)
was slowly added. The suspension was stirred for 10 min after
effervescence had ceased (30 min). The white microcrystalline
product was collected, washed with ethanol, then water, then ethanol,
then hexane and dried in the air (0.547 g, 92\%). The product was
characterised by comparison of the I.R. spectrum with that quoted for
\[ \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \] in ref. 123 [\nu_{\text{CO}} (\text{cm}^{-1}) \quad 2010, 1975, 1950; \nu_{\text{Ru-H}}
(\text{cm}^{-1}) \quad 1878, 1820; \delta_{\text{Ru-H}} (\text{cm}^{-1}) \quad 800].

\[ \text{Ru}(\eta^2-\text{CS}_2)(\text{CO})_2(\text{PPh}_3)_2 \quad \text{Dihapto-carbondisulphidedicarbonylbis-}
\text{(triphenylphosphine)ruthenium(II).} \]

\[ \text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2 \quad (0.5 \text{ g}) \text{ was added to a degassed solution comprised}
of benzene (35 ml) and carbon disulphide (1 ml). The mixture was
stirred for 2.5 h. The solvent volume was reduced to 10 ml and hexane
(30 ml) was added to effect complete crystallisation. The yellow
feathery product was collected and washed with hexane and usually used
without further purification (0.54 g, 97.4\%). Recrystallisation from
dichloromethane-ethanol gave yellow-orange feathery needles. The
product was characterised by comparison of the I.R. spectrum with that of an authentic sample.  

\[ \text{OsHCl(CO)(PPh}_3\text{)}_3 \cdot \text{Chlorohydridocarbonyltrim(} \text{triphenylphosphine)} - \text{osmium(II).} \]  

\[(\text{NH}_4)_2[\text{OsCl}_6] \text{ (2.0 g), triphenylphosphate (12 g) and a small quantity of seed crystals of OsHCl(CO)(PPh}_3\text{)}_3 \text{ in 2-(β-methoxy)ethoxyethanol (methyl digol) (57 ml) were heated under reflux for 1 h. Large white crystals of the product were deposited after 35 min. The mixture was cooled to room temperature and the crystals were filtered, washed with ethanol and hexane and dried at 60°C (4.45 g, 94%).} \]  

\[ \text{OsH}_2\text{(CO)(PPh}_3\text{)}_3 \cdot \text{Dihydridocarbonyltrim(} \text{triphenylphosphine)} - \text{osmium(II).} \]  

\[ \text{OsHCl(CO)(PPh}_3\text{)}_3 \text{ (2.0 g), triphenylphosphate (0.2 g) and sodium hydroxide (0.5 g) were heated under reflux in 2-methoxyethanol (50 ml) for 30 min. The mixture was cooled in an ice-bath and the white crystalline solid was collected and washed with ethanol, water and then ethanol again. The solid was dissolved in dichloromethane with triphenylphosphate (0.1 g) (and filtered through a celite pad if any undissolved NaCl was apparent) and ethanol was added. Removal of dichloromethane afforded white crystals (1.85 g, 95.7%).} \]

\[ [\text{Os(H}_2\text{O)(CO)(PPh}_3\text{)}_3] \text{BF}_4 \cdot \text{Hydroxocarbonyltrim(} \text{triphenylphosphine)} - \text{osmium(II)} \text{tetrafluoroborate.} \]  

\[ \text{OsH}_2\text{(CO)(PPh}_3\text{)}_3 \text{ (1.85 g) was heated gently in a degassed solution comprised of dichloromethane (70 ml), methanol (10 ml) and} \]
tetrafluoroboric acid (ca. 40%) (1 ml) until dissolution had been
affected. The slow evolution of hydrogen was evident. The
dichloromethane was removed and water was added slowly until

crystallisation was complete. (Diethyl ether was also found to be
effective for inducing crystallisation.) Recrystallisation from
dichloromethane-ethanol-water yielded large colourless hexagonal
crystals of the solvate [Osh(H₂O)(CO)(PPh₃)₃]BF₄·(CH₃CH₂OH)·1.5
(2.05 g, 96.5%). ¹H N.M.R. (CDCl₃) shows τ 6.48[q, J(H-H) = 7.3 Hz,
3H, -CH₂-] τ 8.89[t, J(H-H) = 7.2 Hz, 4H, -CH₃]. M.p. 132-138°C.

Anal. Found: C, 59.03; H, 4.66; P, 7.90%. C₅₅H₄₈BF₄O₂OsP₃·
(CH₃CH₂OH)·1.5 requires C, 59.03; H, 4.87; P, 7.87%.

[Osh(CO)₂(PPh₃)₃]BF₄. Hydridodicarbonyltris(triphenylphosphine)osmium(II)-
tetrafluoroborate.

Osh₂(CO)(PPh₃)₃ (1.85 g) was treated as above to afford a
dichloromethane-methanol solution of [Osh(H₂O)(CO)(PPh₃)₃]BF₄. This
solution was then heated under carbon monoxide (60 p.s.i.) to 80°C for
1.5 h. This solution was then usually used as a solution of

[Osh(CO)₂(PPh₃)₃]BF₄. The product can be isolated by adding water
which affords a colourless oil. Recrystallisation of this oil from
ethanol yielded large colourless hexagonal crystals (1.35 g, 65.6%).
M.p. 208-212°C. Anal. Found: C, 59.88; H, 4.30; P, 8.18%.
C₅₆H₄₆BF₄O₂OsP₃ requires C, 60.00; H, 4.14; P, 8.23%.

Os(CO)₂(PPh₃)₃. Dicarbonyltris(triphenylphosphine)osmium(O).

A dichloromethane-methanol solution of [Osh(CO)₂(PPh₃)₃]BF₄ was
prepared as described above from Osh₂(CO)(PPh₃)₃ (1.85 g). The
dichloromethane was removed and methanol was added to bring the total volume of the solution to 60 ml. The solution was then heated to boiling under nitrogen and crushed sodium hydroxide (0.6 g) and triphenylphosphine (0.2 g) were added. The solution was heated under reflux for 1 h. The yellow needles were removed by filtration and washed with ethanol and hexane (1.8 g, 94.8%).

\[
\text{Dihapto-ethylenedicarboxylbis(triphenylphosphine)osmium(II).}
\]

\[
\text{Os(CO)}_2(\text{PPh}_3)_3 \quad (1.0 \text{ g}) \quad \text{was dissolved in degassed benzene (50 ml)}
\]
in a 250 ml flask under an atmosphere of ethylene. The light from a 500 watt quartz-halogen sun-lamp (Thorne) was directed at the flask which was cooled by a constant air flow across the surface. When the solution was quite colourless (1-2 h) the solvent volume was reduced to 10 ml and ethanol was added to effect complete crystallisation (0.757 g, 98%).

\[
\text{Dihapto-carbodisulphidedicarboxylbis-}
\]

\[
\text{(triphenylphosphine)osmium(II).}
\]

\[
\text{Os(η^2-C}_2\text{H}_4)(\text{CO})_2(\text{PPh}_3)_2 \quad (0.5 \text{ g}) \quad \text{was heated under reflux in}
\]
degassed benzene (50 ml) containing 10 ml of a degassed solution of carbon disulphide in benzene (1% w/w, 1.1 equiv.). The solution was heated under reflux for 30 min, and the solvent volume was reduced to 10 ml. Ethanol was added and the pink needles were collected (0.475 g, 89.6%) and used without further purification.
METHYLDITHIOESTER COMPLEXES

[Ru(\(\eta^2-\text{CS}_2\)Me)(CO)\(_2\)(PPh\(_3\))\(_2\)]CF\(_3\)SO\(_3\).  

**Dihapto-dithiomethyleneesterdicarbonyl-bis(triphenylphosphine)ruthenium(II)-trifluoromethanesulphonate.**  

Ru(\(\eta^2-\text{CS}_2\))CO\(_2\)(PPh\(_3\))\(_2\) (0.5 g) was stirred in a dry benzene solution (25 ml) containing methyl triflate (0.2 ml). After 30 min hexane (20 ml) was added and the pale yellow crystals were collected and washed with hexane. Recrystallisation from dichloromethane-ethanol-cyclohexane afforded yellow crystals (0.59 g, 97%). M.p. 125-132°C. Anal. Found: C, 53.42; H, 4.14; P, 6.72%. C\(_{41}\)H\(_{33}\)F\(_2\)O\(_5\)P\(_2\)RuS\(_3\) requires C, 53.41; H, 3.61; P, 6.72%.

[Ru(\(\eta^2-\text{CS}_2\)Me)(CO)(CNR)(PPh\(_3\))\(_2\)]CF\(_3\)SO\(_3\).  

**Dihapto-dithiomethyleneester carbonyl-p-tolylisocyanidebis(triphenylphosphine)ruthenium(II)trifluoromethanesulphonate.**

To Ru(\(\eta^2-\text{CS}_2\))(CO)(CN-p-tolyl)(PPh\(_3\))\(_2\)\(^{109}\) (0.5 g) in dry benzene (25 ml) was added methyl triflate (0.2 ml). After 30 min hexane (20 ml) was added and the pale yellow crystals were collected and washed with hexane. Recrystallisation from dichloromethane-ethanol-cyclohexane afforded large yellow crystals of the solvate [Ru(\(\eta^2-\text{CS}_2\)Me)(CO)(CN-p-tolyl)(PPh\(_3\))\(_2\)]CF\(_3\)SO\(_3\).\(_2\)(H\(_2\)O) \(_0.66\) (0.54 g, 89.4%). \(^1\)H N.M.R. (CDCl\(_3\)) shows \(\delta, 8.15\) [s, 1.33H, H\(_2\)O]. M.p. 182-187°C. Anal. Found: C, 56.20; H, 4.14; N, 1.06%. C\(_{48}\)H\(_{40}\)F\(_{10}\)O\(_4\)P\(_2\)RuS\(_3\).\(_2\)(H\(_2\)O) \(_0.66\) requires C, 56.35; H, 4.07; N, 1.37%.
[Ru(η²-CS₂)₂(Me)(CO)₂(PPh₅)₂]ClO₄. **Dihapto-dithiomethylesterdicarbonylbis-(triphenylphosphine)ruthenium(II) perchlorate.**

[Ru(η²-CS₂)(CO)(CN-p-tolyl)(PPh₅)₂]ClO₄. **Dihapto-dithio-n-propylester-carbonyl-p-tolylisocyanidebis-(triphenylphosphine)ruthenium(II)- perchlorate.**

Ru(η²-CS₂)(CO)(CN-p-tolyl)(PPh₅)₂ (0.3 g) was dissolved in a solution of n-propylbromide and dichloromethane (30 ml, 1:2) and stirred overnight under nitrogen. A solution of sodium perchlorate (0.1 g) in ethanol (25 ml) was added and on removal of the alkyl halide solvents yellow crystals of the title compound formed. Recrystallisation from dichloromethane-ethanol-cyclohexane gave the product as a mixture of yellow needles and yellow chunky crystals. ¹H N.M.R. shows these crystals to contain 0.25 mol dichloromethane of solvation τ, 4.72 [s, 0.5H, CH₂Cl₂] (0.295 g, 86.3%). M.p. 202-206°C. Anal. Found: C, 58.30; H, 4.74; N, 1.38; Cl, 4.96%. C₄₉H₄₄Cl₅NO₅P₂RuS₂(CH₂Cl₂)₀.25 requires C, 58.52; H, 4.44; N, 1.39; Cl, 5.26%.

[Ru(η²-CS₂)₂Me(CO)₂(PPh₅)₂]ClO₄. **Dihapto-dithiomethylesterdicarbonylbis-(triphenylphosphine)ruthenium(II)- perchlorate.**

[Ru(η²-CS₂Me)(CO)₂(PPh₅)₃]CF₃SO₃ (0.3 g) was dissolved in dichloromethane (30 ml) and a solution of sodium perchlorate (0.25 g) in ethanol (20 ml) was added. On removal of the dichloromethane yellow crystals were deposited. These were collected and washed with diethyl ether. Recrystallisation from dichloromethane-ethanol-cyclohexane afforded lemon crystals (0.255 g, 91.5%). M.p. 185-187°C. This compound was further characterised by an X-ray crystal structure. Anal. Found: C, 55.39; H, 4.06; P, 7.35; Cl, 5.24%. C₄₀H₃₃Cl₀.₇P₂RuS₂ requires C, 55.07; H, 3.81; P, 7.10; Cl, 4.06%.
Ru(η²-O₂CMe)(η¹-CS₂Me)(CO)(PPh₃)₂: Dihapto-acetato-monohapto-dithiomethyl-
ester carbonylbis(triphenylphosphine)-
ruthenium(II).

[Ru(η²-CS₂Me)(CO)₂(PPh₃)₂CF₃SO₃] (0.3 g) and lithium acetate
(0.05 g) were dissolved in dichloromethane-ethanol (30 ml, 1:4) and the
solution was heated under reflux for 10 min. The dichloromethane
was removed and the yellow crystals were collected and washed with
ethanol and hexane. Recrystallisation from dichloromethane-ethanol
yielded a mixture of yellow granular crystals and needles (0.255 g,
97.6%). M.p. 178-182°C. Anal. Found: C, 61.42; H, 4.77; P, 7.65%.
C₄₁H₃₆O₃P₂RuS₂ requires C, 61.25; H, 4.51; P, 7.71%.

Ru(η²-S₂CNET₂)(η¹-CS₂Me)(CO)(PPh₃)₂: Dihapto-diethylidithiocarbamato-
monohapto-dithiomethyl estercarbonylbis(triphenylphosphine)ruthenium(II).

[Ru(η²-CS₂Me)(CO)₂(PPh₃)₂CF₃SO₃] (0.3 g) and sodium diethylidithio-
carbamate (0.1 g) in dichloromethane-ethanol solution (30 ml, 1:4)
were stirred for 15 min. The dichloromethane was removed and the yellow
crystals were collected and washed with ethanol and hexane.
Recrystallisation from dichloromethane-ethanol gave yellow crystals
containing 0.25 mol dichloromethane of solvation (0.29 g, 95.5%).

¹H N.M.R. (CDCl₃) shows 7,4.73[ς, 0.5H, CH₂Cl₂]. M.p. 141-143°C.
Anal. Found: C, 58.40; H, 5.03; N, 2.10%. C₄₄H₄₃NOP₂RuS₄(CH₂Cl₂)₀.25
requires C, 58.12; H, 4.80; N, 1.53%.
[Ru(\(\eta^2\)-S\(_2\)CNET\(_2\))(C[SMel]\(_2\))(CO)(PPh\(_3\))\(_2\)]I. \(\text{Dihapto-diethylidithiocarbamatobis-}
(methylthiolato)carbene(carbonylbis-(triphenylphosphine))ruthenium(II)iodide.

Ru(\(\eta^2\)-S\(_2\)CNET\(_2\))(\(\eta^1\)-CS\(_2\)Me)(CO)(PPh\(_3\))\(_2\) (0.2 g) was dissolved in methyl iodide (5 ml) and hexane (30 ml) was added. The deep yellow crystals were collected and recrystallised from dichloromethane-petroleum spirit to give yellow-orange granular crystals (0.23 g, 99%). M.p. 129-132°C. Anal. Found: C, 51.99; H, 4.91; N, 1.28; I, 12.35%.

\(\text{C}_{45}\text{H}_{46}\text{INOP}_2\text{RuS}_4\) requires C, 52.21; H, 4.48; N, 1.35; I, 12.26%.

Ru(CN)(\(\eta^1\)-CS\(_2\)Me)(CO)(PPh\(_3\))\(_2\). \(\text{Cyano-monohapto-dithiomethyleneesterdicarbonylbis(triphenylphosphine)}\)ruthenium(II).

To a cold solution of [Ru(\(\eta^2\)-CS\(_2\)Me)(CO)(PPh\(_3\))\(_2\)]\(\text{CF}_3\text{SO}_3\) (0.3 g) in dichloromethane (10 ml) was added a filtered solution of sodium cyanide (0.05 g) in ethanol (30 ml). The solution was stirred at -5°C for 15 min. The dichloromethane was removed without heating and the salmon needles were collected and washed with ethanol (0.255 g, 98%). M.p. 146-147°C. Anal. Found: C, 61.62; H, 4.59; N, 1.56%.

\(\text{C}_{41}\text{H}_{33}\text{NO}_2\text{P}_2\text{RuS}_2\) requires C, 61.55; H, 4.16; N, 1.75%.

Ru(CN)(\(\eta^2\)-CS\(_2\)Me)(CO)(PPh\(_3\))\(_2\). \(\text{Cyano-dihapto-dithiomethyleneestercarbonylbis-(triphenylphosphine)}\)ruthenium(II).

Ru(CN)(\(\eta^1\)-CS\(_2\)Me)(CO)(PPh\(_3\))\(_2\) (0.15 g) was dissolved in dichloromethane (20 ml) and was heated under reflux for 5 min. Addition of ethanol (20 ml) and removal of dichloromethane gave yellow crystals of the title complex which were washed with ethanol and hexane. \(^1\text{H N.M.R. (CDCl}_3\)
showed the presence of dichloromethane $\tau,4.82\text{[s, 4.8H]}$. The large quantity of dichloromethane is a consequence of the artificially low integral for protons of the complex which occurs because a deuterochloroform solvate is precipitated in the N.M.R. tube. Analysis indicates the presence of 0.5 mol dichloromethane of solvation (0.144 g, 99.3%). M.p. 160 - 162°C. Anal. Found: C, 59.99; H, 4.72; N, 1.80%. $\text{C}_{40}\text{H}_{33}\text{NOP}_{2}\text{RuS}_{2}\{\text{CH}_{2}\text{Cl}_{2}\}_{0.5}$ requires C, 59.81; H, 4.21; N, 1.72%.

RuH($\eta^1$-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$. Hydrido-monohapto-dithiomethylenebis(triphenylphosphine)ruthenium(II).

$[\text{Ru}(\eta^2$-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$]\text{CF}_3\text{SO}_3$ (0.3 g) was dissolved in ethanol (30 ml) and a filtered solution of sodium borohydride (0.05 g) in ethanol (10 ml) was added. The solution was cooled in an ice-bath and stirred for 10 min. The solution was then filtered and washed with ethanol and hexane (0.23 g, 93.2%). Recrystallisation was effected from dichloromethane-ethanol (without heating) to afford pink rectangular crystals (0.2 g, 80%). M.p. 120°C (crystals begin to turn yellow above 60°C).

$[\text{RuH(C(SMe)$_2$}](\text{CO})_2(\text{PPh$_3$})_2]$\text{CF}_3\text{SO}_3$. Hydridobis(methylthiolato)carbene-bis(triphenylphosphine)-dichloromethanesulphonate.

RuH($\eta^1$-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$ (0.3 g) was dissolved in benzene (20 ml) and methyl triflate (0.2 ml) was added. A white crystalline solid formed almost immediately. Hexane (10 ml) was added and the product was collected and washed with hexane. Recrystallisation from dichloromethane-ethanol-cyclohexane gave the title compound as pale yellow crystals.
which contained 0.33 equivalent cyclohexane of solvation (0.32 g, 85.4%). \textsuperscript{1}H N.M.R. (CDCl\textsubscript{3}) shows \(\tau, 8.57\) (s, 4H, C\textsubscript{6}H\textsubscript{12}). M.p. 85°C (melts with decomposition). Anal. Found: C, 54.78; H, 4.55; P, 6.49%. C\textsubscript{42}H\textsubscript{37}F\textsubscript{3}O\textsubscript{5}P\textsubscript{2}Ru\textsubscript{3} (C\textsubscript{6}H\textsubscript{12})\textsubscript{0.33} requires C, 54.71; H, 4.01; P, 6.41%.

\[
\text{OsH(}\eta^1-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2\text{: Hydrido-monohapto-dithioethylstereidicarbonyl-bis(triphenylphosphine)}\text{osmium(II)}. \\
\]

\([\text{Os(}\eta^2-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3 \text{ (0.3 g) was dissolved in ethanol (50 ml), a filtered solution of sodium borohydride (0.05 g) in ethanol (10 ml) was added and the solution was stirred for 15 min. The pink crystals were collected and washed with ethanol and hexane. Recrystallisation from benzene-hexane afforded pink cubes. The X-ray crystal structure shows the crystals to be the hemi-benzene solvate of the title compound (0.265 g, 99%). M.p. 182-184°C. Anal. Found: C, 57.66; H, 5.00; P, 6.89%. C\textsubscript{40}H\textsubscript{33}O\textsubscript{2}O\textsubscript{2}P\textsubscript{2}S\textsubscript{2} (C\textsubscript{6}H\textsubscript{6})\textsubscript{0.5} requires C, 57.32; H, 4.03; P, 6.88%.}

**THIOCARBONYL COMPLEXES**

\[
\text{RuCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2\text{: Dichlorocarbonylthiocarbonylbis(triphenylphosphine)}\text{-ruthenium(II)}. \\
\]

\([\text{Ru(}\eta^2-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3 \text{ (0.3 g) was heated under reflux in a solution comprised of toluene (50 ml), ethanol (5 ml) and concentrated hydrochloric acid (1.5 ml) for 1.5 h. Upon removal of the toluene yellow crystals were deposited which were collected and washed with}


ethanol and hexane (0.24 g, 98%). The product was characterised by comparison of the I.R. spectrum with that of an authentic sample.

Other MX₂(CO)(CS)(PPh₃)₂ complexes were produced similarly.

\[ \text{[Ru(\eta^2-S₂CNET₂)(CO)(CS)(PPh₃)₂]BF₄} \quad \text{Dihapto-diethylidithiocarbamatocarbonyl-thiocarbonylbis(triphenylphosphine)-ruthenium(II)tetrafluoroborate.} \]

Ru(\eta^2-S₂CNET₂)(\eta^1-CS₂Me)(CO)(PPh₃)₂ (0.3 g) was dissolved in dichloromethane-ethanol (30 ml, 1:1) and tetrafluoroboric acid (ca. 40%, 0.2 ml) was added. Upon removal of the dichloromethane cream crystals were deposited which were washed with diethyl ether. Recrystallisation from dichloromethane-ethanol-cyclohexane yielded cream prisms of the solvate \[ \text{[Ru(\eta^2-S₂CNET₂)(CO)(CS)(PPh₃)₂]BF₄·(CH₂Cl₂)·0.5(C₆H₁₂)·0.25} \quad (0.325 g, 97.1%). \]

\(^1\text{H N.M.R. (CDCl₃) shows δ, 4.7 [s, 1H, CH₂Cl₂], 3.57 [s, 3H, C₆H₁₂].} \]

M.p. 193-198°C. Anal. Found: C, 54.53; H, 4.93; N, 1.35%.

\[ \text{C}_{43}\text{H}_{40}\text{BF}_4\text{NOP}_2\text{RuS}_3\cdot(\text{CH}_2\text{Cl}_2)\cdot0.5(\text{C}_6\text{H}_{12})\cdot0.25 \quad \text{requires C, 54.25; H, 4.45; N, 1.41%}. \]

Ru(CO)₂(CS)(PPh₃)₂. \text{Dicarbonylthiocarbonylbis(triphenylphosphine)-ruthenium(0).} \]

RuH(\eta₁-CS₂Me)₂(CO)₂(PPh₃)₂ (0.3 g) was heated in degassed methanol (10 ml) for 30 min. The mixture was cooled on ice and the pale orange crystals were collected and washed with ethanol and hexane (0.13 g, 46.2%). The product was characterised by comparison of the I.R. spectrum with that of an authentic sample.
Os(CO)$_2$ (CS)$_2$ (PPh$_3$)$_2$. Dicarbonylthiocarbonylbis(triphenylphosphine)osmium(O).

Osh$_1$(CS$_2$Me) (CO)$_2$ (PPh$_3$)$_2$ (0.3 g) was heated under reflux in degassed 2-methoxyethanol (10 ml) for 40 min. The mixture was cooled on ice and the yellow-orange crystals were collected and washed with ethanol and hexane (0.24 g, 86.5%). M.p. 195-196°C. Anal. Found: C, 57.32; H, 3.96; P, 7.84%. C$_{39}$H$_{30}$O$_2$OsP$_2$S requires C, 57.48; H, 3.71; P, 7.60%.

**MISCELLANEOUS COMPOUNDS**

RuCl$_2$(CO)(CNPh) (PPh$_3$)$_2$. Dichlorocarbonylphenylisocyanidebis(triphenylphosphine)ruthenium(II).

[Ru(η$^2$-SCNPh)(CO)$_2$(PPh$_3$)$_2$]Cl (0.3 g) was heated under reflux in degassed 2-methoxyethanol (25 ml) containing concentrated hydrochloric acid (2 ml) for 12 h. The solvent was completely removed and the product recrystallised from dichloromethane-ethanol and then dichloromethane-ethanol-cyclohexane. The product was characterised by comparison of the I.R. spectrum with that of an authenticated sample. 109

RuH(η$^2$-S$_2$COEt) (CO) (PPh$_3$)$_2$. Dihapto-($o$-ethyldithiocarbonato)hydridocarbonylbis(triphenylphosphine)ruthenium(II).

RuHCl(CO)(PPh$_3$)$_3$ (0.3 g) was dissolved in dichloromethane (50 ml) and sodium ethylxanthate (0.1 g) in ethanol (20 ml) was added. The solution was warmed gently for 5 min and upon removal of the dichloromethane cream crystals were deposited which were collected and washed with water, ethanol and hexane. Recrystallisation from dichloromethane-ethanol yielded creamy-lemon crystals (0.23 g, 94.1%). M.p. 164-170°C (melts with decomposition). Anal. Found: C, 61.70; H, 4.87%.

C$_{40}$H$_{36}$O$_2$P$_2$RuS$_2$ requires C, 61.92; H, 4.68%. 
RuH\((\eta^2-S_{2}CNMeH)\)(CO)(PPh\(_3\))\(_2\). **Hydrido-dihapto-methyldithiocarbamatocarbonyl-bis(triphenylphosphine)ruthenium(II).**

RuHCl(CO)(PPh\(_3\))\(_3\) (0.3 g) was dissolved in dichloromethane (50 ml) and sodium methyldithiocarbamate (0.1 g) in ethanol (20 ml) was added. The solution was warmed gently for 5 min and cream crystals separated on removal of dichloromethane. These were collected and washed with water, ethanol and hexane. Recrystallisation from dichloromethane-ethanol yielded creamy-lemon crystals (0.23 g, 96%). M.p. 186-191°C (melts with decomposition). Anal. Found: C, 61.24; H, 4.66; N, 1.69%. C\(_{39}\)H\(_{35}\)NOP\(_2\)RuS\(_2\) requires C, 61.56; H, 4.64; N, 1.84%.

RuCl(\(\eta^2-S_{2}CNMeH\))(CO)(PPh\(_3\))\(_2\). **Chloro-dihapto-methyldithiocarbamatocarbonyl-bis(triphenylphosphine)ruthenium(II).**

RuH(\(\eta^2-S_{2}CNMeH\))(CO)(PPh\(_3\))\(_2\) (0.15 g) was heated under reflux in dichloromethane-ethanol solution (30 ml, 4:1) with concentrated hydrochloric acid (0.2 ml) for 15 min. Upon removal of dichloromethane lemon needles formed which were collected and washed with water, ethanol and hexane. Recrystallisation from dichloromethane-ethanol afforded lemon needles containing 0.25 equivalent dichloromethane of solvation (0.155 g, 96.3%). \(^1\)H N.M.R. shows \(\tau, 4.7[s, 0.5H, CH_2Cl_2]\). M.p. 171-173°C. Anal. Found: C, 57.73; H, 4.78; N, 1.54%.

C\(_{39}\)H\(_{34}\)ClNOP\(_2\)RuS\(_2\)(CH\(_2\)Cl\(_2\))\(_{0.25}\) requires C, 57.73; H, 4.26; N, 1.72%.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CS}$</th>
<th>$\nu_{CO}$</th>
<th>$\nu_{CN}$</th>
<th>Other Bands</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCl$_2$(CO)(CS)L$_2$</td>
<td>1302</td>
<td>2050,2040</td>
<td></td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>RuBr$_2$(CO)(CS)L$_2$</td>
<td>1300</td>
<td>2040,2030</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuI$_2$(CO)(CS)L$_2$</td>
<td>1296</td>
<td>2055,2030</td>
<td>290,260 ($\nu_{Os-Cl}$)</td>
<td>61,110</td>
<td></td>
</tr>
<tr>
<td>OsCl$_2$(CO)(CS)L$_2$</td>
<td>1315</td>
<td>2040,2030,2020</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsI$_2$(CO)(CS)L$_2$</td>
<td>1300</td>
<td>2030</td>
<td></td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>RuCl(OClO$_3$) (CO) (CS)L$_2$</td>
<td>1320</td>
<td>2065</td>
<td>1045m,1010s,890w (OCIO$_3$)</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>RuCl$_2$(CNR) (CS)L$_2$</td>
<td>1295</td>
<td></td>
<td>2155</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>RuBr$_2$(CNR) (CS)L$_2$</td>
<td>1295</td>
<td></td>
<td>2145</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>RuI$_2$(CNR) (CS)L$_2$</td>
<td>1290</td>
<td></td>
<td>2130</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>RuI(OClO$_3$) (CNR) (CS)L$_2$</td>
<td>1305</td>
<td></td>
<td>2170</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>[RuCl((CO) (CNR) (CS)L$_2$)ClO$_4$</td>
<td>1335</td>
<td>2075</td>
<td>2200,2160</td>
<td>1090vs (ClO$_4$)</td>
<td>115</td>
</tr>
<tr>
<td>[RuBr((CO) (CNR) (CS)L$_2$)ClO$_4$</td>
<td>1330</td>
<td>2070</td>
<td></td>
<td>2200,2155</td>
<td>1095vs (ClO$_4$)</td>
</tr>
<tr>
<td>[RuI((CO) (CNR) (CS)L$_2$)ClO$_4$</td>
<td>1327</td>
<td>2065</td>
<td></td>
<td>2195,2155</td>
<td>1090vs (ClO$_4$)</td>
</tr>
<tr>
<td>OsCl$_2$(CNR) (CS)L$_2$</td>
<td>1305</td>
<td></td>
<td>2150</td>
<td></td>
<td>110</td>
</tr>
<tr>
<td>[Ru(n$_2$-S$_2$CNET$_2$) (CO) (CS)L$_2$)BF$_4$</td>
<td>1310</td>
<td>2040</td>
<td>1509w</td>
<td>1470w,1280m,1205w,915w,850w; 1050vs (BF$_4$)</td>
<td></td>
</tr>
<tr>
<td>Ru(CO)$_2$(CS)L$_2$</td>
<td>1215</td>
<td>1970,1905</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os(CO)$_2$(CS)L$_2$</td>
<td>1230</td>
<td>1955,1890</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh$_3$; R = p-tolyl) (a) Phosphine bands not quoted in any table; major bands measured in nujol mulls unless otherwise stated in all tables; (b) very strong; (c) strong tending to very strong; (d) measured as petroleum jelly mull; (e) p-tolyl isocyanide bands at 1500 cm$^{-1}$ and near 800 cm$^{-1}$ not quoted in any table; (f) all perchlorate complexes exhibit single sharp strong band near 620 cm$^{-1}$.
<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_{CS}^a)</th>
<th>(v_{CO}^b)</th>
<th>(v_{CN}^c)</th>
<th>Other Bands</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru((n^2-CS_2)(CO)_2)L_2</td>
<td>1118s</td>
<td>2010,1945</td>
<td>645m ((v_{C-S}))</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>Ru((n^2-CS_2)(CO)(CN)R)L_2</td>
<td>1106s,1066m</td>
<td>1914</td>
<td>2120</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>Os((n^2-CS_2)(CO)_2)L_2</td>
<td>1115s</td>
<td>2000,1940</td>
<td>660m ((v_{C-S}))</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>Os((n^2-CS_2)(CO)(CN)R)L_2</td>
<td>1095m,1070m</td>
<td>1905</td>
<td>2120</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>[Ru((n^2-CS_2Me)(CO)_2)L_2]^f</td>
<td>1115mg</td>
<td>2055,1995</td>
<td>675m ((v_{C-S}))</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>[Ru((n^2-CS_2Me)(CO)(CN)R)L_2]^f</td>
<td>1100md</td>
<td>2065</td>
<td>2145</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>[Ru((n^2-CS_2nPr)(CO)(CN)R)L_2]ClO_4</td>
<td>e</td>
<td>2065</td>
<td>2150</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>[Os((n^2-CS_2Me)(CO)_2)L_2]^f</td>
<td>1070m</td>
<td>2050,1995</td>
<td>760w ((v_{C-S})^d)</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>[Os((n^2-CS_2Me)(CO)(CN)R)L_2]ClO_4</td>
<td>e</td>
<td>1955</td>
<td>2130</td>
<td>61,115</td>
<td></td>
</tr>
<tr>
<td>RuCl((n^2-CS_2Me)(CO))L_2</td>
<td>1085md</td>
<td>1948</td>
<td>775m ((v_{C-S}))</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ru((CN)(n^2-CS_2Me)(CO))L_2</td>
<td>1090md</td>
<td>1930</td>
<td>2110w</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ru((CN)(n^2-CS_2Me)(CO))L_2</td>
<td>980m</td>
<td>2060,2000</td>
<td>780w ((v_{C-S})^d)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ru((n^2-O_2CMe)(n^1-CS_2Me)(CO))L_2</td>
<td>1013s</td>
<td>1942</td>
<td>1520w,1465m ((v_{CO})); 795m ((v_{C-S})); 945w</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ru((n^2-S_2CNET_2)(n^1-CS_2Me)(CO))L_2</td>
<td>998m</td>
<td>1930</td>
<td>1490m</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>RuH((n^1-CS_2Me)(CO))L_2</td>
<td>1000m</td>
<td>2050,1970</td>
<td>760w ((v_{C-S})^d); 1360w,1270m,1213w,1145w,915w,845w,935w</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Osh((n^1-CS_2Me)(CO))L_2</td>
<td>1005m</td>
<td>2055,1985,1970</td>
<td>1930w ((v_{RuH})); 800w ((v_{RuH})); 770w ((v_{C-S})); 925w</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>[Ru((n^2-S_2CNET_2)(C[SM]e)_2)(CO))L_2]I</td>
<td>1945</td>
<td>1500m</td>
<td>1370w,1275w,1210w,1150w,895w,850w,850w,995w</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>[RuH((C[SM]e)_2)(CO)_2)L_2]CF_3SO_3</td>
<td>2050,2000</td>
<td>965w,775w (carbene)</td>
<td>1410w,1270vs,1225m,1150m,1030vs,640vs ((CF_3SO_3)); 800w ((v_{RuH})); 373w,925w,765w (carbene)</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Footnotes: \((L = PPh_3; R = p\text{-}toly1)\). (a) medium bands tending to strong;
(b) very strong;
(c) strong tending to very strong;
(d) band partially obscured by nearby phosphine band;
(e) band obscured by perchlorate band at 1090 cm\(^{-1}\);
(f) isolated as perchlorate, trifluoromethanesulphonate and iodide salts;
(g) band quoted for iodide salt;
(h) ClO\(_4\) bands near 1090vs, 620 m-s.
### Table 2.3  I.R. DATA (cm\(^{-1}\)) FOR OTHER COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{\text{CO}}^a)</th>
<th>(\nu_{\text{M-H}})</th>
<th>Other Bands</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuHCl(CO)L(_3)</td>
<td>1924, 1903</td>
<td>2017w</td>
<td>3500w ((\nu_{\text{OH}})); 1625w ((\delta_{\text{OH}})); 1110m, 1060s, 980m (BF(<em>4^−)); 820w ((\delta</em>{\text{RuH}}))</td>
<td>120(b)</td>
</tr>
<tr>
<td>RuH(_2)(CO)L(_3)</td>
<td>1940</td>
<td>1900w, 1960w</td>
<td></td>
<td>122</td>
</tr>
<tr>
<td>[RuH(H(_2)O)(CO)L(_3)]BF(_4^−)</td>
<td>1940</td>
<td>c</td>
<td>1100m, 1010s, 970s (BF(<em>4^−)); 3350w ((\nu</em>{\text{OH}})); 1620w ((\delta_{\text{OH}})); 830w ((\delta_{\text{RuH}}))</td>
<td></td>
</tr>
<tr>
<td>[RuH(H(_2)O)(CO)(_2)L(_2)]BF(_4^−)</td>
<td>2070, 1995</td>
<td>c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RuH(_2)(CO)(_2)L(_2)</td>
<td>2010, 1975, 1950</td>
<td>1878w, 1820w</td>
<td>800m ((\delta_{\text{RuH}}))</td>
<td></td>
</tr>
<tr>
<td>Ru(CO)(_2)L(_3)</td>
<td>1905</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsHCl(CO)L(_3)</td>
<td>1912</td>
<td>2097m</td>
<td>290s ((\nu_{\text{OsCl}}))</td>
<td>108</td>
</tr>
<tr>
<td>OsH(_2)(CO)L(_3)</td>
<td>1950</td>
<td>2051m, 1852m</td>
<td>802m, 790w ((\delta_{\text{OSH}}))</td>
<td>110</td>
</tr>
<tr>
<td>[OsH(H(_2)O)(CO)L(_3)]BF(_4^−)</td>
<td>1930</td>
<td>2080w</td>
<td>1628w ((\delta_{\text{OH}})); 1120m, 1080s, 977m (BF(<em>4^−)); 830w (br) ((\delta</em>{\text{OSH}}))</td>
<td></td>
</tr>
<tr>
<td>[OsH(CO)(_2)L(_3)]BF(_4^−)</td>
<td>1980</td>
<td>2080w, 2042w</td>
<td>1625w ((\delta_{\text{OH}})); 1055vs (BF(<em>4^−)); 800w ((\delta</em>{\text{OSH}}))</td>
<td></td>
</tr>
<tr>
<td>Os(CO)(_2)L(_3)</td>
<td>1895</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os((\eta^2)-C(_2)H(_4))(CO)(_2)L(_2)</td>
<td>1955, 1895</td>
<td></td>
<td>1115m ((\nu_{\text{C=C}}))</td>
<td>110</td>
</tr>
<tr>
<td>RuH((\eta^2)-S(_2)COEt)(CO)L(_2)</td>
<td>1945</td>
<td>1905m</td>
<td>1370m, 1295m, 1215vs, 1160m, 1120w, 1055m, 1045m, 1005w, 970w; 775w ((\delta_{\text{RuH}}))</td>
<td>110</td>
</tr>
<tr>
<td>RuH((\eta^2)-S(_2)CNHMe)(CO)L(_2)</td>
<td>1930</td>
<td>c</td>
<td>3270w ((\nu_{\text{NH}})); 1515m ((\nu_{\text{CN}})); 1350m, 1330w, 1185w, 1028w, 965m; 785vw ((\delta_{\text{RuH}}))</td>
<td></td>
</tr>
<tr>
<td>RuCl((\eta^2)-S(_2)CNHMe)(CO)L(_2)</td>
<td>1944</td>
<td></td>
<td>2950w ((\nu_{\text{NH}})); 1508 m ((\nu_{\text{CN}})); 1344m, 1175w, 1025w, 963m</td>
<td></td>
</tr>
<tr>
<td>RuCl(_2)(CO)(CNPh)L(_2)</td>
<td>1985, 1960</td>
<td></td>
<td>2145vs ((\nu_{\text{CN}}))</td>
<td>109</td>
</tr>
</tbody>
</table>

**Footnotes:**  
(L = PPh\(_3\))  
(a) very strong;  
(b) measured as petroleum jelly mull;  
(c) band not visible.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (τ) and Coupling Constants (Hz)</th>
</tr>
</thead>
</table>
| \([\text{Ru}(\eta^2-\text{S}_{2}CNEt_2)(\text{CO})(\text{CS})L_2]BF_4\) | 9.16, t, 3H, CH\textsubscript{2}-CH\textsubscript{3}, J(HH) = 7  
9.20, t, 3H, CH\textsubscript{2}-CH\textsubscript{3}, J(HH) = 7  
7.13, dq, 4H, -CH\textsubscript{2}-CH\textsubscript{3}, J(HH) = 7  
2.45, d, 32H, Ph\textsuperscript{b,f} |
| \([\text{Ru}(\eta^2-\text{CS}_{2}\text{Me})(\text{CO})_2L_2]CF_3SO_3\) | 7.9, s, 3H, S-CH\textsubscript{3}  
2.42, d, 32H, Ph |
| \([\text{Ru}(\eta^2-\text{CS}_{2}\text{Me})(\text{CO})(\text{CN}-\text{R-tolyl})L_2]CF_3SO_3\) | 7.87, s, 3H, C\textsubscript{6}H\textsubscript{4}-CH\textsubscript{3}  
7.70, s, 3H, S-CH\textsubscript{3}  
3.42, q, 4H, -C\textsubscript{6}H\textsubscript{4}-\textsuperscript{b}  
2.52, m, 33H, Ph |
| \([\text{Ru}(\eta^2-\text{CS}_{2}\text{Pr})(\text{CO})(\text{CN}-\text{R-tolyl})L_2]ClO_4\) | 9.30, t, 3H, CH\textsubscript{2}-CH\textsubscript{3}, J(HH) = 6.5  
8.88, m, 2H, CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{3}  
7.68, s, 3H, C\textsubscript{6}H\textsubscript{4}-CH\textsubscript{3}  
7.53, q, 2H, S-CH\textsubscript{2}-CH\textsubscript{2}-CH\textsubscript{3}, J(HH) = 6.5  
3.37, q, 4H, -C\textsubscript{6}H\textsubscript{4}-  
2.53, m, 30H, Ph |
| \([\text{Os}(\eta^2-\text{CS}_{2}\text{Me})(\text{CO})_2L_2]ClO_4\) | 7.76, s, 3H, S-CH\textsubscript{3}  
2.50, m, 31H, Ph |
| \(\text{Ru}(\text{CN})(\eta^2-\text{CS}_{2}\text{Me})(\text{CO})_2L_2\) | 8.06, s, 3H, S-CH\textsubscript{3}  
2.42, m, 36H, Ph |
| \(\text{Ru}(\text{CN})(\eta^1-\text{CS}_{2}\text{Me})(\text{CO})_2L_2\) | 8.02, s, 3H, S-CH\textsubscript{3}  
2.52, m, 33H, Ph |
| \(\text{Ru}(\eta^2-\text{O}_{2}\text{Me})(\eta^1-\text{CS}_{2}\text{Me})(\text{CO})_2L_2\) | 9.50, s, 3H, O\textsubscript{2}C-CH\textsubscript{3}  
8.10, s, 3H, S-CH\textsubscript{3}  
2.50, m, 30H, Ph |
### Table 2.4 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (τ) and Coupling Constants (Hz)</th>
</tr>
</thead>
</table>
| Ru(\(\eta^2\text{-S}_2\text{CNET}_2\)) (\(\eta^1\text{-CS}_2\text{Me}\)) (CO)\(_2\) \(_2\) | 9.43, t, 3H, CH\(_2\)\text{-CH}_3, J(\(HH\)) = 7  
9.32, t, 3H, CH\(_2\)\text{-CH}_3, J(\(HH\)) = 7  
8.13, s, 3H, S-CH\(_3\)  
7.16, q, 2H, N-CH\(_2\)\text{-CH}_3, J(\(HH\)) = 7.5  
7.03, q, 2H, N-CH\(_2\)\text{-CH}_3, J(\(HH\)) = 7.5  
2.57, m, 34H, Ph |
| RuH(\(\eta^1\text{-CS}_2\text{Me}\)) (CO)\(_2\) \(_2\) | 13.92, t, 1H, Ru-H, J(\(HP\)) = 19.4  
8.16, s, 3H, S-CH\(_3\)  
2.58, m, 55H, Ph |
| OSH(\(\eta^1\text{-CS}_2\text{Me}\)) (CO)\(_2\) \(_2\) | 14.35, t, 1H, Os-H, J(\(HP\)) = 20.2  
8.55, s, 3H, S-CH\(_3\)  
2.52, m, 30H, Ph |
| [Ru(\(\eta^2\text{-S}_2\text{CNET}_2\))(S\text{CMe}_2\)) (CO)\(_2\) \(_2\)I] | 9.45, t, 3H, CH\(_2\)\text{-CH}_3, J(\(HH\)) = 7.5  
9.29, t, 3H, CH\(_2\)\text{-CH}_3, J(\(HH\)) = 7.5  
7.63, d(br), 6H, S-CH\(_3\)  
7.13, m, 4H, N-CH\(_2\)\text{-CH}_3  
2.58, m, 34H, Ph |
| [RuH(S\text{CMe}_2\)) (CO)\(_2\) \(_2\)] \text{CF}_3\text{SO}_3 | 15.13, t, 1H, Ru-H, J(\(HP\)) = 18  
7.70, m, 6H, S-CH\(_3\)  
2.48, m, 30H, Ph |
| [RuH(H\(_2\text{O}\)) (CO)\(_3\) \(_2\)] \text{BF}_4 | 17.27, dt, 1H, Ru-H, J(\(HP_{trans}\)) = 101  
\(\nu\), 6.75, 2H, \(\nu\)H\(_2\text{O}\)  
2.75, m, 45H, Ph |
| [RuH(H\(_2\text{O}\)) (CO)\(_2\) \(_2\)] \text{BF}_4 | 14.30, t, 1H, Ru-H, J(\(HP\)) = 18.5  
\(\delta\), 6.87, s, 2H, \(\delta\)H\(_2\text{O}\)  
2.55, m, 32H, Ph |
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (τ) and Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OSh(H₂O)(CO)L₃]BF₄</td>
<td>17.07, dt, 1H, Os-H, $^2J(\text{HP}_{\text{trans}}) = 84$</td>
</tr>
<tr>
<td></td>
<td>5.47, s, 2H, H₂O</td>
</tr>
<tr>
<td></td>
<td>2.83, m, 5OH, Ph</td>
</tr>
<tr>
<td>[OSh(CO)₂L₃]BF₄</td>
<td>19.41, dt, Os-H, $^2J(\text{HP}_{\text{trans}}) = 42.5$</td>
</tr>
<tr>
<td></td>
<td>$^2J(\text{HP}_{\text{cis}}) = 23.2$</td>
</tr>
<tr>
<td></td>
<td>2.78, Ph</td>
</tr>
<tr>
<td>RuH($\eta^2$-S₂COEt)(CO)L₂</td>
<td>20.60, t, 1H, Ru-H, $^2J(\text{HP}) = 20$</td>
</tr>
<tr>
<td></td>
<td>9.07, t, 3H, CH₂−CH₃, $^2J(\text{HH}) = 7$</td>
</tr>
<tr>
<td></td>
<td>6.39, q, 2H, O−CH₂−CH₃, $^2J(\text{HH}) = 7$</td>
</tr>
<tr>
<td></td>
<td>2.50, m, 3OH, Ph</td>
</tr>
<tr>
<td>RuH($\eta^2$-S₂CNMeH)(CO)L₂</td>
<td>21.31, t, 1H, Ru-H, $^2J(\text{HP}) = 20$</td>
</tr>
<tr>
<td></td>
<td>7.75, d, 3H, N−CH₃, $^2J(\text{HH}) = 5$</td>
</tr>
<tr>
<td></td>
<td>4.37, s(br), 1H, N−H</td>
</tr>
<tr>
<td></td>
<td>2.52, m, 32H, Ph</td>
</tr>
<tr>
<td>RuCl($\eta^2$-S₂CNMeH)(CO)L₂</td>
<td>7.15, d, 3H, N−CH₃, $^2J(\text{HH}) = 5$</td>
</tr>
<tr>
<td></td>
<td>2.71, m, 34H, Ph</td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh₃)  
(a) decomposes in solution, integral unreliable;  
(b) all phenyl resonances quoted as midpoint of multiplet in all $^1$H N.M.R. tables;  
(c) restricted rotation about carbene C-S bond produces isomers;⁵³  
(d) integral cannot be evaluated as no reliable comparison;  
(e) N−H resonance not observed;  
(f) phenyl resonances include CHCl₃ impurities in CDCl₃;  
(g) all H₂O signals disappear on addition of D₂O.
A principal aim of this project was to synthesise complexes containing both the hydrido and thiocarbonyl ligands in order to attempt to observe hydride transfer to the thiocarbonyl ligand and to produce a series of zerovalent complexes by reductive deprotonation of cationic $d^6$ hydrido-containing complexes. Both objectives have been realised and the former is discussed in this chapter. The reductive deprotonation of $d^6$ thiocarbonyl complexes is treated in chapter 4.

The Significance of Hydride Transfer Reactions

Hydride transfer reactions from metal to ligand are fundamental to hydrogenation and other homogeneously catalysed reactions. Several very conspicuous problems confront modern organometallic chemistry where it is apparent that solutions could be partly dependent upon hydride transfer reactions. Two such problems are concerned with gaining an understanding of and producing homogeneous catalysts for the reactions in which nitrogen is reduced to ammonia and carbon monoxide is reduced to methanol and other organic molecules.

$$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$$

$$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$$

Both processes are of outstanding technological importance and are catalysed by heterogeneous transition metals or transition metal compounds. However, both dinitrogen and carbon monoxide are very
inert so that considerable energy is consumed in the industrial processing. The C-O and N-N triple bonds are the strongest chemical bonds known, $257.26 \pm 0.77 \text{ kcal mol}^{-1}$ and $226.8 \pm 1.5 \text{ kcal mol}^{-1}$ respectively. Yet nitrogen-fixing bacteria can produce ammonia from molecular nitrogen and water at ordinary temperatures and pressures using chemically mild reducing agents such as sugars, where the catalyst is the enzyme nitrogenase which contains atoms of molybdenum and iron. Dinitrogen complexes of tungsten and molybdenum have been reduced to ammonia in up to 90% yield and, while metal hydrides are thought not to be involved, the mechanism is still to be determined.

\[
\text{cis-W(N}_2\text{)}_2(\text{PMe}_2\text{Ph})_4 \xrightarrow{\text{H}_2\text{SO}_4^{\text{THF}}} \text{N}_2 + 2\text{NH}_3 + \text{W}^{\text{VI}} \text{ products.}
\]

The reduction of carbon monoxide is not a biologically important process, however, recently there has been an increasing research effort directed towards the problem of developing catalytic cycles which, by reducing carbon dioxide, will reproduce the results of photosynthesis. (The C-O bond strength in carbon dioxide is $127.2 \pm 0.1 \text{ kcal mol}^{-1}$.) This interest has been accentuated by the concern about alternative petrochemical feedstocks. The reduction of carbon dioxide is conceivably more important than processes based on petroleum or coal since the major portion of terrestrial carbon is in the form of carbon dioxide and carbonates. It is reasonable to anticipate that if a technologically useful reaction is discovered then hydride transfer from metal to ligand will be part of the mechanistic description. This is the case in
the synthesis of 1,2-propanediol formates,\textsuperscript{147} formamides,\textsuperscript{148} alkyl formates\textsuperscript{149,150} and formic acid\textsuperscript{151} from carbon dioxide, water and, respectively, methyl oxirane, secondary amines, alcohols and water, which are catalysed by transition metal complexes.

The catalytic synthesis of hydrocarbon products from carbon monoxide and hydrogen is commonly referred to as the Fischer-Tropsch synthesis reaction.\textsuperscript{152} The chemistry detailed in this chapter is of possible relevance to this process. Recall that the problems for organometallic chemistry in dealing with the Fischer-Tropsch synthesis are firstly to find homogeneous catalysts and secondly to endeavour to understand the reaction. The Fischer-Tropsch reaction is at present exclusively dependent upon heterogeneous catalysts which are not highly selective\textsuperscript{153} and are thus wasteful of reagents.\textsuperscript{154} Heterogeneous catalysts do present several advantages over homogeneous catalysts, but the key performance factor which has continued to promote efforts to find homogeneous substitutes is selectivity.\textsuperscript{155} The transition metal cluster complexes $\text{Os}_3(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$\textsuperscript{156,157} and derivatives of $\text{Rh}_6(\text{CO})_{16}$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$\textsuperscript{158} have been reported to function as homogeneous catalysts for the reduction of carbon monoxide. Several mononuclear transition metal complexes promote this reduction stoichiometrically but produce different products -

\[
(\eta^5-C_5\text{Me}_5)_2\text{Zr}(\text{CO})_2 + 2\text{H}_2 \xrightarrow{\text{hv \ or \ 110^\circ\text{C}}} (\eta^5-C_5\text{Me}_5)_2\text{ZrH(OCH}_3\text{)} + \text{CO} \\
\downarrow \text{2HCl} \\
(\eta^5-C_5\text{Me}_5)_2\text{ZrCl}_2 + \text{H}_2 + \text{MeOH} \text{ 159}
\]
However, no homogeneous process is yet in use which is competitive with presently available heterogeneous processes. Considerations such as catalyst separation and capital investment are further problems for homogeneous catalytic processes.

The mechanism of the Fischer-Tropsch reaction has been a subject of considerable speculation, but direct evidence for any of the intermediates in this obviously stepwise process does not exist. A major contribution of organometallic chemistry to surface reactions is to provide well-characterised models of plausible intermediates and for the Fischer-Tropsch reaction formyl complexes are attractive possibilities for the first step. Formaldehyde complexes, for which no organometallic analogues are known, are worthy candidates for the second step, and methoxy complexes, for which numerous organometallic examples exist, provide a logical third step for that part of the reaction sequence that leads to methanol. Hydride migration to the carbonyl ligand has never been observed, probably because the carbonyl ligand is very thermodynamically stable. For carbon monosulphide, the sulphur analogue of carbon monoxide, migration reactions to the
ligand are more likely because the reduction in C-S bond multiplicity which accompanies such processes is more favourable [Chapter 1 section III]. The lower stability of C-S multiple bonds when compared to C-O multiple bonds should also stabilise π-bonded intermediates in the sulphur case. Because sulphur is not "hard" like oxygen, transition metal-sulphur bonds are expected to be more stable than analogous transition metal-oxygen bonds thus adding to the stability of a π-bonded C-S compound such as a thioformaldehyde adduct. For these reasons attempts were made to observe stepwise hydride transfer to the CS ligand resulting eventually in the formation of methyl thiol,

\[ \text{H} \quad \text{CS} \rightarrow \text{H} \quad \text{C} \quad \text{S} \rightarrow \text{H} \quad \text{C} \quad \text{S} \rightarrow \text{H} \quad \text{C} \quad \text{S} \rightarrow \text{H} \quad \text{C} \quad \text{S} \rightarrow \text{H} \quad \text{C} \quad \text{S} \rightarrow \text{H} \quad \text{C} \quad \text{S} \rightarrow \text{M} + \text{CH}_3\text{SH} \].

The work reported in the following sections describes the results of these attempts. The production of the very useful thiocarbonyl complex OsCl\(_2\)(CS)(PPh\(_3\))\(_3\) and hydrido derivatives of this species will be reported first as these complexes are essential precursors to reduction of the CS ligand.

3.1 OsCl\(_2\)(CS)(PPh\(_3\))\(_3\)

It was initially envisaged that hydrido-thiocarbonyl complexes could be produced by hydride incorporation into MX\(_2\)(CO)(CS)(PPh\(_3\))\(_2\)
[M = Ru, Os], or by hydrogenation or protonation of Os(CO)$_2$(CS)(PPh$_3$)$_2$ as has been described for Os(CO)$_3$(PPh$_3$)$_2$.\(^{123,167}\) The synthesis of these precursor thiocarbonyl complexes was described in chapter 2. However, a discovery occurred before these reactions were investigated which considerably simplified the approach to the problem. It will be recalled from the previous chapters that the unsaturated d$^6$ ruthenium complex RuCl$_2$(PPh$_3$)$_3$ is known to react with carbon disulphide to afford a number of dinuclear thiocarbonyl complexes. The corresponding osmium complex, OsCl$_2$(PPh$_3$)$_3$, has a low profile in the literature, from a synthetic point of view, and has been reported only in the context of a structural paper.\(^{140}\) This compound forms quantitatively when (NH$_4$)$_2$[OsCl$_6$] is heated under a nitrogen atmosphere in a t-butanol-water mixture containing an excess of triphenylphosphine. The reaction between OsCl$_2$(PPh$_3$)$_3$, carbon disulphide and excess triphenylphosphine proceeds over several minutes to quantitatively yield the coordinatively saturated thiocarbonyl complex OsCl$_2$(CS)(PPh$_3$)$_3$: 

\[
\text{OsCl}_2(\text{PPh}_3)_3 + \underset{\text{CS}_2/\text{PPh}_3}{\text{benzene}} \rightarrow \text{OsCl}_2(\text{CS})(\text{PPh}_3)_3 + \text{SPh}_3
\]

The product triphenylphosphine sulphide was isolated and characterised by I.R. spectroscopy ($v_{\text{PS}} = 632 \text{ cm}^{-1}$).\(^{168}\) This extremely facile, high yield, one-step synthesis of an osmium thiocarbonyl complex represented a panacea to the problems described in chapter 2. Further desirable characteristics of OsCl$_2$(CS)(PPh$_3$)$_3$ are the presence of labile chloro and phosphine ligands and the absence of any strongly coordinating ligands (such as CO) other than CS. Thus OsCl$_2$(CS)(PPh$_3$)$_3$ is an exceptionally versatile synthetic intermediate
and all of the chemistry reported in the remainder of this thesis emanates from this one single compound.

3.2 Hydrido-Thiocarbonyl Complexes

Compounds in which thiocarbonyl ligands occur in combination with hydrido ligands are very rare and are limited to the examples [WH(CO)(CS)(diphos)\(_2\)]\(^+\), which results from the protonation of W(CO)(CS)(diphos)\(_2\),\(^{98}\) and the iridium complexes IrH(CS)(PPh\(_3\))\(_3\), which is formed by the action of sodium borohydride and excess triphenylphosphine on trans-IrCl(CS)(PPh\(_3\))\(_2\) in ethanol suspension,\(^{14,169}\) [IrH\(_2\)(CO)(CS)(PCy\(_3\))\(_2\)]\(^+\), which is obtained by the hydrogenation of [Ir(CO)]\(_2\)(CS)(PCy\(_3\))\(_2\)\(^+\)\(^{87}\) and IrHCl\(_2\)(CS)(PPh\(_3\))\(_2\), which arises from the oxidative addition of HCl to trans-IrCl(CS)(PPh\(_3\))\(_2\)\(^{79,169}\). Treatment of OsCl\(_2\)(CS)(PPh\(_3\))\(_3\) with sodium hydroxide in boiling 2-methoxyethanol gives OsH\(_2\)(CS)(PPh\(_3\))\(_3\). If ethanol is used as the solvent then OsHCl(CS)(PPh\(_3\))\(_3\) can be observed as an intermediate complex. These reactions are clearly related to the production of OsH\(_2\)(CO)(PPh\(_3\))\(_3\) from OsHCl(CO)(PPh\(_3\))\(_3\) [Chapter 2]. The hydrido ligand is formed by hydride abstraction from the alkoxido ligand of an intermediate complex and the alkoxido ligand is oxidised, in this case to an aldehyde.\(^{170,171}\) The stereochemistry of OsH\(_2\)(CS)(PPh\(_3\))\(_3\) is the same as the well known carbonyl analogue\(^{110}\) and the \(^1\)H N.M.R. spectrum is typical of MH\(_2\)X(PPh\(_3\))\(_3\) compounds with meridional phosphine ligands and cis-hydrido ligands (Table 3.2).

![Chemical structure](image-url)
The I.R. spectra of different samples of OsH$_2$(CS)(PPh$_3$)$_3$ exhibit six bands in the region 1890 cm$^{-1}$ to 2070 cm$^{-1}$ two of which vary in intensity from weak to strong according to the crystallinity of the sample. For each sample four weak bands are found at 2040 cm$^{-1}$, 1960 cm$^{-1}$, 1900 cm$^{-1}$ and 1820 cm$^{-1}$ and are probably combination bands. The two variable bands are exhibited at 2070 cm$^{-1}$ and 1895 cm$^{-1}$.

These latter bands are the most conspicuous features of the I.R. spectra in this region and are assigned to $\nu_{\text{OSh}}$. Two further bands are observed at 800 cm$^{-1}$ and 668 cm$^{-1}$ which vary in unison with $\nu_{\text{OSh}}$ from weak to near medium intensity. These are assigned to the $\delta_{\text{OSh}}$ vibration.

Reaction of OsH$_2$(CS)(PPh$_3$)$_3$ with hydrochloric or hydrobromic acid in dichloromethane-ethanol at ambient temperatures results in the cleavage of one hydrido ligand, accompanied by the rapid evolution of hydrogen, and formation of OsHX(CS)(PPh$_3$)$_3$. If OsHCl(CS)(PPh$_3$)$_3$ is heated under reflux in benzene-ethanol solution containing excess HCl then the slow cleavage of the second hydride ensues to afford OsCl$_2$(CS)(PPh$_3$)$_3$. Thus the process of exchange of chloride for hydride is fully reversible -

\[
\text{OsCl}_2(\text{CS})(\text{PPh}_3)_3 + \text{OH}^-/\text{EtOH} + \text{HCl} \rightarrow \text{OsHCl(CS)(PPh}_3)_3 + \text{OH}^-/\text{ROH} + \text{HCl} \\
(R = \text{CH}_2\text{CH}_2\text{OCH}_3)
\]

If OsH$_2$(CS)(PPh$_3$)$_3$ is treated with HI then a very insoluble white solid is produced which loses weight and darkens slightly on recrystallisation. After the product has been recrystallised from dichloromethane-ethanol several times the weight and appearance of the solid remain constant. The weight reduction corresponds
approximately to the loss of one phosphine ligand. The presence of
water is indicated both in the I.R. and $^1$H N.M.R. spectra
(1 equivalent) and the compound analyses approximately as
OsH$_2$(H$_2$O)(CS)(PPh$_3$)$_2$. That the compound contains only two phosphine
ligands is demonstrated by the nature of the high field hydride
resonance. The triplet pattern is typical of an hydrido ligand cis
to two mutually trans phosphine ligands. The loss of the third
phosphine ligand in this complex is probably a result of the steric
pressure created by the bulky iodo ligand. The trisphosphine
intermediate could not be characterised in a pure form.

Like the carbonyl analogue, OsH$_2$(CS)(PPh$_3$)$_3$ reacts with
tetrafluoroboric acid to afford an aquo-containing cationic complex,
[OsH(H$_2$O)(CS)(PPh$_3$)$_3$]BF$_4^-$, which forms crystals of the 1:1 aquo solvate
from dichloromethane-ethanol-water. The perchlorate analogue was
also isolated and characterised and the I.R. [see Chapter 2, 2.5]
and $^1$H N.M.R. spectra and elemental analysis data indicate that this
compound is also best formulated as [OsH(H$_2$O)(CS)(PPh$_3$)$_3$]ClO$_4^-$.  

Treatment of OsHCl(CS)(PPh$_3$)$_3$ with silver perchlorate in
acetonitrile yields the cation [OsH(MeCN)$_2$(CS)(PPh$_3$)$_2$]ClO$_4^-$. The
carbonyl analogue [OsH(MeCN)$_2$(CO)(PPh$_3$)$_2$]ClO$_4^-$ has an extensive
chemistry, but the further chemistry of the thiocarbonyl complex
was not explored since the more desirable substitutes
[OsH(H$_2$O)(CS)(PPh$_3$)$_3$]X [X = BF$_4^-$, ClO$_4^-$] [cf. Chapter 2] have been
prepared.

The $^1$H N.M.R. spectra of the monohydrido-trisphosphine
complexes show that the geometry
is general, as it can be established from the coupling pattern of
the hydride resonance with the $^{31}$P nuclei that the hydrido ligand is
$\textit{trans}$ to one phosphine ligand and $\textit{cis}$ to two mutually $\textit{trans}$ phosphine
ligands. The coupling constants are within the normal range for
this geometry$^{110}$ [Table 3.2], which is usually observed for
$\text{OsHXL}(\text{PPh}_3)_3$ complexes.$^{110,172,173}$ A sharp well resolved band
near 2100 cm$^{-1}$ in the I.R. spectrum of each compound is assigned to
$\nu_{\text{OSH}}$ and a weak poorly resolved band near 800 cm$^{-1}$ to $\delta_{\text{OSH}}$. The
behaviour of $\nu_{\text{CS}}$ in these complexes [Table 3.1] illustrates the
π-acid nature of the CS ligand. The value of $\nu_{\text{CS}}$ decreases with
the electronegativity of the $\textit{trans}$ halo ligand.

One phosphine ligand in $\text{OsHX(CS)(PPh}_3)_3$ is labile and is
readily displaced by the neutral ligands carbon monoxide [see
section 3.3] and $\text{p}$-tolylisocyanide. In keeping with the marked
$\textit{trans}$ effect of the hydrido ligand it is expected that the displaced
phosphine will be that $\textit{trans}$ to the hydrido ligand. Grundy found
that $\text{OsHCl(CO)(PPh}_3)_3$ reacts with neutral ligands $L$ [$L = \text{CN-}$
$p$-tolyl, $\text{P(OCH}_2)_3\text{CCH}_3$, $\text{P(OMe}_3$, $\text{PMe}_2\text{Ph}$, $\text{P(OPh)}_3$] to give the compound
$\text{OsHCl(CO)L(PPh}_3)_2$ containing mutually $\textit{trans}$ triphenylphosphine ligands
and hydride $\textit{trans}$ to $L$.$^{110}$ However, when $\text{mer-OsHCl(CS)(PPh}_3)_3$ is
treated with $\text{p}$-tolylisocyanide a compound of composition
$\text{OsHCl(CS)(CNR)(PPh}_3)_2$ [$R = p$-tolyl] is formed which exhibits an hydride
\(^1\)H N.M.R. triplet at the very high field value of \(\tau\), 23.78. This value can be compared with the corresponding value for 
\(\text{OsHCl(CO)(CNR)}(\text{PPh}_3)_2\) \(\tau\), 14.76 (hydride \textit{trans} to CNR) or for 
\(\text{OsHCl(CO)}_2(\text{PPh}_3)_2\) \(\tau\), 13.70 (hydride \textit{trans} to CO). The high field value of \(\tau\), 23.78 suggests that \(\text{OsHCl(CS)(CNR)}(\text{PPh}_3)_2\) has geometry 
I (figure 3.1) since hydride resonances at similar high field values were found for the complexes \(\text{RuHX(CO)(CNR)}(\text{PPh}_3)_2\) with hydrido \textit{trans} to the halo ligand.\(^{109}\) Indeed, high field hydride resonances are generally found for hydrido ligands that are \textit{trans} to halo ligands.\(^{174, 175}\)

\[
\text{H} \quad \text{L} \quad \text{CS} \quad \text{RNC} \quad \text{L} \quad \text{Cl} \\
\text{Os} \\
\text{L} \quad \text{Cl} \\
\text{II} \\
\text{H} \quad \text{L} \quad \text{CS} \quad \text{Cl} \\
\text{Os} \\
\text{L} \quad \text{CNR} \\
\text{III} \\
\]

Figure 3.1 (L = PPh\(_3\), R = p-tolyl)

It is worth noting, however, that the hydride resonance in 
\(\text{OsH}_2(\text{CS})(\text{PPh}_3)_3\) for hydride \textit{trans} to CS occurs at \(\tau\), 20.43 which is higher than the corresponding value for the carbonyl (\(\tau\), 17.34) or p-tolylisocyanide (\(\tau\), 15.20) analogues so that geometry III (figure 3.1) cannot be totally discounted.

Isomer I isomerises on heating in benzene to produce a further isomer which displays a hydride triplet resonance at \(\tau\), 12.75. That this isomer has geometry II and not geometry III is demonstrated by the facile transfer of the hydrido ligand to the thiocarbonyl ligand which occurs when this compound is treated with carbon monoxide (implying \textit{cis} hydrido and thiocarbonyl ligands, section 3.3).
Attempts to produce isomer I by a substitution reaction in boiling ethanol between chloride ion and the labile phosphine-containing cation \([\text{OsH(CS)(CN-}p\text{-toly}l)(\text{PPh}_3)_3]^+\) (hydride trans to phosphine [Chapter 4]) resulted in the formation of the thermodynamically stable isomer II.

Thus, in contrast to the carbonyl analogue, \(\text{OsHCl(CS)(PPh}_3)_3\) does not react with \(p\)-tolylisocyanide to first produce isomer II therefore suggesting that the five-coordinate intermediate \(\text{OsHCl(CS)(PPh}_3)_2\), which results from phosphine dissociation, isomerises to favour coordination of the isocyanide ligand in the site trans to the thiocarbonyl ligand. Although the pronounced trans effect of the CS ligand has been observed by other workers [Chapter 1, section IIIA(i)] this result implies that the CS ligand has a stronger trans effect than the hydrido ligand. Since the latter is also known to have a very marked trans effect the description of this reaction as a dissociative process must be regarded with suspicion until appropriate kinetic studies have been conducted.

Other recorded \(^1\text{H N.M.R. hydride resonance data for thiocarbonyl complexes are also included in Table 3.2, but are of limited value for comparison purposes. The hydrido ligand is coordinated through an octahedral face in [WH(CO)(CS)(diphos)_2]CF_3SO_3 and occupies an apical position of a trigonal bipyramid in IrH(CS)(PPh}_3)_3. All the hydrido complexes reported in this work are octahedral as is [IrH}_2(\text{CO})(\text{CS})(\text{PCy}_3)_2]ClO_4 which contains cis hydrido and trans phosphine ligands.
3.3 Hydride Transfer Reactions

Hydride transfer from metal to ligand has been achieved in this laboratory for coordinated isocyanide and the nitrosyl ligand. Similar reactions are probably also involved in the reduction of some tungsten carbene complexes with hydrogen to afford alkanes, although the intermediate alkyl complexes could not be isolated.

The hydrido complexes OsHX(CS)(PPh_3)_3 [X = Cl, Br] and OsHCl(CS)(CNR)(PPh_3)_2 [R = p-tolyl, hydride trans to CNR] which contain mutually cis hydrido and thiocarbonyl ligands have the desirable stereochemistry for investigating migratory-insertion reactions to produce a thioformyl group.

When a benzene solution of each of these colourless compounds is stirred under carbon monoxide (40 p.s.i.) an intense blue colouration develops and the addition of n-hexane affords blue crystals of the monodentate thioformyl-containing complexes OsX(CHS)(CO)_(2)(PPh_3)_2 and OsCl(CHS)(CO)(CNR)(PPh_3)_2.

(CNR = CN-p-tolyl in subsequent text)
The intermediate complexes OsHX(CO)(CS)(PPh₃)₂ can be isolated if only one equivalent of carbon monoxide is reacted with OsHX(CS)(PPh₃)₃, but in the presence of excess carbon monoxide at room temperature the thioformyl complexes are the only products observed. That the transfer reaction is reversible is demonstrated by the regeneration of OsHCl(CO)(CS)(PPh₃)₂ when OsCl(CHS)(CO)₂(PPh₃)₂ is heated in dichloromethane for nine hours. Considerable decomposition accompanies this reaction.

The thioformyl complexes exhibit very characteristic I.R. and ¹H N.M.R. properties. Two medium intense bands in the I.R. spectrum of each complex occur near 1000 cm⁻¹ and 1200 cm⁻¹ which can be attributed to the monodentate thioformyl ligand. Since monodentate dithioester complexes also display a medium intense I.R. band near 1000 cm⁻¹ [Table 2.2] it is likely that the similar band for the thioformyl complexes is primarily a ν₃S₂ vibration. A further weak band near 2830 cm⁻¹ is assigned to the νCH vibration of the thioformyl ligand [Table 3.3]. The thioformyl proton appears in the ¹H N.M.R. spectrum in the very low field range of τ, -6.93 to τ, -7.73 and weak coupling with the ³¹P nuclei (τ, 3 Hz) is observed [Table 3.4]. Thus a large downfield shift of approximately 20 p.p.m. occurs for the ¹H N.M.R. resonance of the transferred hydride [τ, 12.75 for OsHCl(CS)(CNR)(PPh₃)₂]. The formyl proton resonance has also been found at very low field values, e.g., τ, -5 to -6.⁶⁶

Upon dissolution in polar solvents such as dichloromethane or chloroform the characteristic blue colour of the thioformyl complexes changes slowly to an intense red. This colour change occurs rapidly if ethanol is added. However, addition of sufficient ethanol to
induce crystallisation or addition of \( n \)-hexane results in the deposition of blue crystals of the original thioformyl complex. This colour change is accompanied by the partial disappearance of the thioformyl proton resonance in the \( ^1H \) N.M.R. spectra and, in the case of OsCl(CHS)(CO)(CNR)(PPh\(_3\))\(_2\), the appearance of a broad weak signal at \( \tau, -3.23 \). It is presumed that this behaviour is caused by a reversible displacement of halo ligand in solution accompanied by the formation of a \( \pi \)-bonded thioformyl ligand. Bidentate thioacyl complexes [Chapter 6] are a very intense red or maroon colour. Attempts to isolate the cationic

\[
\begin{align*}
\text{L}_n \text{Os} & \quad \text{C=S} \\
& \xrightarrow{\text{X}} \\
& \text{L}_n \text{Os} \quad \text{C} \quad \text{H} \\
& + \quad \text{X}^{-}
\end{align*}
\]

product by recrystallisation in the presence of excess perchlorate ion or by addition of silver perchlorate to remove chloride ion were not successful.

Surprisingly, the intermediate compounds OsHX(CO)(CS)(PPh\(_3\))\(_2\) [\( X = \text{Cl}, \text{Br} \)] do not exhibit a hydride resonance in deuterobenzene or deuterochloroform in the \( ^1H \) N.M.R. at 40°C. Yet carbonylation of the \( ^1H \) N.M.R. samples leads to the formation of the thioformyl complexes and \( \nu_{OSH} \) and \( \delta_{OSH} \) bands can be observed in the I.R. spectra. This is in contrast to OsHCl(CS)(CNR)(PPh\(_3\))\(_2\) (hydride \( \text{trans} \) to CNR) which exhibits both a hydride resonance and forms a thioformyl complex. One apparent explanation for this anomalous behaviour is that an equilibrium, which is fast on the N.M.R. time scale, exists between OsHX(CO)(CS)(PPh\(_3\))\(_2\) and the five-coordinate
intermediate OsX(CHS)(CO)(PPh$_3$)$_2$. This intermediate is trapped by carbon monoxide to give the thioformyl products.

The complex OsHCl(CS)(CNR)(PPh$_3$)$_2$ (hydrido trans to chloro ligand) does not undergo hydride transfer when treated with carbon monoxide. This behaviour is not unprecedented in that Christian found that of the three isolated isomers of RuHL(CO)(CNR)(PPh$_3$)$_2$ [H trans to (i) CO, (ii) CNR, (iii) I] only the first could be induced to undergo hydride migration to the isocyanoide ligand.$^{109,176}$

Nor does a thioformyl complex form when OsH(n$_2^2$-S$_2$CNET$_2$)(CS)(PPh$_3$)$_2$ is heated in benzene under carbon monoxide and heating of OsH(n$_1$-S$_2$CNET$_2$)(CO)(CS)(PPh$_3$)$_2$ in dichloromethane or benzene does not afford a tractable product. These complexes were produced by reaction of [OsH(H$_2$O)(CS)(PPh$_3$)$_3$]BF$_4$ and [OsH(CO)(CS)(PPh$_3$)$_3$]BF$_4$ [Chapter 4], respectively, with diethylidithiocarbamate ion.

Hydride transfer to form a thioformyl ligand represents a logical first step in the complete reduction of carbon monosulphide to methyl thiol. The corresponding reactions are not observed for OsHX(CO)$_2$(PPh$_3$)$_2$ or for OsHCl(CO)(CNR)(PPh$_3$)$_2$. In the following section the reactions of the thioformyl ligand are discussed. One of these reactions [section 3.4(ii)] encompasses the problem of the further reduction of the thioformyl ligand to a thioformaldehyde-containing complex.
3.4 Reactions of Thioformyl Complexes

(i) Carbene Formation and Derived Products

When methyl triflate is added to a benzene solution containing a thioformyl complex a rapid colour change from blue to bright yellow occurs and yellow crystals soon begin to deposit. Addition of n-hexane affords the resulting methylthiolato carbene complexes [OsX(CHSMe)(CO)]_2(PPh_3)_2(CF_3SO_3) and [OsCl(CHSMe)(CO)(CNR)(PPh_3)_2(CF_3SO_3) in quantitative yields. The \( \nu_{CO} \) and \( \nu_{CN} \) bands are observed to increase on methylation of the thioformyl ligand as expected for the formation of cationic species. The thioformyl bands near 1000 cm\(^{-1}\) and 1200 cm\(^{-1}\) are replaced by a broad/weak medium intense band near 960 cm\(^{-1}\) [Table 3.4] which is attributable to the carbene ligand. No band is observed in the 2800 cm\(^{-1}\) to 2950 cm\(^{-1}\) region of the I.R. spectra obtained in Kel-F mulls which can be unambiguously assigned to a carbene \( \nu_{CH} \) vibration. On methylation an upfield shift occurs for the thioformyl proton resonance in the \(^1\)H N.M.R. spectra of approximately 2 p.p.m. [Table 3.4], but the carbene proton no longer exhibits a simple triplet coupling pattern with the \(^{31}\)P nuclei. Instead one broad singlet for each complex near \( \tau, -5 \) which has the approximate profile of an overlapping binomial pentet is observed and the S-methyl signal is also a structured singlet near \( \tau, 8.6 \). It is unlikely that this structuring is due to geometrical isomers of the carbene ligand, i.e.

\[
\begin{align*}
\text{Os} & \quad \text{S} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H}
\end{align*}
\]
since a larger separation of signals is observed for such isomerism [Table 2.4 note (c)] as in $[\text{OsCl} \left( \text{CH}_{3}\text{Me} \right) \left( \text{CO} \right) \left( \text{CNR} \right) \left( \text{PPh}_3 \right)_2] \text{CF}_3 \text{SO}_3$ (see below). Coupling within the carbene ligand and long range coupling with the $^{31}\text{P}$ nuclei is the probable source of this structuring.

These secondary carbene complexes have proved to be very useful synthetic intermediates and, in keeping with the generally recognized electrophilic character of the carbene carbon atom, are reactive towards nucleophiles. Treatment of $[\text{OsCl} \left( \text{CH}_{3}\text{Me} \right) \left( \text{CO} \right) \left( \text{PPh}_3 \right)_2] \text{CF}_3 \text{SO}_3$ with excess methylamine affords the iminoformyl complex $\text{OsCl} \left( \text{CHNMe} \right) \left( \text{CO} \right)_2 \left( \text{PPh}_3 \right)_2$. The reaction proceeds through the intermediate carbene-containing cation $[\text{OsCl} \left( \text{CHNMe} \right) \left( \text{CO} \right)_2 \left( \text{PPh}_3 \right)_2]^{+}$ which can be isolated in poor yield when one equivalent of amine is used -

![Chemical Structure](image)

The iminoformyl complex is protonated by perchloric acid to return the intermediate carbene cation.

Both the iminoformyl and the carbene complexes are well-defined by characteristic features in the I.R. and $^{1}\text{H}$ N.M.R. spectra. A weak to medium intense band at $2740 \text{ cm}^{-1}$ and a strong band at $1589 \text{ cm}^{-1}$ are assigned to $\nu_{\text{CH}}$ and $\nu_{\text{CN}}$ respectively for the iminoformyl ligand. For the carbene complex $\nu_{\text{CN}}$ is observed at $1610 \text{ cm}^{-1}$ and $\nu_{\text{NH}}$ at $3175 \text{ cm}^{-1}$ and $3240 \text{ cm}^{-1}$, but no unambiguous carbene $\nu_{\text{CH}}$ band can be discerned in the KBr-F spectrum. The $^{1}\text{H}$ N.M.R. spectrum of $\text{OsCl} \left( \text{CHNMe} \right) \left( \text{CO} \right)_2 \left( \text{PPh}_3 \right)_2$
displays two structured singlets at $\tau = -0.73$ [1H, Os-C-H] and $\tau = 7.45$ [3H, N-CH$_3$]. The complex structuring observed in both signals is probably the result of coupling within the iminoformyl ligand and of long range coupling with the $^{31}$P nuclei. The carbene complex [OsCl(CHNHMe)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$ exhibits similar $^1$H N.M.R. behaviour.

The thiolato-carbene complexes are so reactive with nucleophiles that a reaction occurs between the solids and moist air which results in the evolution of methyl thiol. When [OsX(CHSMe)(CO)$_2$(PPh$_3$)$_2$]CF$_3$SO$_3$ [X = Cl, Br] are recrystallised from dichloromethane-ethanol-water, without heating, white crystals of the formyl-containing complexes OsX(CHO)(CO)$_2$(PPh$_3$)$_2$ are deposited. The hydrolysis reaction is suppressed by acid and recrystallisation of [OsCl(CHSMe)(CO)$_2$(PPh$_3$)$_2$]CF$_3$SO$_3$ from dichloromethane-ethanol containing perchloric acid gives [OsCl(CHSMe)(CO)$_2$(PPh$_3$)$_2$]ClO$_4$. The I.R. spectra of the formyl complexes contain a strong sharp $\nu_{\text{CO}}$ band near 1600 cm$^{-1}$ and two weak to medium intense sharp $\nu_{\text{CH}}$ bands between 2500 cm$^{-1}$ and 2700 cm$^{-1}$ for the formyl ligand. Similar I.R. behaviour is exhibited by [(Ph$_3$P)$_2$N][Fe(CHO)(CO)$_4$]$_{166}$ [Table 3.3]. However, the osmium formyl complexes are contaminated by OsHX(CO)$_2$(PPh$_3$)$_2$ and if the formyl complexes are recrystallised from any of the solvents dichloromethane, chloroform or benzene with ethanol then carbon monoxide displacement is rapid and formation of OsHX(CO)$_2$(PPh$_3$)$_2$ is quantitative. Solid samples appear indefinitely stable in the absence of light. Similar behaviour was observed for [Fe(CHO)(CO)$_4$]$^-$, but the formation of [FeH(CO)$_4$]$^-$ in solution was much slower.$^{166(a)}$ The solution instability of OsX(CHO)(CO)$_2$(PPh$_3$)$_2$ prevented further characterisation
of these compounds. A transient signal was observed at \( \tau, -4.4 \) in the \(^1\)H N.M.R. spectrum of \( \text{OsBr(CHO)(CO)}_2(PPh_3)_2 \) when the solid formyl was dissolved in CDCl\(_3\) and the region between \( \tau, -5 \) to \( \tau, -3, \) scanned immediately [cf. \( \text{[Fe(CHO)(CO)}_4]^\text{\textsuperscript{+}} \), \( \tau, -4.95 \)]. It has been suggested\(^{95}\) that \( \text{OsCl(CHO)(CO)}_2(PPh_3)_2 \) may be involved in the fast reaction of \( \text{Os(CO)}_3(PPh_3)_2 \) with HCl which gives \( \text{OsCl}_2(\text{CO})_2(PPh_3)_2 \).\(^{181}\) However, when \( \text{OsCl(CHO)(CO)}_2(PPh_3)_2 \) is added to a dichloromethane–ethanol solution containing HCl, \( \text{OsHCl(CHO)(CO)}_2(PPh_3)_2 \) is obtained and there is no evidence to suggest the formation of any \( \text{OsCl}_2(\text{CO})_2(PPh_3)_2 \).

The isocyanide-containing thiolato-carbene complex \( \text{[OsCl-(CHSMe)(CO)(CNR)}(PPh_3)_2]_{\text{CF}_3SO_3} \) is more resistant to hydrolysis than the dicarboxyl analogues and reacts only very slowly with water to produce the formyl complex \( \text{OsCl(CHO)(CO)(CNR)}(PPh_3)_2 \). This hydrolysis is base catalysed and in dichloromethane-ethanol-water solution containing NaOH hydrolysis proceeds rapidly and \( \text{OsCl(CHO)(CO)(CNR)}(PPh_3)_2 \) can be isolated in a pure form. In contrast, if base is added to the hydrolysis reactions of \( \text{[OsX(CHSMe)(CO)}_2(PPh_3)_2]_\text{\textsuperscript{+}} \) then the only products observed are \( \text{OsHX(CHO)}_2(PPh_3)_2 \). Recrystallisation of \( \text{OsCl(CHO)(CO)(CNR)}(PPh_3)_2 \) from dichloromethane-ethanol or dichloromethane-hexane occurs without apparent decomposition [I.R. \( \nu \text{CO} 1965 \text{ vs}, 1950 \text{ vs}, 1602 \text{ s}, 1596 \text{ s}, 1572 \text{ w} \text{m}; \nu \text{CH} 2685 \text{ w}, 2564 \text{ w}, 2515 \text{ w} \text{m} \)]. That only one geometrical isomer of \( \text{OsCl(CHO)(CO)(CNR)}(PPh_3)_2 \) is formed is indicated by the presence of only one broad singlet formyl proton resonance in the \(^1\)H N.M.R. spectrum at \( \tau, -4.45 \). As found for the thioformyl complexes, \( \text{OsCl(CHO)(CO)(CNR)}(PPh_3)_2 \) is alkylated by methyl triflate. The resulting methoxy-carbene-containing product \( \text{[OsCl(CHMe)(CO)(CNR)}(PPh_3)_2]_{\text{CF}_3SO_3} \) is the sole example of a stable
ligand-reaction derivative of an isolated formyl-containing complex. Two separate signals are observed in the $^1$H N.M.R. spectrum for the $\text{CHO}_\text{Me}$ and $O-\text{CH}_3$ resonances $[\tau, -3.05, 0.5\text{H}, \tau, -2.03, 0.3\text{H}, \text{CHO}_\text{Me}; \tau, 5.38, 2\text{H}, \tau, 6.03, 1\text{H}, O-\text{CH}_3]$ indicating the presence of geometrical isomers for the carbene ligand, i.e.

The same structuring is observed in each of the broad singlet resonances, as was noted for the carbene and iminoformyl complexes discussed above, indicating coupling within the carbene ligand and with the $^{31}\text{P}$ nuclei. Formyl complexes have been prepared by the reaction of $\text{Na}_2[\text{Fe(CO)}_4]$ with acetic formic anhydride or by treating carbonyl complexes of iron, chromium and tungsten with trialkoxy- and trialkyl-borohydrides. $^{166}$ Other formyl complexes have been proposed as intermediates in a number of reactions$^{158,182}$ and, as already noted, as key intermediates in the Fischer-Tropsch synthesis. $^{164}$ No secondary alkoxy-carbene complexes have been reported, nor has there been any recorded general route available to secondary carbene complexes $^{166c}$ as has been discovered in this series of results [Scheme 3.1]. Such complexes are of interest as potential reagents for organic synthesis. $^{183}$

(ii) Further Reduction of the Thioformyl Ligand

In seeking other compounds which might provide further examples of hydride migration to CS Keith Town endeavoured to prepare

$\text{IrH}_3(\text{CS})(\text{PPh}_3)_2$ by oxidative addition of hydrogen to $\text{IrH(CS)(PPh}_3)_3$
\[ \text{IrH}_3(\text{CS})(\text{PPh}_3)_2 \] \[ \text{IrH}_2(\text{SMe})(\text{PPh}_3)_3 \]

Surprisingly, the yellow crystalline product of hydrogen addition to \( \text{IrH}(\text{CS})(\text{PPh}_3)_3 \) was identified not as the expected \( \text{IrH}_3(\text{CS})(\text{PPh}_3)_2 \) but instead as the compound \( \text{IrH}_2(\text{SMe})(\text{PPh}_3)_3 \).

The formation of the methyl-containing compound can be explained by successive hydride transfer to the thiocarbonyl ligand yielding first a thioformyl complex, then a thioformaldehyde complex and finally a methylthiolato complex as shown in the proposed mechanism depicted in Scheme 3.2.

Under the reaction conditions [benzene solvent, \( \text{H}_2 \) at 2 atm., 6 h] for complete reaction of 0.5 g of \( \text{IrH}(\text{CS})(\text{PPh}_3)_3 \) the postulated intermediates could not be isolated, suggesting that the hydride transfers are fairly rapid. However, that a thioformyl complex of iridium(III) is a reasonable intermediate was shown by the independent synthesis of a stable example,

\[ \text{IrCl}_2(\text{CO})(\text{CS})(\text{PPh}_3)_2][\text{I}_3] \xrightarrow{\text{NaBH}_4/\text{EtOH}} \text{IrCl}_2(\text{CHS})(\text{CO})(\text{PPh}_3)_2 \]
The complete reduction of an osmium thiocarbonyl complex to an hydrido-thiolato-containing complex by one single stepwise reaction has not been achieved but, in addition to the thioformyl complexes described above, osmium analogues of the intermediates proposed in Scheme 3.2 have been separately prepared and characterised. The same sequence of reduction events depicted in Scheme 3.2 for carbon monosulphide has been proposed by some authors to occur in the Fischer-Tropsch reduction of carbon monoxide to methanol.\textsuperscript{152(a),153}

Although several thiolketal complexes are known in which the ligand is bound either through sulphur\textsuperscript{185,186,187} or through both sulphur and carbon,\textsuperscript{188} no stable complexes of monomeric thioaldehydes or of thioformaldehyde have been described. The cyclic trimer of thioformaldehyde can function as a ligand.\textsuperscript{189} Pure thioformaldehyde has been generated by the high temperature decomposition of 1,2,4-trithiolan\textsuperscript{190} or of methylsulphenylichloride\textsuperscript{191} and has been established as a constituent of the interstellar medium.\textsuperscript{192} Two approaches to the problem of synthesising an osmium complex of the unstable thioformaldehyde monomer have been investigated: (i) inducing the transfer of both hydrides of OsH\textsubscript{2}(CS)(PPh\textsubscript{3})\textsubscript{3} through reaction with carbon monoxide and (ii) reaction of the thioformyl complex OsCl(CHS)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} with NaBH\textsubscript{4} (Scheme 3.3).

Because of the inertness of OsH\textsubscript{2}(CS)(PPh\textsubscript{3})\textsubscript{3}, vigorous conditions are necessary [CO at 4 atm. (ca. 60 p.s.i.), 140°C for 1 h] to induce any reaction to occur and two colourless products which vary in relative yields are obtained. One product is an exceptionally insoluble complex which can be shown by qualitative elemental analysis
to contain sulphur and which exhibits two $\nu_{\text{CO}}$ bands in the I.R. spectrum at 1930 cm$^{-1}$ and 1990 cm$^{-1}$. It is thought that this complex probably contains thioformaldehyde as a bridging ligand, but attempts to form derivatives by treatment with acid or methyl iodide have not been successful. The second product is
Os(\(\eta^2\)-CH\(\text{S}\))\((\text{CO})_2(\text{PPh}_3)_2\).

Gentle heating of the thioformyl complex OsCl(CHS)(\text{CO})_2(\text{PPh}_3)_2 in dichloromethane containing an ethanolic solution of sodium borohydride produces a gradual colour change which eventually affords a faintly yellow solution. Removal of dichloromethane affords colourless crystals of the thioformaldehyde adduct Os(\(\eta^2\)-CH\(\text{S}\))\((\text{CO})_2(\text{PPh}_3)_2\) in high yield which are contaminated by small quantities of an unidentified product \(v_{\text{CO}}\) bands at 2025 cm\(^{-1}\) and 1942 cm\(^{-1}\). The pure thioformaldehyde adduct can be obtained by recrystallisation from dichloromethane-benzene, but the yield is considerably reduced by this purification procedure. Purification prior to methylation with methyl triflate did not prove necessary since the impurity did not interfere with this reaction and could be easily separated from the methylated product (see below). The interesting observation can be made from Table 3.5 that the \(v_{\text{CO}}\) bands

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v_{\text{CO}}) (cm(^{-1}))</th>
<th>(1^H) N.M.R. Data (CDCl(_3))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os((\eta^2)-C(_2)H(_4))(\text{CO})_2(\text{PPh}_3)_2</td>
<td>1955,1895</td>
<td>9.55, t, 4H, (^3)J(HP)=7 Hz</td>
<td>110</td>
</tr>
<tr>
<td>Os((\eta^2)-CH(_2)S)(\text{CO})_2(\text{PPh}_3)_2</td>
<td>1985,1915</td>
<td>9.1, t, 4H, (^3)J(HP)=4.6 Hz</td>
<td>194</td>
</tr>
<tr>
<td>Os((\eta^2)-S(_2))(\text{CO})_2(\text{PPh}_3)_2</td>
<td>1998,1944</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os((\eta^2)-S(_2)Me)(\text{CO})_2(\text{PPh}_3)_2]ClO(<em>4)</em></td>
<td>2045,1980</td>
<td>8.0, s, 3H, S-CH(_3)</td>
<td>194</td>
</tr>
</tbody>
</table>

of the adducts of Os(\text{CO})_2(\text{PPh}_3)_2 represented increase with the unsaturated addend according to the series H\(_2\)C=CH\(_2\) < S=CH\(_2\) < S\(_2\) < S\(_2\)Me\(^+\). The degree of electron transfer from metal to ligand thus increases in
the same order and the \( \nu_{\text{CO}} \) values indicate that \( S=\text{CH}_2 \) is more tightly bound than \( \text{C}_2\text{H}_4 \). As numerous ethylene adducts of low valent metal centres are known many thioformaldehyde adducts ought to be stable. The stabilisation of highly reactive organic molecules by coordination to a transition metal centre is a feature of organometallic chemistry.

Treatment of \( \text{Os}(\eta^2-\text{CH}_2\text{S})(\text{CO})_2(\text{PPh}_3)_2 \) with hydrochloric acid in dichloromethane-ethanol rapidly yields the methylthiolato-containing complex \( \text{OsCl(SMe)}(\text{CO})_2(\text{PPh}_3)_2 \) (probably via initial protonation at the metal). If this compound is heated gently in the same reaction medium methyl thiol elimination ensues to afford \( \text{OsCl}_2(\text{CO})_2(\text{PPh}_3)_2 \) [Scheme 3.3]. Thus suitable examples are now available for each of the intermediates postulated in the hydrogenation of \( \text{CS} \) in \( \text{IrH(CS)}(\text{PPh}_3)_3 \). 102

In contrast, alkylation with methyl triflate occurs at the sulphur atom to yield a dihapto-methylthiolatomethyl complex, \( [\text{Os}(\eta^2-\text{CH}_2\text{SMe})(\text{CO})_2(\text{PPh}_3)_2]^+ \). Chloride ion brings about ring-opening, forming \( \text{OsCl(}^1-\text{CH}_2\text{SMe})(\text{CO})_2(\text{PPh}_3)_2 \) and further methylation with methyl triflate affords the dimethylsulphonium methylide complex \( [\text{OsCl}(^1-\text{CH}_2\text{SMe}_2)(\text{CO})_2(\text{PPh}_3)_2]^+ \). Complexes of the methylthiolatomethyl ligand have been known for some time 195 and palladium and platinum complexes of both these same ligands have recently been derived from oxidative addition of \( \text{ClCH}_2\text{SMe} \) to \( \text{Pd(} \text{PPh}_3)_4 \) and \( \text{Pt(} \text{PPh}_3)_4 \) respectively, followed by methylation. 196 The thioformaldehyde complex and the methylated derivatives exhibit a medium to weak band in the I.R. spectrum near 560 cm\(^{-1}\) which is in the lower end of the range found for the \( \nu_{\text{CS}} \) vibration of aliphatic sulphides.
EXPERIMENTAL

HYDRIDO COMPLEXES

OsCl₂(PPH₃)₃.

Dichlorotris(triphenylphosphine)osmium(II).

(NH₄)₂[OsCl₆] (2.0 g) and triphenylphosphine (8.4 g) were heated under reflux in a degassed solution of t-butanol (300 ml) and water (120 ml) until the suspension turned a deep green (3 - 5 days). The reaction often proceeded via an orange suspension in which case the longer reaction period was found to be necessary. The mixture was allowed to cool to room temperature and the green crystals were washed with ethanol and hexane and allowed to dry at room temperature (4.56 g, 95.5%).

OsCl₂(CS)(PPH₃)₃.

Dichlorothiocarbonyltris(triphenylphosphine)osmium(II).

OsCl₂(PPh₃)₃ (2.0 g) and triphenylphosphine (1.0 g) were heated under reflux for 30 min in a carefully degassed solution comprised of benzene (50 ml) and carbon disulphide (5 ml). During this period the green suspension dissolved rapidly leaving a dark brown solution from which white crystals of the title compound gradually deposited. The solvent volume was reduced to 20 ml and ethanol (50 ml) was added. After removal of the benzene, filtration gave white needles which were washed with ethanol and hexane and dried at room temperature (2.05 g, 98.2%). An analytical sample was recrystallised from dichloromethane-ethanol,
but the crude product was used for further experimentation.  
M.p. 201-205°C. Anal. Found: C, 60.17; H, 4.43; P, 8.55%.

\[ C_{55}H_{45}Cl_2OsP_3S \] requires C, 60.49; H, 4.15; P, 8.51%.

\[ OsH_2(CS)(PPh_3)_3 \]

Dihydridothiocarbonyltris(triphenylphosphine)osmium(II).

\[ OsCl_2(CS)(PPh_3)_3 \] (2.0 g), triphenylphosphine (0.1 g) and sodium hydroxide (0.5 g) were heated under reflux in 2-methoxy-ethanol (20 ml) for 20 min. The resulting suspension was cooled on ice. Filtration gave vivid white crystals which were redissolved in dichloromethane and filtered through a celite pad. Ethanol was added and on removal of the dichloromethane vivid white crystals deposited (1.72 g, 91.8%). M.p. 174-176°C. Anal. Found: C, 64.58; H, 5.00; P, 8.95%. 
\[ C_{55}H_{47}OsP_3S \] requires C, 64.56; H, 4.67; P, 9.08%.

\[ OsCl(CS)(PPh_3)_3 \]

Chlorohydridothiocarbonyltris(triphenylphosphine)osmium(II).

\[ OsH_2(CS)(PPh_3)_3 \] (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol (10 ml) and concentrated hydrochloric acid (0.5 ml) were added. Vigorous hydrogen evolution ensued and when this had ceased the dichloromethane was removed to afford vivid white crystals which formed vivid white crystals of the hemidichloromethane solvate when recrystallised from dichloromethane-ethanol (1.06 g, 98.6%). \[ ^1H \text{N.M.R. (CDCl}_3 \] shows \[ \tau, 4.73 \text{ [s, 1H, CH}_2Cl_2 \]. M.p. 171-174°C. Anal. Found: C, 60.52; H, 4.61; P, 8.17%. 
\[ C_{55}H_{46}ClOsP_3S-(CH_2Cl_2)0.5 \] requires C, 60.59; H, 4.30; P, 8.45%.
OshBr(CS)(PPh$_3$)$_3$.

Bromohydridothiocarbonyltris(triphenylphosphine)osmium(II).

Osh$_2$(CS)(PPh$_3$)$_3$ (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol and concentrated hydrobromic acid (ca. 49%, 0.5 ml) were added. Vigorous hydrogen evolution ensued and when this had ceased the dichloromethane was removed to afford white crystals which formed crystals of the solvated complex OshBr(CS)(PPh$_3$)$_3$(CH$_2$Cl$_2$)$_{0.33}$ on recrystallisation from dichloromethane-ethanol (1.07 g, 96.9%). $^1$H N.M.R. (CDCl$_3$) shows $\tau$, 4.78 [s, 0.66 H, CH$_2$Cl$_2$]. M.p. 176-180°C. Anal. Found: C, 58.71; H, 4.24; P, 8.20%. $C_{55}H_{46}$BrOsP$_3$S.(CH$_2$Cl$_2$)$_{0.33}$ requires C, 58.79; H, 4.16; P, 8.22%.

OshI(H$_2$O)(CS)(PPh$_3$)$_2$.

Hydridoiodoaquothiocarbonylbis(triphenylphosphine)osmium(II).

Osh$_2$(CS)(PPh$_3$)$_3$ (0.3 g) was dissolved in dichloromethane (20 ml) and ethanol (10 ml) containing tetrafluoroboric acid (ca. 40%, 0.1 ml) and sodium iodide (0.1 g), which had been first dissolved in water (2 ml), was added. The solution was stirred for 5 min and on removal of the dichloromethane cream crystals separated which were collected and washed with water, ethanol and hexane. The solid was recrystallised four times from dichloromethane-ethanol to yield cream crystals (0.25 g, 94.2%). M.p. 130-132°C. Anal. Found: C, 48.25; H, 3.79; P, 6.42%. $C_{37}H_{33}$TOOsP$_2$S requires C, 49.11; H, 3.68; P, 6.85%.
Hydridoaquothiocarbonyltris(triphenylphosphine)osmium(II)-
tetrafluoroborate.

Osh₂(CS)(PPh₃)₃ (1.0 g) was dissolved in dichloromethane (25 ml), and ethanol (10 ml) and tetrafluoroboric acid (ca. 40%, 0.5 ml) were added. After effervescence had ceased the solvent volume was reduced to 5 ml. Slow addition of water effected crystallisation of white needles which were washed with an ethanol-water mixture (1:1) and dried at room temperature (1.05 g, 95.3%). An analytical sample was recrystallised from dichloromethane-ethanol-water.

M.p. 140-143°C. Anal. Found: C, 58.61; H, 4.83; P, 8.48%.

C₅₅H₄₈BF₄OoP₃S requires C, 58.61; H, 4.29; P, 8.24%.

Hydridoaquothiocarbonyltris(triphenylphosphine)osmium(II)perchlorate.

Osh₂(CS)(PPh₃)₃ (1.0 g) was dissolved in degassed dichloromethane (25 ml), and ethanol (10 ml) and perchloric acid (70%, 0.5 ml) were added. After effervescence had ceased the solvent volume was reduced to 5 ml. Air contact with the solution was kept to a minimum. Slow addition of water effected crystallisation of white crystals of the 1:1 aquo solvate which were washed with an ethanol-water mixture (1:1) and dried at room temperature (1.07 g, 94.6%). ¹H N.M.R. (CDCl₃) shows T, 8.02 [s, 2H, H₂O]. Recrystallisation as for BF₄⁻ salt.

M.p. 123-125°C. Anal. Found: C, 57.16; H, 4.39; P, 8.06%.

C₅₅H₄₈ClO₅OoP₃S.H₂O requires C, 57.06; H, 4.35; P, 8.03%.
[Osh(MeCN)₂(CS)(PPh₃)₂]ClO₄.

Hydridobis(acetonitrile)thiocarbonylbis(triphenylphosphine)osmium(II)- perchlorate.

OshCl(CS)(PPh₃)₃(CH₂Cl₂)₀.₅ (0.1 g) was heated under reflux in acetonitrile (50 ml) with silver perchlorate (0.19 g, 1 eq.) for 15 min. The white crystalline solid was collected on a celite pad, washed with ethanol and discarded. The filtrate and washings were evaporated to 10 ml and ethanol and cyclohexane were added. After removal of the acetonitrile the white crystals were collected and washed with cyclohexane (0.08 g, 93.6%). An analytical sample was recrystallised from dichloromethane-ethanol-cyclohexane.

M.p. 158-160°C. Anal. Found: C, 52.99; H, 4.03; P, 6.59%.

C₄₁H₃₇Cl₄O₄S₂P₂ requires C, 52.31; H, 3.96; P, 6.58%.

OshCl(CS)(CNR)(PPh₃)₂.

Chlorohydridothiocarbonylp-tolylisocyanidebis(triphenylphosphine)- osmium(II).

a) Isomer - Hydrido trans to chloro ligand.

OshCl(CS)(PPh₃)₃(CH₂Cl₂)₀.₅ (1.0 g) was dissolved in benzene (50 ml) and p-tolylisocyanide (0.11 g, 1.03 eq.) was added. The solution volume was lowered to 15 ml and hexane was added to afford a yellow solid which was collected and washed with hexane. Recrystallisation from dichloromethane-ethanol gave a yellow crystalline solid which was contaminated by the isomer with hydride trans to isocyanide and which contained 0.25 mole of dichloromethane of solvation (0.67 g, 78.9%). ¹H N.M.R. (CDCl₃) shows τ, 4.75 [s, 0.5H, CH₂Cl₂].
M.p. 133-135°C.  

**Anal.** Found: C, 58.58; H, 4.46; N, 1.51; P, 6.69%.  

\[
\text{C}_{45}\text{H}_{36}\text{ClNO}_{2}\text{S}_{2}\cdot(\text{CH}_2\text{Cl}_2)_{0.25}
\]
requires C, 58.21; H, 4.16; N, 1.50; P, 6.63%.

b) **Isomer** — **Hydride trans to isocyanide.**

(i) \(\text{OsHCl(CS)(CNR)(PPh}_3)_2\) [H trans Cl] (0.5 g) in benzene solution (30 ml) was heated under reflux for 2 h. Ethanol (30 ml) was added and upon evaporation of the solvent mixture white crystals deposited (0.46 g, 94.2%). M.p. 239-241°C.  

**Anal.** Found: C, 58.99; H, 4.19; N, 1.61%. \(\text{C}_{45}\text{H}_{38}\text{ClNO}_{2}\text{S}\) requires C, 59.23; H, 4.09; N, 1.54%.

(ii) \([\text{OsH(CS)(CNR)(PPh}_3]_3\text{ClO}_4\) (0.3 g, see Chapter 4) and lithium chloride (0.1 g) were heated in ethanol solution under reflux for 2 h. The white crystalline solid was collected and washed with ethanol and hexane (0.215 g, 97.3%). M.p. 239-241°C.

**OsHCl(CO)(CS)(PPh}_3)_2.**

**Chlorohydridocarbonylthiocarbonylbis(triphenylphosphine)osmium(II).**

\(\text{OsHCl(CS)(PPh}_3)_3\cdot(\text{CH}_2\text{Cl}_2)_{0.5}\) (0.3 g) was dissolved in benzene (50 ml) in a closed flask and carbon monoxide (6.5 ml at 1 atm. and 20°C, \(\alpha\). 1 eq.) was introduced through a rubber septum. The solution was shaken for 15 min. The volume of the solution was reduced to 10 ml and hexane was added to afford cream crystals which were washed with hexane. Recrystallisation from dichloromethane-hexane gave cream cubes (0.2 g, 89.1%). M.p. 188-190°C.  

**Anal.** Found: C, 54.93; H, 3.82; P, 7.60%. \(\text{C}_{38}\text{H}_{31}\text{ClO}_{0}\text{O}_{2}\text{S}\) requires C, 55.43; H, 3.80; P, 7.52%.
OsHBr(CO)(CS)(PPh₃)₂.

Bromohydridocarbonylthiocarbonylbis(triphenylphosphine)osmium(II).

OsHBr(CS)(PPh₃)₃(CH₂Cl₂)₀·₃₃ (0.3 g) was dissolved in benzene (50 ml) in a closed flask and carbon monoxide (6.2 ml at 1 atm. and 20°C, ca. 1 eq.) was introduced through a rubber septum. The solution was shaken for 15 min. The volume of the solution was reduced to 10 ml and ethanol was added to afford pale yellow crystals which were washed with ethanol. Recrystallisation from dichloromethane-ethanol gave pale yellow crystals (0.21 g, 91.2%).

M.p. 182-185°C. Anal. Found: C, 52.38; H, 3.80; P, 7.26%.

C₁₈H₃₁BrOOS₂P₂S₂ requires C, 52.59; H, 3.60; P, 7.14%.

OsH(n²-S₂CNET₂)₃(CS)(PPh₃)₂.

Dihapto-diethylidithiocarbamatohydridothiocarbonylbis(triphenylphosphine)-
osmium(II).

[OsH(H₂O)(CS)(PPh₃)₃]BF₄ (0.3 g) was dissolved in ethanol (30 ml) and sodium diethylidithiocarbamate (0.1 g) in ethanol (10 ml) was added. The solution was stirred for 30 min and the yellow crystals were collected and washed with ethanol. Recrystallisation from dichloromethane-ethanol gave lemon needles (0.19 g, 78.6%).

M.p. 235-238°C. Anal. Found: C, 55.82; H, 4.65; N, 1.64;
P, 6.78%. C₄₂H₄₁NO₃P₂S₂ requires C, 55.55; H, 4.55; N, 1.54;
P, 6.82%.

OsH(n¹-S₂CNET₂)(CO)(CS)(PPh₃)₂.

Monohapto-diethylidithiocarbamatohydridocarbonylthiocarbonylbis(triphenyl-
phosphine)osmium(II).

[OsH(H₂O)(CS)(PPh₃)₃]BF₄ (0.3 g) was dissolved in dichloromethane
(10 ml) and ethanol (20 ml) and the solution was stirred under carbon monoxide (60 p.s.i.) for 1.5 h. The dichloromethane was removed and sodium diethyldithiocarbamate (0.1 g) was added. The solution was stirred for 30 min and the yellow crystals were collected and washed with ethanol. Recrystallisation from dichloromethane-ethanol gave yellow-orange crystals. \(^1\)H N.M.R. (CDCl\(_3\), DMSO) showed that these crystals contain dichloromethane of solvation (\(\tau\), 4.3) but the compound was too insoluble to obtain an accurate integral. Analysis indicates the presence of 0.33 mol dichloromethane (0.21 g, 81.8%). M.p. 154°C. Anal. Found: C, 53.92; H, 3.67%.

\(\text{C}_4\text{H}_{41}\text{NOOsP}_2\text{S}_3\cdot(\text{CH}_2\text{Cl}_2)_{0.33}\) requires C, 53.96; H, 4.35%.

**THIOFORMYL COMPLEXES AND DERIVATIVES**

OsCl(CHS)(CO)\(_2\)\(\text{PPh}_3\)\(_2\).

**Chlorothioformydicarbonylbis(triphenylphosphine)osmium(II).**

OsHCl(CS)(PPh\(_3\)\(_3\)'\(\text{CH}_2\text{Cl}_2\)\(_0.5\) (1.0 g) was stirred in dry benzene (20 ml) under carbon monoxide (40 p.s.i.) for 1 h. Hexane was added to afford sky blue crystals which were washed with hexane.

\(^1\)H N.M.R. (C\(_6\)D\(_6\)) shows presence of 0.66 mol \(n\)-hexane of solvation [\(\tau\), 9.13, 8.80, 2 m, 9.3 H, C\(_6\)H\(_{14}\)] (0.82 g, 99.3%). M.p. 128-130°C. Anal. Found: C, 57.05; H, 4.48; P, 6.59%. C\(_{39}\)H\(_{31}\)Cl\(_2\)OsP\(_2\)S.-

\(\text{C}_6\text{H}_{14}\)\(_0.66\) requires C, 56.83; H, 4.44; P, 6.81%.

OsBr(CHS)(CO)\(_2\)\(\text{PPh}_3\)\(_2\).

**Bromothioformydicarbonylbis(triphenylphosphine)osmium(II).**

OsHBr(CS)(PPh\(_3\)\(_3\)'\(\text{CH}_2\text{Cl}_2\)\(_0.33\) (1.0 g) was treated as above to afford
blue crystals of OsBr(CHS)(CO)₂(PPh₃)₂·C₆H₁₄ (0.85 g, 97.9%). ¹H N.M.R. (C₆D₆) shows presence of 1 mol n-hexane of solvation [τ, 9.10, 8.77, 2 m, 14 H, C₆H₁₄]. M.p. 161-162°C. Anal. Found: C, 55.13; H, 4.74; P, 6.44%. C₃₉H₃₁BrO₂OsP₂S·(C₆H₁₄) requires C, 55.04; H, 4.62; P, 6.31%.

OsCl(CHS)(CO)(CNR)(PPh₃)₂'H₂O

Chlorothioformylcarbonyl-p-tolylisocyanidebis(triphenylphosphine)-osmium(II).

OsHCl(CS)(CNR)(PPh₃)₂ [hydrido trans to chloro ligand] (1.0 g) was stirred in dry benzene (30 ml) under carbon monoxide (40 p.s.i.) for 1.5 h. The intense blue colouration which is characteristic of the thioformyl complexes developed more slowly than in either of the above two complexes. Hexane was added to afford sky blue needles which were washed with hexane and dried at room temperature (1.0 g, 97.0%). An analytical sample was recrystallised from dry benzene-petroleum spirit to give sky blue needles which were washed with petroleum spirit. M.p. 205-207°C. Anal. Found: C, 58.73; H, 4.38; N, 1.53%. C₄₆H₃₈ClNOO₂S₂S requires C, 58.74; H, 4.38; N, 1.49%. 
[OsCl(CHSMe)(CO)\(_2\)(PPh\(_3\))\(_2\)]CF\(_3\)SO\(_3\).

Chlorodicarbonylmethylthiolatocarbenebis(triphenylphosphine)osmium(II)-trifluoromethanesulphonate.

OsCl(CHS)(CO)\(_2\)(PPh\(_3\))\(_2\).C\(_6\)H\(_4\)O.66 (0.5 g) was dissolved in benzene (25 ml) and methyl triflate (0.2 ml) was added. After stirring for 10 min hexane (10 ml) was added and the yellow crystals were collected and washed with benzene and hexane. \(^1\)H N.M.R. (CDCl\(_3\)) shows the presence of benzene of solvation \(\tau\), 2.63 [s, 4H, C\(_6\)H\(_6\)] giving the composition [OsCl(CHSMe)(CO)\(_2\)(PPh\(_3\))\(_2\)CF\(_3\)SO\(_3\).C\(_6\)H\(_6\)]0.66 (0.58 g, 98.6%). M.p. 138-140°C. Anal. Found: C, 50.70; H, 4.12; P, 5.63%.

\(\text{C}_{41}^\text{H}_{34}^\text{ClF}_5^\text{O}_5^\text{OsP}_2\text{SO}_3\).C\(_6\)H\(_6\)0.66 requires C, 50.62; H, 3.59; P, 5.80%.

[OsCl(CHSMe)(CO)\(_2\)(PPh\(_3\))\(_2\)]ClO\(_4\).

Chlorodicarbonylmethylthiolatocarbenebis(triphenylphosphine)osmium(II)- perchlorate.

[OsCl(CHSMe)(CO)\(_2\)(PPh\(_3\))\(_2\)CF\(_3\)SO\(_3\).C\(_6\)H\(_6\)]0.66 (0.3 g) was recrystallised from dichloromethane-ethanol (30 ml, 2:1) containing perchloric acid (70%, 0.1 ml) to afford pale yellow crystals (0.24 g, 88.4%). M.p. 260-264°C. Anal. Found: C, 50.24; H, 3.61%. C\(_40\)H\(_{34}\)Cl\(_2\)O\(_6\)OsP\(_2\)S requires C, 49.74; H, 3.55%.

[OsBr(CHSMe)(CO)\(_2\)(PPh\(_3\))\(_2\)]CF\(_3\)SO\(_3\).

Bromodicarbonylmethylthiolatocarbenebis(triphenylphosphine)osmium(II)-trifluoromethanesulphonate.

OsBr(CHS)(CO)\(_2\)(PPh\(_3\))\(_2\).C\(_6\)H\(_4\)O (0.5 g) was treated with methyl
triflate in dry benzene as above to yield yellow crystals. $^1$H N.M.R. 
(CDCl$_3$) shows $\tau$, 2.65 [s, 6H] attributable to benzene of solvation
giving the composition [OsBr(CHSMe)(CO)$_2$(PPh$_3$)$_2$]CF$_3$SO$_3$. C$_{44}$H$_{34}$BrF$_2$O$_5$Sp$_2$S$_2$ (C$_{6}$H$_{6}$)$_2$ required C, 49.60; H, 3.54; P, 5.44%.

C$_{41}$H$_{34}$BrF$_2$O$_5$Sp$_2$S$_2$. (C$_{6}$H$_{6}$)$_2$ required C, 49.60; H, 3.54; P, 5.44%.


Chlorocarbonylmethylthiolatocarbene-p-tolylisocyanidebis(triphenylphosphine)-
osmium(II)trifluoromethanesulphonate.

OsCl(CHS)(CO)(CN)(PPh$_3$)$_2$ (0.5 g) was treated with methyl triflate
in dry benzene to yield yellow crystals. $^1$H N.M.R. (CDCl$_3$) shows
$\tau$, 2.75 [s, 1H] attributable to benzene of solvation giving the
composition [OsCl(CHSMe)(CO)(CN)(PPh$_3$)$_2$]CF$_3$SO$_3$. (C$_{6}$H$_{6}$)$_2$ 0.167.

M.p. 195-200°C. Anal. Found: C, 53.04; H, 4.17; N, 1.21%.

C$_{48}$H$_{41}$ClF$_3$NO$_5$Sp$_2$S$_2$. (C$_{6}$H$_{6}$)$_2$ requires C, 52.66; H, 3.79; N, 1.25%.
Chlorodicarbonyl-N-methylaminocarbenebis(triphenylphosphine)osmium(II) perchlorate.

\[ \text{OsCl(ChNHMe)}(\text{CO})_2\text{(PPh}_3\text{)}_2\text{ClO}_4 \]

\[ \text{[OsCl(CHSMe) (CO)}_2\text{(PPh}_3\text{)}_2\text{]}\text{CF}_3\text{SO}_3\text{. (C}_6\text{H}_6\text{)}_{0.66} \]

(0.3 g) was dissolved in dichloromethane (30 ml) and 1 ml of a solution of methylamine in ethanol (ca. 33%) was added. Perchloric acid (70%, 0.5 ml) was added and on reduction of the solvent volume white crystals were deposited which were collected and washed with ethanol and hexane (0.24 g, 87.7%). An analytical sample was recrystallised from dichloromethane-ethanol-cyclohexane to afford colourless crystals. M.p. 205-207°C. Anal. Found: C, 50.43; H, 4.08; N, 1.63%. 

\[ \text{C}_{40}\text{H}_{35}\text{Cl}_2\text{NO}_2\text{O}_2\text{S}_2 \]

requires C, 50.64; H, 3.72; N, 1.48%.

Chloromethyliminoformylidicarbonylbis(triphenylphosphine)osmium(II).

\[ \text{OsCl(ChNHMe)}(\text{CO})_2\text{(PPh}_3\text{)}_2\text{ClO}_4 \]

(0.2 g) was dissolved in dichloromethane-ethanol (30 ml, 3:1) and a solution of sodium hydroxide (0.1 g) in ethanol (10 ml) was added. Upon reduction of the solvent volume white feathery crystals formed which were collected and washed with ethanol. Recrystallisation was achieved from dichloromethane-ethanol (0.179 g, 100%). M.p. 220-222°C. Anal. Found: C, 56.48; H, 4.55; N, 2.01%. 

\[ \text{C}_{40}\text{H}_{34}\text{ClNO}_2\text{O}_2\text{S}_2 \]

requires C, 56.63; H, 4.04; N, 1.65%.
OsCl(CHO)(CO)₂(PPh₃)₂.

**Chloroformylidicarbonylbis(triphenylphosphine)osmium(II).**

\[ [\text{OsCl(CHSMe)(CO)}_2(PPh_3)_2]CF_3SO_3\cdot(C_6H_6)_{0.66} \] 
(0.3 g) was recrystallised from dichloromethane (40 ml) - ethanol (10 ml) - water (5 ml) by removal of dichloromethane under reduced pressure without the application of heat. The white crystals were collected and washed with ethanol (0.22 g). I.R. indicates a mixture of OsCl(CHO)(CO)₂(PPh₃)₂ and OsHCl(CO)₂(PPh₃)₂ (α: 9:1) but further purification was not possible [section 3.4(i)].

OsBr(CHO)(CO)₂(PPh₃)₂.

**Bromoformylidicarbonylbis(triphenylphosphine)osmium(II).**

\[ [\text{OsBr(CHSMe)(CO)}_2(PPh_3)_2]CF_3SO_3\cdot(C_6H_6) \] 
(0.3 g) was treated as above to afford white crystals (0.21 g). I.R. indicates a mixture of OsBr(CHO)(CO)₂(PPh₃)₂ and OsHBr(CO)₂(PPh₃)₂ (α: 4:1) but further purification was not possible [section 3.4(i)].

OsCl(CHO)(CO)(CN)(PPh₃)₂.

**Chloroformylcarbonyl-p-tolylisocyanidebis(triphenylphosphine)osmium(II).**

\[ [\text{OsCl(CHSMe)(CO)CN}(PPh_3)_2]CF_3SO_3\cdot(C_6H_6)_{0.167} \] 
(0.3 g) was dissolved in dichloromethane (30 ml) and a solution of ethanol (20 ml) and water (5 ml) containing sodium hydroxide (0.05 g) was added. Upon reduction of the solvent volume white crystals deposited which were collected and washed with ethanol (0.13 g, 52.4%). An analytical sample was recrystallised from dichloromethane-hexane.
M.p. 151-153°C (darkens above 130°C). Anal. Found: C, 59.44; H, 4.74; N, 1.36%. $\text{C}_{46}\text{H}_{38}\text{ClNO}_{2}\text{OsP}_{2}$ requires C, 59.77; H, 4.14, N, 1.52%.

\[
[\text{OsCl(CHOME)}(\text{CO})(\text{CNR})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3.
\]

Chlorocarbonylmethoxycarbene-$p$-tolylisocyanidebis(triphenylphosphine)osmium(II)trifluoromethanesulphonate.

OsCl(CHO)(CO)(CNR)(PPh$_3$)$_2$ (0.1 g) was dissolved in dry benzene (10 ml) and methyl triflate (0.03 ml) was added. After stirring for 5 min hexane was added and the solvent was decanted from the oily solid which was washed twice with hexane. Recrystallisation from dichloromethane-hexane yielded pale lemon crystals which were collected and washed with hexane and dried at room temperature. The crystals contain 1.0 equivalent dichloromethane of solvation (0.11 g, 86.7%). $^1$H N.M.R. (CDCl$_3$) shows $\tau$, 4.70 [s, 2H, CH$_2$Cl$_2$]. M.p. 108-112°C. Anal. Found: C, 49.20; H, 4.02; N, 1.17%.

$\text{C}_{48}\text{H}_{41}\text{ClF}_3\text{NO}_5\text{OsP}_2\text{S.CH}_2\text{Cl}_2$ requires C, 50.15; H, 3.69; N, 1.19%.

Os($^2$-$\text{CH}_2\text{S}$)(CO)$_2$(PPh$_3$)$_2$.

Dithapto-thioformaldehydedicarbonylbis(triphenylphosphine)osmium(II).

OsCl(CHS)(CO)$_2$(PPh$_3$)$_2$.($\text{C}_6\text{H}_{14}$)$_{0.66}$ (0.5 g) was heated under reflux in a solution of dichloromethane (30 ml) and ethanol (10 ml)
containing sodium borohydride (0.1 g) for 30 min. Evaporation of the dichloromethane yielded cream crystals which were collected and washed with water and ethanol. The solid was dissolved in dichloromethane and the solution passed through a celite pad. Ethanol was added and the dichloromethane removed to afford cream crystals (0.43 g). Recrystallisation from dichloromethane-benzene afforded white crystals of the solvate Os(η²-CH₂S)(CO)₂(PPh₃)₂(CH₂Cl₂)₀.₂₅ which were collected and washed with ethanol (0.23 g, 46.7%). ¹H N.M.R. (CDCl₃) shows τ, 4.73 [s, 0.5 H, CH₂Cl₂]. M.p. 193-195°C. Anal. Found: C, 56.49; H, 4.15; P, 7.65%. C₃₉H₃₂O₂OsP₂S(CH₂Cl₂)₀.₂₅ requires C, 56.25; H, 3.91; P, 7.39%.

OsCl(SMe)(CO)₂(PPh₃)₂·

Chloromethylthiolatodicarbonyl bis(triphenylphosphine) osmium(II).

Os(η²-CH₂S)(CO)₂(PPh₃)₂(CH₂Cl₂)₀.₂₅ (0.15 g) was dissolved in dichloromethane (30 ml) and ethanol (10 ml) containing concentrated hydrochloric acid (0.01 ml) was added. Removal of the dichloromethane afforded yellow ochre crystals which were collected and washed with ethanol (0.145 g, 94.9%). An analytical sample was recrystallised from dichloromethane-ethanol to give yellow ochre crystals. M.p. 185-188°C. Anal. Found: C, 54.94; H, 4.00; P, 6.57%. C₃₉H₃₃ClO₂OsP₂S requires C, 54.89; H, 3.90; P, 7.26%.
OsCl₂(CO)₂(PPh₃)₂,

Dichlorodicarbonyl bis(triphenylphosphine) osmium(II).

OsCl(SMe)(CO)₂(PPh₃)₂ (0.1 g) was dissolved in dichloromethane (20 ml) and ethanol (10 ml) containing concentrated hydrochloric acid (0.05 ml) was added. The solution was heated under reflux for 5 min during which time the evolution of methyl thiol occurred as evidenced by the very characteristic odour of the effluent gas. Removal of dichloromethane afforded white crystals (0.095 g, 96.3%) characterised by comparison of the I.R. spectrum with that of an authenticated sample.¹¹⁰

[Os(n²-CH₂SMe)(CO)₂(PPh₃)₂]CF₃SO₃.

Dihapto-methylthiolatomethyl dicarbonyl bis(triphenylphosphine) osmium(II)-trifluoromethanesulphonate.

Os(n²-CH₂S)(CO)₂(PPh₃)₂(CH₂Cl₂)₀.₅ (0.3 g) was stirred in dry benzene (30 ml) and methyl triflate (0.1 ml) was added. After 20 min hexane (10 ml) was added and the white crystals were collected and washed with hexane (0.35 g, 97.9%). An analytical sample was recrystallised from dichloromethane-ethanol-cyclohexane to yield white crystals of the solvate [Os(n²-CH₂SMe)(CO)₂(PPh₃)₂]CF₃SO₃·H₂O.¹¹¹

¹H N.M.R. (CDCl₃) shows τ, 8.40 [s, 2H, H₂O], I.R. (cm⁻¹) shows ν₁OH 3500 (w, br), δ₁OH 1625 (w). M.p. 235-238°C. Anal. Found; C, 49.27; H, 4.01; P, 6.44%. C₄₁H₃₅F₃O₅OsP₂S₂·H₂O requires C, 49.29; H, 3.73; P, 6.20%.
OsCl(η¹-CH₂SMe)₂(CO)₂(PPh₃)₂.

Chloro-monohapto-methylthiolatomethtylidodicarbonylbis(triphenylphosphine)-osmium(II).

[Os(η²-CH₂SMe)₂(CO)₂(PPh₃)₂]CF₃SO₃·H₂O (0.3 g) and lithium chloride (0.1 g) were heated under reflux in ethanol solution (20 ml) for 15 min. The white crystals were collected and washed with ethanol (0.24 g, 90.5%). An analytical sample was recrystallised from dichloromethane-ethanol. M.p. 167-168°C. Anal. Found: C, 55.34; H, 4.39; P, 7.32%. C₄₀H₃₅Cl₂O₅P₂S₂S requires C, 55.39; H, 4.07; P, 7.14%.

[OsCl(η¹-CH₂SMe₂)₂(CO)₂(PPh₃)₂]CF₃SO₃.

Chloro-monohapto-dimethylsulphoniummethylidodicarbonylbis(triphenylphosphine)osmium(II)trifluoromethanesulphonate.

OsCl(η¹-CH₂SMe)₂(CO)₂(PPh₃)₂ (0.2 g) was dissolved in dry benzene (20 ml) and methyl triflate (0.05 ml) was added. After 10 min stirring hexane (10 ml) was added and the white crystals were collected and washed with hexane (0.23 g, 96.7%). An analytical sample was recrystallised from dichloromethane-ethanol-cyclohexane to give white crystals of the solvate [OsCl(η¹-CH₂SMe₂)₂(CO)₂(PPh₃)₂]CF₃SO₃·(C₆H₁₂)₀.₆₆(H₂O)₂. ¹H N.M.R. (CDCl₃) shows τ, 8.53 [s, 8H, C₆H₁₂], τ, 7.70 [s, 4H, H₂O]. M.p. 183-187°C. Anal. Found: C, 49.21; H, 4.46; P, 5.49%. C₄₂H₃₈ClF₃O₅P₂S₂S·(C₆H₁₂)₀.₆₆(H₂O)₂ requires C, 49.17; H, 4.48; P, 5.51%.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CS}^a$</th>
<th>$\nu_{Osh}$</th>
<th>$\delta_{Osh}$</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsCl$_2$(CS) L$_3$</td>
<td>1290</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsH$_2$(CS) L$_3$</td>
<td>1233</td>
<td>2070s, 800w,</td>
<td>1895s, 775w</td>
<td></td>
</tr>
<tr>
<td>OsHCl(CS) L$_3$</td>
<td>1280</td>
<td>2100wm</td>
<td>820w</td>
<td></td>
</tr>
<tr>
<td>OsHBr(CS) L$_3$</td>
<td>1273</td>
<td>2110wm</td>
<td>810w</td>
<td></td>
</tr>
<tr>
<td>OsHI(H$_2$O)(CS)L$_2$</td>
<td>1295</td>
<td>2110wm</td>
<td>818w</td>
<td>3400w ($\nu_{OH}$); 1600w ($\delta_{OH}$)</td>
</tr>
<tr>
<td>[OsH(H$_2$O)(CS)L$_3$]BF$_4$</td>
<td>1297</td>
<td>2060w</td>
<td>820w</td>
<td>3600w, 3500w ($\nu_{OH}$); 1625w ($\delta_{OH}$); 1110m, 1065s, 975m (BF$_4$)</td>
</tr>
<tr>
<td>[OsH(H$_2$O)(CS)L$_3$]ClO$_4$</td>
<td>1295</td>
<td>2070w</td>
<td>818w</td>
<td>3400w ($\nu_{OH}$); 1625w ($\delta_{OH}$); 1095vs (ClO$_4$)</td>
</tr>
<tr>
<td>[OsH(MeCN)$_2$(CS)L$_3$]ClO$_4$</td>
<td>1297</td>
<td>2110w</td>
<td>837w</td>
<td>1095vs (ClO$_4$)</td>
</tr>
<tr>
<td>OsHCl(CS)(CNR)L$_2$ [CS trans to Cl + CS trans to CNR]</td>
<td>1276 1950w</td>
<td></td>
<td></td>
<td>245s vs ($\nu_{CN}$)</td>
</tr>
<tr>
<td>OsHCl(CS)(CNR)L$_2$ [CS trans to Cl]</td>
<td>1282</td>
<td>1957wm</td>
<td></td>
<td>2145vs ($\nu_{CN}$)</td>
</tr>
<tr>
<td>OsHCl(CO)(CS)L$_2$</td>
<td>1295</td>
<td>1960m</td>
<td>825w, 785w</td>
<td>2050vs ($\nu_{CO}$)</td>
</tr>
<tr>
<td>OsHBr(CO)(CS)L$_2$</td>
<td>1300</td>
<td>1958ms</td>
<td>820w, 787w</td>
<td>2050vs ($\nu_{CO}$)</td>
</tr>
<tr>
<td>OsH($\eta^2$-S$_2$CNET)$_2$(CS)L$_2$</td>
<td>1262</td>
<td>2070w</td>
<td>780w</td>
<td>1488m, 1450w, 1360w, 1213w, 1148w, 915w, 850w</td>
</tr>
<tr>
<td>OsH($\eta^1$-S$_2$CNET)$_2$(CO)(CS)L$_2$</td>
<td>1290</td>
<td>c</td>
<td>c</td>
<td>1115vs ($\nu_{C=S}$); 665m ($\nu_{C-S}$)</td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh$_3$; R = p-tolyl)  
(a) very strong;  
(b) band obscured by arene $\delta_{CH}$ at 818 cm$^{-1}$;  
(c) band not visible.
### Table 3.2 $^1$H N.M.R. DATA (CDCl$_3$) FOR HYDRIDO-THIOCARBONYL COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydride Chemical Shift (δ) and Coupling Constants (Hz)</th>
<th>Other Assignments</th>
</tr>
</thead>
</table>
| ![Diagram](image) | 20.43, dtd, $^a$H$_1$  
$^2$J(H$_1$P$_1$) = 26.2  
$^2$J(H$_1$P$_2$) = 23.3  
$^2$J(H$_1$H$_2$) = 5.5  
17.32, dtd, $^a$H$_2$  
$^2$J(H$_2$P$_1$) = 28.0  
$^2$J(H$_2$P$_2$) = 60.5 | 2.91, m, 46H, Ph |
| ![Diagram](image) | 15.50, dt, $^2$J(HP$_1$) = 24.5  
$^2$J(HP$_2$) = 93.0 | 2.81, m, 48H, Ph |
| OsHBr(CS)$_3$ | 16.04, dt, $^2$J(HP$_1$) = 24.0  
$^2$J(HP$_2$) = 89.0 | 2.93, m, 45H, Ph |
| OsH$_2$(H$_2$O)(CS)$_2$ | 20.27, t, $^2$J(HP) = 16.4 | 7.27, s (br), 2H, H$_2$O  
2.45, m, 47H, Ph |
| [OsH$_2$(H$_2$O)(CS)$_3$]BF$_4$ | 15.18, dt, $^2$J(HP$_1$) = 25.0  
$^2$J(HP$_2$) = 82.6 | 6.23, s (br), 2H, H$_2$O  
2.78, m, 49H, Ph |
| [OsH$_2$(H$_2$O)(CS)$_3$]ClO$_4$ | 15.20, dt, $^2$J(HP$_1$) = 24.5  
$^2$J(HP$_2$) = 82.0 | 6.26, s (br), 2H, H$_2$O  
2.73, m, 50H, Ph |
| [Os(MeCN)$_2$(CS)$_2$]ClO$_4$ | 20.90, t, $^2$J(HP) = 15.0 | 8.00, s, 3H, CH$_3$CN  
8.58, s, 3H, CH$_3$CN  
2.77, m, 32H, Ph |
| OsHCl(CS)(CNR)$_2$ | 23.78, t, $^2$J(HP) = 13.2 | 7.75, s, 3H, C$_6$H$_4$-CH$_3$  
3.53, q, H, -C$_6$H$_4$-  
2.42, m, 47H, Ph |
Table 3.2 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydride Chemical Shift (τ) and Coupling Constants (Hz)</th>
<th>Other Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSHCl(CS) (CNR)L₂ (H trans to CNR).</td>
<td>12.75, t, ²J(HP) = 19.0</td>
<td>7.67, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.30, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.35, m, 31H, Ph</td>
</tr>
<tr>
<td>OSHCl(CO) (CS)L₂</td>
<td>e</td>
<td>2.41, m, Ph</td>
</tr>
<tr>
<td>OSHBr(CO) (CS)L₂</td>
<td>e</td>
<td>2.50, m, Ph</td>
</tr>
<tr>
<td>OSH(n²-S₂CNET₂) (CS)L₂</td>
<td>19.63, t, ²J(HP) = 18.0</td>
<td>9.32, t, 3H, CH₂-CH₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J(HH) = 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.25, t, 3H, CH₂-CH₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J(HH) = 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.17, q, 2H, N-CH₂-CH₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.05, q, 2H, N-CH₂-CH₃,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.64, m, 31H, Ph</td>
</tr>
<tr>
<td>OSH(n¹-S₂CNET₂) (CO) (CS)L₂</td>
<td>²</td>
<td></td>
</tr>
<tr>
<td>IrH(CS)L₃</td>
<td>14</td>
<td>23.0, q, ²J(HP) = 25</td>
</tr>
<tr>
<td>[IrH₂(CO) (CS) (PCY₃)₂]ClO₄</td>
<td>87</td>
<td>19.95, t, ²J(HP) = 25±2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24.05, t</td>
</tr>
<tr>
<td>[WH(CO) (CS) (diphos)]⁻</td>
<td>98</td>
<td>12.79, tt, ²J(HP) = 72</td>
</tr>
<tr>
<td>CP₃SO₃</td>
<td></td>
<td>²J(HP') = 13</td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh₃; R = p-toly1)
(a) dtd = double triplet of doublets;
(b) ref.110, p26 for ¹H N.M.R. table of OSH₂XL₃ compounds;
(c) meridional phosphines and H trans to phosphine as for OSHCl(CS)L₃;
(d) includes Ph resonances for isomer H trans to CNR also present;
(e) no hydride resonance observed [section 3.2];
(f) too insoluble for ¹H N.M.R.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CO}$</th>
<th>$\nu_{CN}$</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>THIOFORMYL COMPLEXES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OsCl(CHS)(CO)$_2$L$_2$</td>
<td>2050,1970</td>
<td></td>
<td>2867w ($\nu_{CH}$); 1190ms, 1010m (CHS)</td>
</tr>
<tr>
<td>OsBr(CHS)(CO)$_2$L$_2$</td>
<td>2040,2021</td>
<td>1978,1953$^d$</td>
<td>2865w ($\nu_{CH}$); 1190ms, 1011m (CHS)</td>
</tr>
<tr>
<td>OsCl(CHS)(CO)(CNR)L$_2$</td>
<td>1972</td>
<td>2130vs</td>
<td>2840w ($\nu_{CH}$); 1184m, 1000m (CHS)</td>
</tr>
<tr>
<td><strong>DERIVATIVES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OsCl(CHSMe)(CO)$_2$L$_2$]$^+$$^b$</td>
<td>2050,1996</td>
<td></td>
<td>965wm$^e$ (carbene)$^c$</td>
</tr>
<tr>
<td>[OsBr(CHSMe)(CO)$_2$L$_2$]CF$_3$SO$_3$</td>
<td>2055,1995</td>
<td></td>
<td>965wm$^e$ (carbene)$^c$</td>
</tr>
<tr>
<td>[OsCl(CHSMe)(CO)(CNR)L$_2$]CF$_3$SO$_3$</td>
<td>2003</td>
<td>2155vs</td>
<td>954wm$^e$ (carbene)$^c$</td>
</tr>
<tr>
<td>[OsCl(CHNHMe)(CO)$_2$L$_2$]ClO$_4$</td>
<td>2060,1982</td>
<td>1610s$^g$</td>
<td>3245w, 2975w ($\nu_{NH}$); 810w (carbene)$^f$</td>
</tr>
<tr>
<td>OsCl(CHNMe)(CO)$_2$L$_2$</td>
<td>2030,1953</td>
<td>1589s</td>
<td>2747wm ($\nu_{CH}$); 970w (iminoformyl)</td>
</tr>
<tr>
<td>OsCl(CHO)(CO)$_2$L$_2$</td>
<td>2020,1960$^h$</td>
<td></td>
<td>2660w, 2540w ($\nu_{CH}$); 1610s (v$_{C=O}$)</td>
</tr>
<tr>
<td>OsBr(CHO)(CO)$_2$L$_2$</td>
<td>2040,1970$^h$</td>
<td></td>
<td>2695w, 2555w ($\nu_{CH}$); 1609ms (v$_{C=O}$)</td>
</tr>
<tr>
<td>OsCl(CHO)(CO)(CNR)L$_2$</td>
<td>1965,1950</td>
<td>2120vs</td>
<td>2685w, 2564w, 2515wn ($\nu_{CH}$); 1602s, 1596s, 1572wm (v$_{C=O}$)</td>
</tr>
<tr>
<td>[Fe(CHO)(CO)$_4$]$^{1,}$</td>
<td>2018w, 1930s, 1902vs</td>
<td></td>
<td>2690, 2540 ($\nu_{CH}$); 1607 (v$_{C=O}$)</td>
</tr>
<tr>
<td>[Fe(CHO)(CO)$_3$P[OPh]$_3$]$^k$</td>
<td>1960m, 1872vs</td>
<td></td>
<td>2515w ($\nu_{CH}$); 1584m (v$_{C=O}$)</td>
</tr>
<tr>
<td>[OsCl(CHMe)(CO)(CNR)L$_2$]CF$_3$SO$_3$</td>
<td>2005</td>
<td>2155</td>
<td>1240s (carbene)$^c$</td>
</tr>
</tbody>
</table>
Table 3.3 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{CO}$</th>
<th>$\nu_{CN}$</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os($\eta^2$-CH$_2$S) (CO)$_2$L$_2$</td>
<td>1985,1915</td>
<td></td>
<td>558m ($\nu_{CS}$)</td>
</tr>
<tr>
<td>OsCl(SMe)(CO)$_2$L$_2$</td>
<td>2038,1950</td>
<td></td>
<td>558m ($\nu_{CS}$)</td>
</tr>
<tr>
<td>[Os($\eta^2$-CH$_2$SMe)(CO)$_2$L$_2$]CF$_3$SO$_3$</td>
<td>2035,1954</td>
<td></td>
<td>565m ($\nu_{CS}$)</td>
</tr>
<tr>
<td>OsCl($\eta^1$-CH$_2$SMe)(CO)$_2$L$_2$</td>
<td>2025,2005,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1952,1934</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OsCl($\eta^1$-CH$_2$SMe$_2$)(CO)$_2$L$_2$]CF$_3$SO$_3$</td>
<td>2035,1957</td>
<td></td>
<td>570w ($\nu_{CS}$)</td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh$_3$; R = p-tolyl)

(a) very strong;
(b) isolated as CF$_3$SO$_3^-$ and ClO$_4^-$ salts;
(c) CF$_3$SO$_3$ bands at 1270vs, 1225m, 1150s, 1030vs, 640vs;
(d) solid state splitting gives multiple bands;
(e) broad band;
(f) perchlorate bands ca.1095vs, 620s;
(g) \(\delta_{NH}\) obscured by this band;
(h) $\nu_{CO}$ bands due to OsX(CHO)(CO)$_2$L$_2$ and OsHX(CO)$_2$L$_2$;
(i) in THF solution$^{166(a)}$;
(j) for Na$^+$ salt; isolated as [(Ph$_3$P)$_2$N]$^+$ salt, I.R. dependent upon cation;
(k) in THF solution$^{166(b)}$. 

164.
Table 3.4 $^1$H N.M.R. DATA (CDCl$_3$) FOR THIOFORMYL AND DERIVED COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ($\delta$) and Coupling Constants (Hz)</th>
</tr>
</thead>
</table>
| OsCl(CHS)(CO)$_2$L$_2$ | a) 2.47, m, 34H, Ph  
-6.93, t, 1H, -CHS, $^3$J(HP) = 2.2  
b) in C$_6$D$_6$: 2.58, m, 30H, Ph  
-7.73, t, 1H, -CHS, $^3$J(HP) = 2.5 |
| OsBr(CHS)(CO)$_2$L$_2$ | a) 2.62, m, 36H, Ph  
-7.19, t, -CHS, $^3$J(HP) = 2.3  
b) in C$_6$D$_6$: 2.41, m, 31H, Ph  
-7.86, t, 1H, -CHS, $^3$J(HP) = 2.5 |
| OsCl(CHS)(CO)(CNR)L$_2$ | 7.68, s, 3H, C$_6$H$_4$CH$_3$  
3.35, q, 4H, -C$_6$H$_4$C  
2.61, m, 32H, Ph  
-7.50, t, 1H, CHS, $^3$J(HP) = 2.3 |
| [OsCl(CHSMe)(CO)$_2$L$_2$]CF$_3$SO$_3$ | 7.60, m, 3H, S-CH$_3$  
2.48, m, 34H, Ph  
-4.70, m, 1H, -CHSMe |
| [OsCl(CHSMe)(CO)$_2$L$_2$]ClO$_4$ | 7.63, m, 3H, S-CH$_3$  
2.47, m, 35H, Ph  
-4.70, m, 1H, -CHSMe |
| [OsBr(CHSMe)(CO)$_2$L$_2$]CF$_3$SO$_3$ | 7.65, m, 3H, S-CH$_3$  
2.50, m, 30H, Ph  
-4.68, m, 1H, -CHSMe |
| [OsCl(CHSMe)(CO)(CNR)L$_2$]CF$_3$SO$_3$ | 7.67, m, 6H, S-CH$_3$ + C$_6$H$_4$CH$_3$  
3.05, q, 4H, -C$_6$H$_4$C  
2.50, m, 33H, Ph  
-4.91, m, 1H, -CHSMe |
Table 3.4 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (t) and Coupling Constants (Hz)</th>
</tr>
</thead>
</table>
| [OsCl(CHNHMe)(CO)₂L₂]ClO₄ | 7.57, m, 3H, N-CH₃  
2.43, m, 3OH, Ph  
-0.13, m, 1H, -CHNHMe  
-0.48, s(br), 1H, N-H<sup>a</sup> |
| OsCl(CHNMe)(CO)₂L₂ | 6.15, m, 3H, N-CH₃  
2.48, m, 31H, Ph  
-0.73, m, 1H, -CHNMe |
| OsBr(CHO)(CO)₂L₂ | -4.4, s(br), transient signal |
| OsCl(CHO)(CO)(CNR)L₂ | 6.55, s, 3H, C₆H₄-CH₃  
3.35, q, 4H, -C₆H₄-  
2.50, m, 33H, Ph  
-4.45, m, 1H, -CHO |
| [Fe(CHO)(CO)₄]<sup>–</sup> | 166(a) |
| [Et₄N][trans-Fe(CHO)(CO)₃(P[OPh]₃)<sup>b</sup>]<sup>166(b)</sup> | -4.95, s<sup>b</sup>  
-4.82, d, <sup>3</sup>J(HP) = 44.4 |
| [Fe(CHO)(CO)₃(PPh₃)<sup>–</sup>]<sup>166(b)</sup> | -5.5, d, <sup>3</sup>J(HP) = 24 |
| [Cr(CHO)(CO)₅]<sup>–</sup> | 166(b) |
| [Cr(CHO)(CO)₄L]<sup>–</sup> | 166(b) |
| [W(CHO)(CO)₅]<sup>–</sup> | 166(b) |
| OsCl(CHOME)(CO)(CNR)L₂]CF₃SO₃ | 7.67, s, 3H, C₆H₄-CH₃  
6.03, m, 1H, O-CH₃  
5.38, m, 2H, O-CH₃  
3.28, m, 4H, -C₆H₄-  
2.47, m, 3OH, Ph  
-2.03, s(br), 0.3H, -CHOME  
-3.05, s(br), 0.5H, -CHOME |
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ($\tau$) and Coupling Constants (Hz)</th>
</tr>
</thead>
</table>
| Os($\eta^2$-CH$_2$S)(CO)$_2$L$_2$ | 9.1, t, 2H, CH$_2$S, $^{3}$J(HP) = 4.6  
2.88, m, 33H, Ph |
| OsCl(SMe)(CO)$_2$L$_2$ | 8.67, s, 3H, S-CH$_3$  
2.45, m, 33H, Ph |
| [Os($\eta^2$-CH$_2$SMe)(CO)$_2$L$_2$]CF$_3$SO$_3$ | 8.26-8.14, m, $^C$-CH$_2$SMe  
8.18, s, S-CH$_3$  
2.50, m, 30H, Ph |
| OsCl($\eta^1$-CH$_2$SMe)(CO)$_2$L$_2$ | 8.47, s, 3H, S-CH$_3$  
8.18, t, 2H, -CH$_2$SMe, $^{3}$J(HP) = 9  
2.42, m, 33H, Ph |
| [OsCl($\eta^1$-CH$_2$SMe$_2$)(CO)$_2$L$_2$]CF$_3$SO$_3$ | 7.95, s, 6H, -CH$_2$S(CH$_3$)$_2$  
7.58, t, 2H, -CH$_2$SMe$_2$, $^{3}$J(HP) = 7  
2.38, m, 30H, Ph |

(L = PPh$_3$, R = p-toly1) (a) exchanges with D$_2$O;  
(b) $^{13}$C N.M.R. data also available;  
(c) triplet pattern obscured by S-Me signal.
CHAPTER 4

ZEROVALENT THIOCARBONYL COMPLEXES OF OSMIUM

Low valent transition metal complexes have provided a source of curiosity for organometallic chemists for many years and much of the rapid development of the field is based on the remarkable reactivity and usefulness of such complexes. A unifying conceptual approach is provided by the notion of oxidative addition.\textsuperscript{130} Oxidative addition reactions provide scope to introduce a large number of saturated or unsaturated molecules into the coordination sphere of the transition metal centre and this synthetic utility has motivated much of the interest of this group in low valent complexes. At least one elementary step in all homogeneously catalysed reactions, for which the mechanisms are known, is an oxidative addition reaction and it is reasonable to assume that this feature is general to all homogeneously catalysed processes. Our interest has been to contribute to the field of low valent transition metal chemistry and in this chapter the synthesis and some of the reactions of a number of $d^8$ osmium thiocarbonyl complexes are described.

Two separate approaches have successfully afforded stable low valent transition metal complexes. One has been to use very bulky ligands which provide a form of kinetic stability by blocking the access of potential reactants, such as electrophiles, to the metal centre. A consequence of this method is that coordinatively unsaturated complexes often arise because of steric pressure.\textsuperscript{198}
The alternative more common approach is to fabricate low valent complexes containing strong $\pi$-acid ligands which reduce the reactivity of the metal centre by removing substantial amounts of electron density. Data obtained from physical measurements and the results of chemical reactions have shown that CS is a strong $\pi$-acceptor ligand [Chapter 1] and therefore an excellent candidate for stabilising low valent complexes.

4.1 Synthesis and Reactions of Zerovalent Complexes

In chapter 2 an improved synthetic route to the $d^8$ osmium complex Os(CO)$_2$(PPh$_3$)$_3$ was discussed. This route is based on the facile high yield synthesis of the dihydrido complex OsH$_2$(CO)(PPh$_3$)$_3$. An analogous route is applicable to the derivation of Os(CO)(CS)(PPh$_3$)$_3$ based on the intermediate complex OsH$_2$(CS)(PPh$_3$)$_3$, which was discussed in chapter 3. Thus OsH$_2$(CS)(PPh$_3$)$_3$ reacts with perchloric acid to afford [OsH(H$_2$O)(CS)(PPh$_3$)$_3$]ClO$_4$ which can be carbonylated to yield [OsH(CO)(CS)(PPh$_3$)$_3$]ClO$_4$. This latter cation is very difficult to isolate as a solid and has eluded satisfactory elemental analysis. The cation has the geometry

![Diagram](image)

(L = PPh$_3$)

as shown by the coupling pattern of the hydrido ligand with the $^{31}$P nuclei [Table 4.2]. This geometry was also found for [OsH(CO)$_2$(PPh$_3$)$_3$]$^+$ [Chapter 2]. Halide ions displace phosphine from [OsH(CO)(CS)(PPh$_3$)$_3$]$^+$ to yield neutral complexes which are
assumed to be OsHX(CO)(CS)(PPh$_3$)$_2$ [X = Br, I]. The I.R. spectra indicate that these complexes, which have not been further characterised, are not the same isomers as those discussed in chapter 3. Treatment of [OsH(CO)(CS)(PPh$_3$)$_3$]$^+$ (generated in situ) in degassed methanol solution with sodium hydroxide affords the trisphosphine zerovalent complex Os(CO)(CS)(PPh$_3$)$_3$ as a tan crystalline solid in very high yield (Scheme 4.1). This deprotonation reaction is faster (ca. 10 min in methanol under reflux) than the corresponding reaction of [OsH(CO)$_2$(PPh$_3$)$_3$]$^+$ (ca. 40 min in methanol under reflux) suggesting that CS is a stronger π-acceptor than CO in these complexes, thus stabilising the zerovalent state.

Addition of carbon monoxide or p-tolylisocyanide to a carefully degassed benzene solution of the labile phosphine-containing Os(CO)(CS)(PPh$_3$)$_3$ affords the d$^8$ complexes Os(CO)$_2$(CS)(PPh$_3$)$_2$ and Os(CO)$_2$(CS)(CN)$_2$(PPh$_3$)$_2$ respectively. This synthesis of Os(CO)$_2$(CS)(PPh$_3$)$_2$ is superior to the methyl thiol elimination from OsH(η$^1$-CS$_2$Me)(CO)$_2$(PPh$_3$)$_2$ discussed in chapter 2.

Os(CO)(CS)(PPh$_3$)$_3$ also reacts with ethylene in degassed benzene when exposed to the light from a quartz-halogen lamp to afford Os(η$^2$-C$_2$H$_4$)(CO)(CS)(PPh$_3$)$_2$, but the reaction is reversible and, in the presence of the displaced phosphine, does not proceed to completion. Instead mixtures of Os(η$^2$-C$_2$H$_4$)(CO)(CS)(PPh$_3$)$_2$ and Os(CO)(CS)(PPh$_3$)$_3$ are obtained, even after many hours reaction time. A pure sample of the ethylene adduct can be obtained by repeated reaction of these mixtures with ethylene (3 cycles). This process effects gradual removal of the displaced phosphine and the equilibrium
Os(CO)(CS)(PPh₃)₃ + C₂H₄ ⇌ Os(η²-C₂H₄)(CO)(CS)(PPh₃)₂ + PPh₃

is shifted in favour of the ethylene adduct. Benzene washing of the solid mixtures effectively removes the zervalent contaminant and also affords pure Os(η²-C₂H₄)(CO)(CS)(PPh₃)₂. Ethylene loss occurs readily in solution as evidenced by the $^1$H N.M.R. signal for free ethylene which is observed in deuterochloroform solutions of this adduct as a sharp singlet at $\tau$, 4.6.¹¹⁰ An unambiguous assignment for the coordinated ethylene signal has not been possible. The analogous dicarbonyl ethylene adduct contains a substantially less labile ethylene ligand¹¹⁰ and this comparison demonstrates that CS is stabilising the zervalent state more effectively than CO in these molecules.

Reaction of Os(CO)(CS)(PPh₃)₃ with carbon disulphide in degassed benzene leads to the formation of the π-bonded CS₂ adduct Os(η²-CS₂)(CO)(CS)(PPh₃)₂ in very high yield. In contrast to the dicarbonyl analogue the formation of an intermediate ethylene adduct¹¹⁰ is not necessary since Os(η²-CS₂)(CO)(CS)(PPh₃)₂ is obtained as a pure product from this reaction (Scheme 4.1). The production of dithiocarbonyl-containing complexes from this adduct is discussed in section 4.2.

Perchloric acid reacts instantaneously with Os(CO)(CS)(CNR)(PPh₃)₂ in degassed dichloromethane-ethanol solution to afford [OsH(CO)(CS)(CNR)(PPh₃)₂]ClO₄$. There are three possible geometries for this cation (figure 4.1, $^1$H N.M.R. shows trans phosphine ligands). Since the actual geometry is probably dependent upon the site of protonation of the zervalent complex the cation [OsH(CO)(CS)(CNR)(PPh₃)₂]$^+$ is a worthy candidate for a future X-ray crystal structure analysis.
The isocyanide-triphenylphosphine-containing zerovalent complex \( \text{Os(CS)(CNR)(PPh}_3)_3 \) \([R = p\text{-toly}]\) can be obtained by reductive deprotonation of the cation \([\text{OsH(CS)(CNR)(PPh}_3)_3]^+\) in basic ethanol. This latter complex is produced from the reaction of excess triphenylphosphine with \([\text{OsH(H}_2\text{O)(CNS)(CNR)(PPh}_3)_2]^+\text{ClO}_4^-\) which in turn is formed from the action of silver perchlorate on \(\text{OsCl}_3(\text{CNS})(\text{CNR})(\text{PPh}_3)_2\) \([\text{H trans to CNS}]\) in dichloromethane-ethanol solution (Scheme 4.1). The reductive deprotonation of \([\text{OsH(CS)(CNR)(PPh}_3)_3]^+\) is much slower (ca. 8 h in ethanol under reflux) than the reductive deprotonation of \([\text{OsH(CS)(CO)(PPh}_3)_3]^+\) (ca. 10 min in methanol under reflux). A similar rate difference is observed in the analogous reductive deprotonation reactions to yield \(\text{Os(CO)(CNR)(PPh}_3)_3\) and \(\text{Os(CO)}_2(\text{PPh}_3)_3\). The slower rates for deprotonation of the isocyanide-containing hydrido cations is a reflection of the greater net donor properties of \(p\text{-toly}l\)isocyanide when compared with carbonyl.

All the solid zerovalent thiocarbonyl complexes react with air on standing to produce a surface darkening. This occurs most rapidly for the isocyanide-containing complexes where surface deterioration is apparent after several days and least rapidly for \(\text{Os(CO)}_2(\text{CNS})(\text{PPh}_3)_2\). Persistent attempts to obtain satisfactory
Scheme 4.1  \((L = \text{PPh}_3; \; R = \text{p-toly1})\)
elemental analyses have returned analytical figures 1-2% low in carbon for all but Os(CO)$_2$(CS)(PPh$_3$)$_2$. Consequently, the formulations of these air-sensitive compounds have been confirmed by the complete characterisation of derivatives. Os(CS)(CNR)(PPh$_3$)$_3$ when treated with perchloric acid in degassed dichloromethane-ethanol returns [OsH(CS)(CNR)(PPh$_3$)$_3$]ClO$_4$. Os(CS)(CNR)(PPh$_3$)$_3$ exhibits an unusual ν$_{CN}$ band which is very broad (250 cm$^{-1}$) with two prominent peaks at 1950s and 1820s. This atypical behaviour is also exhibited by other isocyanide complexes discussed in chapter 6.

4.2 Synthesis of Dithiocarbonyl Complexes

In chapter 1 approximately two hundred reported thiocarbonyl complexes were discussed, but examples of well-characterised complexes containing more than one thiocarbonyl ligand other than the osmium examples which have resulted from this work are limited to CpMn(CO)(CS)$_2$,$^{31}$ which was produced in only 20% yield, and CpRe(CO)(CS)$_2$,$^{36}$ CpMn(CS)$_3$,$^{31}$ and Ni(CS)$_n$ [n = 1-4]$^{8,9}$ which have been detected by spectroscopic means only. That so few multi-thiocarbonyl complexes have been reported is a consequence of synthetic limitations. Several of the synthetic procedures that have afforded monothiocarbonyl complexes [Chapter 1, section I] have been employed here for the general design of obtaining dithiocarbonyl complexes of osmium and, as is discussed below, only the acid cleavage of dithioester ligands has been successful.
The multithiocarbonyl complexes \( \text{CpMn(CO)(CS)}_2 \), \( \text{CpMn(CS)}_3 \), \( \text{CpRe(CO)(CS)}_2 \), and \( \text{CpMn(CS)}_3 \) are produced by the reactions of the complexes \( \text{CpMn(CO)(CS)}_2(\text{C}_8\text{H}_{14}) \), \( \text{CpRe(CO)}_2(\text{THF}) \), and \( \text{CpMn(CS)}_2(\text{C}_8\text{H}_{14}) \) respectively with carbon disulphide and excess triphenylphosphine. Treatment of \( \text{OsCl}_2(\text{PPh}_3)_3 \) with carbon disulphide and triphenylphosphine in benzene yields \( \text{OsCl}_2(\text{CS})(\text{PPh}_3)_2 \), but extended heating of this monothiocarbonyl complex in toluene with excess triphenylphosphine and carbon disulphide does not give a dithiocarbonyl complex. Instead the bright crimson zwitterion-containing compound \( [\text{OsCl(\eta}^2-\text{S}_{2}\text{CPh}_3)(\text{CS})(\text{PPh}_3)_2]^{+} \) is obtained quantitatively and this complex has been characterised as the perchlorate salt.

Similarly, while heating of the hydrido-\textit{monohapto}-dithioester-containing complex \( \text{OsH(\eta}^1-\text{CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2 \) in 2-methoxyethanol cleanly yields \( \text{Os(CO)}_2(\text{CS})(\text{PPh}_3)_2 \), the heating in a variety of degassed solvents of \( \text{OsH(\eta}^1-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2 \) (see below) produces a product which is difficult to handle and which I.R. evidence suggests does not contain \( \text{Os(CO)}_2(\text{CS})(\text{PPh}_3)_2 \).

Methyl triflate reacts rapidly with \( \text{Os(\eta}^2-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2 \) to give \( [\text{Os(\eta}^2-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2]^{+}\text{CF}_3\text{SO}_3^{-} \). Reaction of this salt, or of \( \text{Os(\eta}^2-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2 \) directly with aqueous \( \text{HX} \) [\( \text{X} = \text{Cl, Br} \)] in benzene-ethanol (2:1) under reflux, results in loss of CO and MeSH (or \( \text{H}_2\text{S} \)) and quantitative formation of the dithiocarbonyl complexes \( \text{OsX}_2(\text{CS})_2(\text{PPh}_3)_2 \). The pale yellow complexes have a \textit{cis} arrangement of the thiolethcarbonyl ligands as indicated by the appearance of two very strong \( \nu_{\text{CS}} \) bands in the I.R. spectra (Table 4.1).

The bidentate dithioester ligand in \( [\text{Os(\eta}^2-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2]^{+} \) is opened by introduction of the diethylthiocarbamato ligand.
forming $\text{Os}(\eta^2-\text{S}_2\text{CNET}_2)(\eta^1-\text{CS}_2\text{Me})(\text{CS})(\text{PPh}_3)_2$ via the isolatable intermediate $\text{Os}(\eta^1-\text{S}_2\text{CNET}_2)(\eta^1-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2$. Hydro-sulphide ion also opens the ring to afford $\text{Os}(\text{SH})(\eta^1-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2$ which, it was anticipated, might have given $\text{Os}(\eta^2-\text{CS}_2)(\text{CO})(\text{CS})(\text{PPh}_3)_2$ on heating by elimination of methyl thiol. Methyl thiol is certainly lost in the solid state or on heating in a number of solvents of varying boiling points and polarity, but the principal product in each case is indicated by I.R. evidence to be $\text{Os}(\eta^2-\text{CS}_2\text{Me})(\text{CS})(\text{PPh}_3)_2$. Ring-opening is also effected by borohydride to yield $\text{OsH}(\eta^1-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2$, but halide ion reacts with $[\text{Os}(\eta^2-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2]^+$ on heating to give $\text{OsX}(\eta^2-\text{CS}_2\text{Me})(\text{CS})(\text{PPh}_3)_2$ [$X = \text{Cl, I}$].

As was previously noted in chapter 2, by comparison with $\eta^2-\text{CS}_2\text{Me}$ ligands, $\eta^1-\text{CS}_2\text{Me}$ ligands are rapidly cleaved by reaction with acids and $\text{Os}(\eta^2-\text{S}_2\text{CNET}_2)(\eta^1-\text{CS}_2\text{Me})(\text{CS})(\text{PPh}_3)_2$ with $\text{HClO}_4$ gives the dithiocarbonyl cation $[\text{Os}(\eta^2-\text{S}_2\text{CNET}_2)(\text{CS})(\text{PPh}_3)_2]^+$ where the CS ligands are again cis. Methyl triflate also reacts rapidly with $\text{Os}(\eta^2-\text{S}_2\text{CNET}_2)(\eta^1-\text{CS}_2\text{Me})(\text{CS})(\text{PPh}_3)_2$ to yield the carbene-containing complex $[\text{Os}(\eta^2-\text{S}_2\text{CNET}_2)(\text{C}[\text{SMe}]_2)(\text{CS})(\text{PPh}_3)_2\text{CF}_3\text{SO}_3]^-$. No quantitative studies of the mechanism of thiocarbonyl formation in these systems have been undertaken, but all evidence favours similar processes to those considered in section 2.3 for monothiocarbonyl analogues of these complexes.

The only known examples of coordinatively unsaturated complexes of $d^8$ osmium or ruthenium are $\text{RuX(NO)}(\text{PPh}_3)_2$ [$X = \text{Cl, Br, I, OH}$] where electronic stabilisation is provided by the strongly electron-withdrawing nitrosyl ligand. Because of very considerable
π-acceptor properties [Chapter 1], CS is a particularly suitable ligand to choose in attempting to lower the basicity of the metal centre to the point where a coordinatively unsaturated $d^8$ osmium complex will become available. The lability found in the ethylene adduct $\text{Os}(\eta^2-\text{C}_2\text{H}_4)(\text{CO})(\text{CS})(\text{PPh}_3)_2$ supports this contention. This project has now reached the point where a reasonable avenue of investigation is to seek a coordinatively unsaturated $d^8$ complex such as $\text{Os(CS)}_2(\text{PPh}_3)_2$. Apart from a further result discussed in chapter 6 it has not been possible to investigate this and other aspects of the chemistry of the compounds reported in this chapter within the time limitations of this project. It is anticipated that $\text{Os(CO)}(\text{CS})(\text{PPh}_3)_3$ and the other zerovalent complexes will prove to be very useful synthetic intermediates which, like the carbonyl and isocyano analogue\textsuperscript{110}, will exhibit an extensive chemistry.
Scheme 4.2 (L = PPh₃; X = Cl, Br; X' = Cl, I)
EXPERIMENTAL

ZEROVALENT COMPLEXES

\([\text{OsH}_2(\text{CO})(\text{CS})(\text{PPh}_3)_3]\text{ClO}_4\).

Hydridocarbonylthiocarbonyltris(triphenylphosphine)osmium(II) perchlorate.

\(\text{OsH}_2(\text{CS})(\text{PPh}_3)_3\) (2.0 g) was dissolved in dichloromethane (50 ml) and methanol (50 ml) containing perchloric acid (70% w/w; 1 ml) was added. After hydrogen evolution had ceased the solution was stirred under an atmosphere of carbon monoxide for 2 h. The dichloromethane was removed and the resulting methanolic solution was used as a solution of the title compound for further reactions. A solid sample was obtained by adding water to precipitate the cationic complex as a pale yellow oil. The oil was dissolved in dichloromethane (30 ml) and washed twice with water (40 ml). Ethanol (2 ml) was added and the solution volume lowered to 10 ml. The rapid addition of petroleum spirit afforded a white floccular solid (2.1 g, 93.4%). M.p. 117-119°C.

\(\text{Os(CO)}(\text{CS})(\text{PPh}_3)_3\).

Carbonylthiocarbonyltris(triphenylphosphine)osmium(II).

\(\text{OsH}_2(\text{CS})(\text{PPh}_3)_3\) (2.0 g) was treated as above to produce a methanolic solution of \([\text{OsH(CO)}(\text{CS})(\text{PPh}_3)_3]\text{ClO}_4\) which was made up to a total volume of 60 ml with methanol and triphenylphosphine (0.2 g) was added. A stream of nitrogen was passed through the solution for 10 min and the degassed solution was then heated under reflux and
crushed sodium hydroxide (1.0 g) was added. After 20 min the solution was allowed to cool to room temperature and the tan crystals were collected and washed with methanol and hexane and allowed to dry at room temperature (2.0 g, 97.5%). M.p. 159–161°C.

\[
\text{Os(CO)}_2\text{(CS)}(\text{PPh}_3)_2.
\]

**Dicarboxyldithiocarbonylbis(triphenylphosphine)osmium(0).**

Os(CO)(CS)(PPh\textsubscript{3})\textsubscript{3} (0.5 g) in degassed benzene (25 ml) was heated under carbon monoxide (100 p.s.i.) to 160°C until a pale-yellow solution had formed. Ethanol was added and removal of the benzene afforded yellow-orange crystals which were collected and washed with ethanol and hexane (0.34 g, 87.5%). The compound could be recrystallised without substantial loss from dichloromethane-ethanol to give orange platelets. M.p. 195–196°C. Characterisation was achieved by comparison of the I.R. spectrum with that of an authentic sample [Chapter 2].

\[
\text{Os(CO)}(\text{CS})(\text{CNR})(\text{PPh}_3)_2.
\]

**Carboxyldithiocarbonyl-p-tolylisocyanidebis(triphenylphosphine)osmium(0).**

Os(CO)(CS)(PPh\textsubscript{3})\textsubscript{3} (0.5 g) in degassed benzene (10 ml) and p-tolylisocyanide (0.06 g, 1.07 eq.) in degassed methanol (10 ml) were mixed and heated under reflux for 1 h. Addition of degassed methanol (60 ml) gave orange crystals which were collected and washed with methanol (0.26 g, 60.3%). M.p. 150–151°C.
Dihapta-ethylenecarbonylthiocarbonylbis(triphenylphosphine)osmium(II).

(a) Os(CO)(CS)(PPh₃)₃ (1.0 g) was stirred in degassed benzene (120 ml) in a 250 ml pyrex flask under an atmosphere of ethylene. The light from a 500 watt quartz-halogen sun-lamp (Thorne) was directed at the flask which was cooled by a constant air flow across the surface. After 2 h the light source was removed and the solvent volume was reduced to 10 ml under reduced pressure with a continuous ethylene stream being passed through the solution. Ethanol was added to give a brown solid and the solvent volume was further reduced in open conditions. The brown solid was collected and washed with benzene until only a yellow crystalline solid remained which was washed with ethanol and dried at room temperature (0.12 g, 15.5%). M.p. 124-128°C.

Anal. Found: C, 58.33; H, 5.18; P, 7.74%. C₄₀H₃₄O₃S₂P₂S requires C, 58.95; H, 4.21; P, 7.60%.

(b) The above process was repeated but hexane was used instead of ethanol to isolate the brown solid which was not washed with benzene but was instead reacted with ethylene in benzene as above. A further brown solid was similarly isolated from this reaction and a further repetition of the reaction gave a yellow solid (0.38 g, 48.9%) which was characterised by comparison of the I.R. spectrum with that of a sample produced by method (a).
Dihapto-carbendisulphidecarbonylthiocarbonylbis(triphenylphosphine)-
osmium(II).

Os(CO)(CS)(PPh₃)₃ (1.0 g) was heated under reflux in degassed benzene (60 ml) containing carbon disulphide (0.15 ml) for 30 min. The solvent volume was lowered to 20 ml, ethanol was added and the remaining benzene was removed. The yellow-orange feathery crystals were collected and washed with ethanol (0.8 g, 97.3%). M.p. 155-157°C. Anal. Found: C, 54.21; H, 3.81; P, 6.81%. C₃₉H₃₀OsP₂S₃ requires C, 54.28; H, 3.50; P, 7.18%.

[OsH(CO)(CS)(CNR)(PPh₃)₂]ClO₄

Hydridocarbonylthiocarbonylp-tolylisocyanidebis(triphenylphosphine)-
osmium(II) perchlorate.

Os(CO)(CS)(CNR)(PPh₃)₂ (0.1 g) was added to a solution of ethanol (10 ml) containing perchloric acid (ca. 70%: 0.1 ml) and dichloromethane (20 ml) was added. On removal of the dichloromethane colourless crystals deposited which were collected and washed with ethanol and hexane (0.1 g, 90%). Recrystallisation from dichloromethane-ethanol-cyclohexane afforded white needles of the solvate [OsH(CO)(CS)(CNR)(PPh₃)₂]ClO₄·(C₆H₁₂)₀.₆₇. "H N.M.R. (CDCl₃) shows τ, 7.88 [s, 8H, C₆H₁₂]. M.p. 151-153°C. Anal. Found: C, 56.44; H, 4.47; N, 1.27%. C₄₆H₃₈ClNO₅OsP₂S·(C₆H₁₂)₀.₆₇ requires C, 56.62; H, 4.37; N, 1.32%.
[Osh(H₂O) (CS) (CNR) (PPh₃)₂]ClO₄.

Hydridoaquothiocarbonyl-p-tolylisocyanidebis(triphenylphosphine)-
osmium(II) perchlorate.

OshCl(CS) (CNR) (PPh₃)₂ [H trans to CNR] (0.5 g) was dissolved in dichloromethane (40 ml). Silver perchlorate (0.114 g, 1 eq.) in ethanol (15 ml) was added and the mixture was stirred for 15 min. Removal of the dichloromethane gave white crystals which were collected and washed with ethanol and hexane (0.51 g, 93.6%). Recrystallisation from dichloromethane-ethanol gave large colourless crystals. M.p. 179-180°C. Anal. Found: C, 54.73; H, 4.32; N, 1.48%. C₄₅H₄₀ClNO₅OsP₂S requires C, 54.34; H, 4.05; N, 1.41%.

[Osh(CS) (CNR) (PPh₃)₃]ClO₄.

Hydridothiocarbonyl-p-tolylisocyanidetriss(triphenylphosphine)osmium(II) perchlorate.

[Osh(H₂O) (CS) (CNR) (PPh₃)₂]ClO₄ (0.5 g) and triphenylphosphine (0.16 g) were heated under reflux in toluene (30 ml) for 2 h. Hexane was added and the lemon crystals were collected and washed with hexane (0.61 g, 97.9%). Recrystallisation from dichloromethane-ethanol-cyclohexane gave large lemon crystals. M.p. 180°C. Anal. Found: C, 61.27; H, 4.32; N, 1.18; P, 7.79%. C₆₃H₅₃ClNO₄OsP₃S requires C, 61.08; H, 4.31; N, 1.13; P, 7.50%. 
Thiocarbonyl-p-tolylisocyanidetris(triphenylphosphine)osmium(0).

\[ \text{OsH(CS(CNR)(PPh}_3)_3 \]ClO_4 \] (0.2 g) was heated under reflux in degassed ethanol (25 ml) containing triphenylphosphine (0.05 g) and sodium hydroxide (0.1 g) was added. After 8 h the solution was allowed to cool to room temperature and the red-orange crystals were collected and washed with ethanol and dried at room temperature (0.15 g, 81.6%). M.p. 141-143°C.

**DITHIOCARBONYL COMPLEXES**

\[ \text{[OsCl}_2(n^2-S_2CPPh}_3)(CS)(PPh}_3)_2 \]ClO_4.  

Chlorotriphenylphosphoniodithiocarboxylato-S,S'-thiocarbonylbis-(triphenylphosphine)osmium(II) perchlorate.

OsCl_2(CS)(PPh)_3 (0.3 g) and triphenylphosphine (0.1 g) were heated under reflux in a solvent medium comprised of dichloromethane (20 ml), carbon disulphide (10 ml) and methanol (10 ml) for 2 days. A deep violet-red colour formed during the first 10 min and the solution did not change in appearance thereafter. The solution was cooled to room temperature and sodium perchlorate (0.1 g) in ethanol (20 ml) was added. Upon removal of dichloromethane deep maroon crystals formed which were collected and washed with ethanol and hexane (0.33 g, 97.5%). Recrystallisation from dichloromethane-ethanol-cyclohexane gave deep maroon crystals. M.p. 203-206°C.

**Anal.** Found: C, 54.56; H, 3.88; P, 7.69%. C_{56}H_{45}Cl_2OsP_3S_3 requires C, 54.58; H, 3.68; P, 7.54%. 
[Os(η²-CS₂Me)(CO)(CS)(PPh₃)₂]CF₃SO₃·

**Dihapto-dithiomethyleneestercarbonylthiocarbonylbis(triphenylphosphine)-osmium(II)trifluoromethanesulphonate.**

Os(η²-CS₂)(CO)(CS)(PPh₃)₂ (0.5 g) was stirred in dry benzene (10 ml) and methyl triflate (0.2 ml) was added. After 5 min hexane (5 ml) was added and the lemon-yellow crystals were collected and washed with hexane. Recrystallisation from dichloromethane-ethanol-cyclohexane gave lemon-yellow crystals of the hemidichloromethane solvate (0.59 g, 95.2%). ¹H N.M.R. (CDCl₃-DMSO) shows τ, 4.53 [s, 1H, CH₂Cl₂]. M.p. 176-180°C. Anal. Found: C, 46.43; H, 3.68; P, 5.67%. C₄₁H₃₃F₃O₄OsP₂S₄(CH₂Cl₂)₀.₅ requires C, 46.60; H, 3.20; P, 5.79%.

OsH(η¹-CS₂Me)(CO)(CS)(PPh₃)₂.

**Hydrido-monohapto-dithiomethyleneestercarbonylthiocarbonylbis(triphenylphosphine)osmium(II).**

To [Os(η²-CS₂Me)(CO)(CS)(PPh₃)₂]CF₃SO₃·(CH₂Cl₂)₀.₅ (0.3 g) in ethanol (40 ml) was slowly added a filtered solution of sodium borohydride (0.1 g) in ethanol (25 ml). The solution was stirred for 15 min and the solvent volume was reduced without the application of heat. The red crystals were collected and washed with ethanol. Recrystallisation from dichloromethane-ethanol afforded light red crystals (0.23 g, 93.3%). M.p. 138-140°C. Anal. Found: C, 54.75; H, 4.15; P, 7.28%. C₄₀H₃₄O₄OsP₂S₃ requires C, 54.65; H, 3.90; P, 7.05%.
OsCl$_2$(CS)$_2$(PPh$_3$)$_2$.

Dichlorodithiocarbonylbis(triphenylphosphine)osmium(II).

(a) [Os($\eta^2$-CS$_2$Me) (CO) (CS) (PPh$_3$)$_2$]CF$_3$SO$_3$·(CH$_2$Cl)$_2$ 0.5 (0.15 g) was heated under reflux with concentrated hydrochloric acid (0.5 ml) in a solvent mixture comprised of benzene (20 ml) and ethanol (40 ml) for 1.5 h. The benzene was removed to afford pale lemon crystals which were collected and washed with ethanol. Recrystallisation from dichloromethane-ethanol gave pale lemon platelets (0.12 g, 97.9%). M.p. 280-285°C.

Anal. Found: C, 52.56; H, 3.83; P, 7.39%. C$_{30}$H$_{30}$Cl$_2$OsP$_2$S$_2$ requires C, 52.23; H, 3.46; P, 7.09%.

(b) Os($\eta^2$-CS$_2$) (CO) (CS) (PPh$_3$)$_2$ (0.3 g) was heated under reflux with concentrated hydrochloric acid (0.5 ml) in a solvent mixture comprised of toluene (50 ml) and ethanol (20 ml) for 2 h. The solvent volume was reduced to 5 ml and ethanol (50 ml) was added. The lemon platelets were collected, washed with ethanol and recrystallised from dichloromethane-ethanol to give lemon platelets (0.28 g, 92.2%).

OsBr$_2$(CS)$_2$(PPh$_3$)$_2$.

Dibromodithiocarbonylbis(triphenylphosphine)osmium(II).

Os($\eta^2$-CS$_2$) (CO) (CS) (PPh$_3$)$_2$ (0.3 g) was heated under reflux with hydrobromic acid (ca. 49%, 0.5 ml) as above for 2 h. Recrystallisation of the crude product gave lemon platelets (0.3 g, 89.6%). M.p. 290-295°C. Anal. Found: C, 47.69; H, 3.59; P, 6.48%. C$_{30}$H$_{30}$Br$_2$OsP$_2$S$_2$ requires C, 47.41; H, 3.14; P, 6.43%. 

Os(\(\eta^1\)-S\(_2\)CNEt\(_2\))(\(\eta^1\)-CS\(_2\)Me)(CO)(CS)(PPh\(_3\))\(_2\).

**Monohapto-diethyl-dithiocarbamato-monohapto-dithiomethylester-carbonyl-thiocarbonylbis(triphenylphosphine)osmium(II).**

\[\text{[Os}(\eta^2\text{-CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3\cdot(\text{CH}_2\text{Cl}_2)_{0.5} \] (0.5 g)

was stirred in ethanol solution (60 ml) and sodium diethyl-dithiocarbamate (0.15 g) in ethanol (10 ml) was added. After 20 min stirring the volume was reduced without application of heat and the pink crystals were collected and washed with ethanol (0.45 g, 93.8%). Recrystallisation from dichloromethane-ethanol without application of heat gave pink crystals. M.p. 112°C. Anal.

Found: C, 52.98; H, 4.40; N, 1.35%. C\(_{45}\)H\(_{43}\)NOOs\(_2\)S\(_3\) requires C, 52.66; H, 4.22; N, 1.35%.

Os(\(\eta^2\)-S\(_2\)CNEt\(_2\))(\(\eta^1\)-CS\(_2\)Me)(CS)(PPh\(_3\))\(_2\).

**Dihapto-diethyl-dithiocarbamato-monohapto-dithiomethylester-thiocarbonyl-bis(triphenylphosphine)osmium(II).**

Os(\(\eta^1\)-S\(_2\)CNEt\(_2\))(\(\eta^1\)-CS\(_2\)Me)(CO)(CS)(PPh\(_3\))\(_2\) (0.4 g) was heated under reflux in dichloromethane (30 ml) for 1 h. The solvent volume was reduced to 10 ml and petroleum spirit (50 ml) was added to give yellow crystals (0.2 g). That some decomposition had occurred was evidenced by a strong smell of methyl thiol in the filtrate. The solvents were entirely removed from the filtrate and the yellow oil was recrystallised from dichloromethane-petroleum spirit to give further yellow crystals (0.14 g). Recrystallisation of the total product from dichloromethane-petroleum spirit gave yellow crystals (total yield 0.34 g, 87.4%). M.p. 163-170°C.
Anal. Found: C, 52.43; H, 4.48; N, 1.35%. \( C_{44}H_{43}NO_{2}P_{2}S_{5} \)
requires C, 52.94; H, 4.34; N, 1.40%.

\[
\text{Os(}^{1}\text{-CS}_{2}\text{Me})(\text{SH})(\text{CO})(\text{CS})(\text{PPh}_{3})_{2}\text{).}
\]

\textit{Monohapto-dithiomethylesterhydrosulphidocarbonylthiocarbonylbis- (triphenylphosphine)osmium(II).}

\[
[\text{Os(}^{2}\text{-CS}_{2}\text{Me})(\text{CO})(\text{CS})(\text{PPh}_{3})_{2}\text{]}\text{CF}_{3}\text{SO}_{3}\cdot(\text{CH}_{2}\text{Cl}_{2})_{0.5} \quad (0.2 \text{ g})
\]
is stirred in ethanol solution (30 ml) and sodium hydrosulphide (0.1 g) in ethanol (10 ml) was added. The solvent volume was reduced without application of heat and the orange crystals were collected and washed with ethanol and petroleum spirit (0.15 g, 88%). M.p. 165°C. Solid smells strongly of methyl thiol. Recrystallisation from dichloromethane-ethanol results in decomposition. Anal. Found: C, 53.36; H, 4.18; P, 7.05%.

\[
C_{40}H_{34}O_{2}P_{2}S_{4} \text{ requires C, } 52.73; \text{ H, } 3.76; \text{ P, } 6.80%.
\]

\[
\text{OsCl(}^{2}\text{-CS}_{2}\text{Me})(\text{CS})(\text{PPh}_{3})_{2}\text{).}
\]

\textit{Chloro-dikapto-dithiomethylesterthiocarbonylbis(triphenylphosphine)- osmium(II).}

\[
[\text{Os(}^{2}\text{-CS}_{2}\text{Me})(\text{CO})(\text{CS})(\text{PPh}_{3})_{2}\text{]}\text{CF}_{3}\text{SO}_{3}\cdot(\text{CH}_{2}\text{Cl}_{2})_{0.5} \quad (0.15 \text{ g})
\]
and lithium chloride (0.1 g) were heated under reflux in ethanol (25 ml) for 30 min. After cooling to room temperature the yellow crystals were collected and washed with ethanol (0.12 g, 96.6%). Recrystallisation from dichloromethane-ethanol yielded a yellow crystalline solid which was too insoluble for N.M.R. measurements. However, digestion in DMSO showed the presence of dichloromethane
Analyses indicate the composition

\[ \text{OsCl(} \eta^2-\text{CS}_2\text{Me})(\text{CS})\text{(PPh}_3\text{)}_2\cdot(\text{CH}_2\text{Cl}_2\text{)}\cdot0.2 \]

M.p. 240°C.

Anal. Found: C, 52.26; H, 3.87; P, 6.88%. \( \text{C}_{39}\text{H}_{33}\text{ClOsP}_2\text{S}_3\cdot(\text{CH}_2\text{Cl}_2\text{)}\cdot0.2 \)

requires C, 52.17; H, 3.73; P, 6.86%.

\[ \text{Os(} \eta^2-\text{CS}_2\text{Me})\text{I(} \text{CS})\text{(PPh}_3\text{)}_2\cdot \]

**Dihapto-dithiomethylesteriodiiodothiocarbonylbis(triphenylphosphine)-
osmium(II).**

\[ \text{[Os(} \eta^2-\text{CS}_2\text{Me})(\text{CO})\text{(CS})\text{(PPh}_3\text{)}_2\cdot\text{CP}_3\text{SO}_3\cdot(\text{CH}_2\text{Cl}_2\text{)}\cdot0.5 \]

(0.1 g) and lithium iodide (0.1 g) were heated under reflux in ethanol (25 ml) for

3 h. The pale yellow crystals were collected and washed with

ethanol (0.082 g, 89.8%). Recrystallisation from dichloromethane-

ethanol gave lemon-yellow needles. M.p. 230-231°C.

Anal.

Found: C, 48.52; H, 3.74; P, 6.55%. \( \text{C}_{39}\text{H}_{33}\text{IoP}_2\text{S}_3 \)

requires C, 47.95; H, 3.41; P, 6.34%.

\[ \text{[Os(} \eta^2-\text{SCN}_2\text{Et}_2\text{)}\text{(CS})_2\text{(PPh}_3\text{)}_2\cdot\text{ClO}_4\cdot \]

**Dihapto-diethylidithiocarbatodithiocarbonylbis(triphenylphosphine)-
osmium(II) perchlorate.**

\[ \text{Os(} \eta^2-\text{SCN}_2\text{Et}_2\text{)}\{(\eta^1-\text{CS}_2\text{Me})(\text{CS})\text{(PPh}_3\text{)}_2 \]

(0.3 g) was dissolved in dichloromethane (20 ml) and perchloric acid (ca. 70%, 0.1 ml) in

ethanol (10 ml) was added. The solution was warmed gently for

5 min and the dichloromethane was removed to afford yellow crystals

(0.3 g, 95%). Recrystallisation from dichloromethane-ethanol-
cyclohexane gave yellow crystals. M.p. 193-195°C.

Anal. Found:

C, 49.41; H, 3.94; N, 1.82%. \( \text{C}_{43}\text{H}_{40}\text{Cl}_4\text{OsP}_2\text{S}_4 \)

requires C, 49.16; H, 3.84; N, 1.33%.
\[ \text{[Os(}\eta^2-S_2\text{CNET}_2\text{)(C[SMe]_2)(CS)(PPh}_3\text{)_2]}\text{CF}_3\text{SO}_3 \].

**Dihapto-diethylidithiocarbamatobis(methylthiolato)carbenethiocarbonylbis(triphenylphosphine)osmium(II)trifluoromethanesulphonate.**

Os(\eta^2-S_2\text{CNET}_2)(\eta^1-CS_2\text{Me})(\text{CS})(\text{PPh}_3)_2 (0.15 g) was stirred in dry benzene (20 ml) and methyl triflate (0.1 ml) was added. After 10 min stirring hexane (5 ml) was added and the yellow crystals were collected and washed with hexane (0.175 g, 100%).

Recrystallisation from dichloromethane-ethanol-cyclohexane gave yellow needles of the solvate [Os(\eta^2-S_2\text{CNET}_2)(\text{C[SMe]_2})(\text{CS})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3(\text{C}_6\text{H}_{12})1/12. M.p. 202-209°C. Anal. Found: C, 48.00; H, 4.51; N, 1.14%. C_{46}H_{46}F_3NO_3OsP_2S_6(\text{C}_6\text{H}_{12})1/12 requires C, 47.76; H, 4.05; N, 1.20%.
### Table 4.1 I.R. DATA (cm\(^{-1}\)) FOR THIOCARBONYL COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_{\text{CS}})</th>
<th>(\nu_{\text{CO}})</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OSH(CO)((\text{CS})_2)](\text{ClO}_4)</td>
<td>1310</td>
<td>2045</td>
<td>1955m ((\nu_{\text{OH}}); 785w ((\delta_{\text{OSH}}))</td>
</tr>
<tr>
<td>Os(CO)((\text{CS})_2)</td>
<td>1230</td>
<td>1890, 1870</td>
<td>2060vs, 2036vs ((\nu_{\text{CN}}))</td>
</tr>
<tr>
<td>Os(CO)((\text{CS})_2)</td>
<td>1230</td>
<td>1955, 1890</td>
<td>1150w ((\nu_{\text{CC}}))</td>
</tr>
<tr>
<td>Os(CO)((\text{CS})_2)</td>
<td>1232, c</td>
<td>1890, 1865</td>
<td>1112s, 664m ((\nu_{\text{CS}}))</td>
</tr>
<tr>
<td>Os(n(^2)-C(_2)H(_4))((\text{CO})((\text{CS})_2)</td>
<td>1237</td>
<td>1945</td>
<td>2165vs ((\nu_{\text{CN}}))</td>
</tr>
<tr>
<td>Os(n(^2)-CS(_2))((\text{CO})((\text{CS})_2)</td>
<td>1280</td>
<td>2020, 1995, 1975, 1965</td>
<td>3200w(br) ((\nu_{\text{OH}}); 1958w(br) ((\nu_{\text{OSH}}); 1620w ((\delta_{\text{OSH}}); 1120vs, 1045vs, 930w, 623s ((\text{ClO}_4))</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1286</td>
<td>2159</td>
<td>2063w ((\nu_{\text{OSH}})(b, f))</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1222</td>
<td>2159</td>
<td>1950s(vbr), 1820s(vbr) ((\nu_{\text{CN}})); 1605w</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1288</td>
<td>2070, 2040, 1997</td>
<td>1190wm, 980m, 625s, 560s ((\text{S}_2\text{Cl})_b)</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1300</td>
<td>2159</td>
<td>1090, 765, (CS(_2))Me</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1260</td>
<td>1980</td>
<td>1883m ((\nu_{\text{OSH}}); 1005m ((\nu_{\text{C-S}}); 932wh</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1260</td>
<td>1980</td>
<td>1012m, 765w ((\text{CS}_2))Me; 1465w, 1409m, 1375w, 1357w, 1260s, 1211s, 1130m, 988w, 960w, 917w, 835w</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1290</td>
<td>2030</td>
<td>1190wm, 980m, 625s, 560s ((\text{S}_2\text{Cl})_b)</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1263</td>
<td>2030</td>
<td>1490ms, 1375w, 1355w, 1213w, 1148w, 931w, 849w</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1293</td>
<td>2040</td>
<td>1019wm, 800w ((\text{CS}_2))Me</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1282</td>
<td>2040</td>
<td>1063wm, 800m, 787wm (CS(_2))Me</td>
</tr>
<tr>
<td>Os((\text{CS})_2)((\text{CN})_2)Cl(_2)</td>
<td>1280</td>
<td>2040</td>
<td>1065wm, 790m (CS(_2))Me</td>
</tr>
</tbody>
</table>
| [OSH(CS)(CS)(CS)]\(\text{ClO}_4\) | 1350, i | 2040 | 1513s, 920w, 850w
| [OSH(CS)(CS)(CS)]\(\text{ClO}_4\) | 1265, j | 2040 | 1140w, 1222s, 1150s, 1030vs, 640vs (\(\text{CF}_3\text{SO}_3\)); 980w, 925w, 780w (carbene); 1513s, 1359m, 1210w, 935w, 895w, 850w |

**Footnotes:** (L = PPh\(_3\), R = p-tolyl)  
(a) very strong; (b) perchlorate bands ca. 1095vs, 620s; (c) solid state splitting gives multiple bands; (d) \(\text{CH}_2\) \(\nu_{\text{CH}}\) bands not discernible in Kel-F spectrum; (e) \(\nu_{\text{OSH}}, \delta_{\text{OSH}}\) not discernable; (f) \(\delta_{\text{OSH}}\) obscured by phosphine or CNR bands near 800; (g) bands partially obscured by overlapping phosphine bands; (h) \(\delta_{\text{OSH}}\) and \(\nu_{\text{CS}}\) obscured by phosphine band at 745; (i) measurement quoted for Kel-F mull; (j) band also incorporates \(\text{S}_2\text{CNET}_2\) vibration near 1270 w-m; (k) band also incorporates \(\text{CF}_3\text{SO}_3\) vibration near 1270vs;
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ) and Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os($n^2$-C$_2$H$_4$) (CO) (CS)L$_2$</td>
<td>2.58, m, Ph $^a,b$</td>
</tr>
<tr>
<td>[O$_2$H] (CO) (CS) (CNR)L$_2$</td>
<td>16.57, t, 1H, Os-H, $^2$J(HP) = 13.5</td>
</tr>
<tr>
<td></td>
<td>7.64, s, 3H, C$_6$H$_4$-$^-$CH$_3$</td>
</tr>
<tr>
<td></td>
<td>3.23, q, 4H, -C$_6$H$_4$-$^-$</td>
</tr>
<tr>
<td></td>
<td>2.45, m, 30H, Ph</td>
</tr>
<tr>
<td>[O$_2$H$_2$] (CO) (CS) (CNR)L$_2$</td>
<td>11.98, t, 1H, Os-H, $^2$J(HP) = 18</td>
</tr>
<tr>
<td></td>
<td>7.67, s, 3H, C$_6$H$_4$-$^-$CH$_3$</td>
</tr>
<tr>
<td></td>
<td>3.12, q, 4H, -C$_6$H$_4$-$^-$</td>
</tr>
<tr>
<td></td>
<td>2.42, m, 32H, Ph</td>
</tr>
<tr>
<td>[O$_2$HCS(CNR) L$_3$]</td>
<td>17.65, dt, Os-H, $^2$J(HP) = 50,</td>
</tr>
<tr>
<td></td>
<td>2J(HP $^c$) = 24.5</td>
</tr>
<tr>
<td></td>
<td>7.60, s, 3H, C$_6$H$_4$-$^-$CH$_3$</td>
</tr>
<tr>
<td></td>
<td>3.40, q, 4H, -C$_6$H$_4$-$^-$</td>
</tr>
<tr>
<td></td>
<td>2.78, m, 48H, Ph</td>
</tr>
<tr>
<td>[O$_2$(n$^2$-CS$_2$Me) (CO) (CS)L$_2$</td>
<td>7.72, s, 3H, S-CH$_3$</td>
</tr>
<tr>
<td></td>
<td>2.44, m, 30H, Ph</td>
</tr>
<tr>
<td>O$_2$H(n$^1$-CS$_2$Me) (CO) (CS)L$_2$</td>
<td>16.38, t, 1H, Os-H, $^2$J(HP) = 21.2</td>
</tr>
<tr>
<td></td>
<td>8.47, s, 3H, S-CH$_3$</td>
</tr>
<tr>
<td></td>
<td>2.50, m, 30H, Ph</td>
</tr>
<tr>
<td>O$_2$(n$^1$-S$_2$CNEt$_2$) (n$^1$-CS$_2$Me) (CO) (CS)L$_2$</td>
<td>9.20, t, 3H, NCH$_2$-CH$_3$, J(HH) = 7.3</td>
</tr>
<tr>
<td></td>
<td>8.98, t, 3H, NCH$_2$-CH$_3$, J(HH) = 7.6</td>
</tr>
<tr>
<td></td>
<td>8.03, s, 3H, S-CH$_3$</td>
</tr>
<tr>
<td></td>
<td>6.22, m, 4H, N-CH$_2$-CH$_3$</td>
</tr>
<tr>
<td></td>
<td>2.41, m, 32H, Ph</td>
</tr>
</tbody>
</table>
Table 4.2 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ((\tau)) and Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os((\eta^1-\text{CS}_2\text{Me})\text{(SH)}(\text{CO})(\text{CS})\text{L}_2)</td>
<td>8.00, s, 3H, S-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.50, m, 1H, S-H</td>
</tr>
<tr>
<td></td>
<td>2.53, m, 46H, (^f) Ph</td>
</tr>
<tr>
<td>Os((\eta^2-\text{S}_{\text{CNET}_2})\text{(\eta^1-\text{CS}_2\text{Me})(\text{CS})L}_2)</td>
<td>9.52, t, 3H, NCH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>9.23, t, 3H, NCH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>8.18, s, 3H, S-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.38, q, 2H, N-CH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>7.01, q, 2H, N-CH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>2.50, m, 34H, Ph</td>
</tr>
<tr>
<td>[Os((\eta^2-\text{S}_{\text{CNET}_2})(\text{CS})_2\text{L}_2)]\text{ClO}_4</td>
<td>9.32, t, 6H, NCH₂-CH₃, (J(\text{HH}) = 7.2)</td>
</tr>
<tr>
<td></td>
<td>7.22, q, 4H, N-CH₂-CH₃, (J(\text{HH}) = 7.2)</td>
</tr>
<tr>
<td></td>
<td>2.40, m, 32H, Ph</td>
</tr>
<tr>
<td>[Os((\eta^2-\text{S}_{\text{CNET}_2})(\text{C[SMe}_2)(\text{CS})L}_2)]\text{CF}_3\text{SO}_3</td>
<td>9.43, t, 3H, NCH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>9.20, t, 3H, NCH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>7.74, s, 3H, S-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.65, s, 3H, S-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.36, q, 2H, N-CH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>7.04, q, 2H, N-CH₂-CH₃, (J(\text{HH}) = 7.1)</td>
</tr>
<tr>
<td></td>
<td>2.47, m, 32H, Ph</td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh₃; R = p-tolyl)

(a) no accurate comparison for integral determination;
(b) unambiguous assignment for C₂H₄ signal has not been possible;
(c) meridional phosphines and H \(\text{trans}\) to phosphine as for \([\text{OsH(CO)(CS)L}_3]\text{ClO}_4\);
(d) in DMSO/CDCl₃ \([\text{DMSO} = \text{(CD}_3)_2\text{SO}\] for \(^1\text{H N.M.R.}\);
(e) OsX\((\eta^2-\text{CS}_2\text{Me})\text{(CS)L}_2\) \([X = \text{Cl, I}]\) too insoluble for \(^1\text{H N.M.R.}\);
(f) compound decomposes in solution.
CHAPTER 5

NUCLEOPHILIC ATTACK AT THE THIOCARBONYL LIGAND

The extent of \( \sigma \)-donation from a two-electron donor ligand is dependent upon the charge at the metal centre. An increase in positive charge at the metal centre causes greater \( \sigma \)-donation and, where appropriate, decreased \( \pi \)-acceptance by the ligand, thereby enhancing the susceptibility of the ligand donor atom to nucleophilic attack. This elementary consideration allows chemists to design ligand-reaction derived products since the charge at the metal centre can be adjusted either by changing the oxidation state or the other ligands in the coordination sphere. The most outstanding example of the synthetic utility of nucleophilic ligand reactions is the very considerable contribution published by Fischer's group concerning carbene\(^{179}\) and carbyne\(^{200}\) complexes. This work is based on the attack of nucleophiles, mainly carbanions, at the carbonyl ligand. Nucleophilic attack at the carbonyl and isocyanide ligands has been studied in this laboratory and for the cation \([\text{OsCl(CO)}_2(\text{CNR})(\text{PPh}_3)_2]^+\) the results of this work are summarised in Scheme 5.1.\(^{116}\) These reactions illustrate clearly that the site of nucleophilic attack, where there are alternatives, is dependent upon the nature of the incoming nucleophile.
Scheme 5.1 \( (L = \text{PPh}_3; \ R = p\text{-tolyl}; \ R' = H, \text{Me}; \ \text{all reactions high yield}) \)

The reactions of the thiocarbonyl ligand with nucleophiles were reviewed in chapter 1 [section III B(i)] and separate reviews have treated the same topic for the carbonyl\(^{201}\) and isocyanide\(^{202}\) ligands. As was noted in chapter 1, the available results suggest that the thiocarbonyl ligand tends to undergo reactions with nucleophiles more readily than the carbonyl ligand. Also reaction of the isocyanide-thiocarbonyl-containing cation \([\text{CpFe(CNPh)}_2\text{(CS)}]^{+}\) with \(\text{C}_6\text{H}_{11}\text{NH}_2\) gave rise to attack at the CS carbon atom.\(^{68}\) The thiocarbonyl ligand in \(\text{M(CO)}_5\text{(CS)}\) \([\text{M} = \text{Cr, Mo, W}]\) reacts with primary and secondary alkylamines and reactions of uncharged nucleophiles with the isocyanide ligand in neutral complexes have been commonly reported.\(^{202}\) This has not been
the case for the carbonyl ligand which, in neutral complexes, usually reacts only with very potent anionic nucleophiles.

As evidence to the importance of the charge at the metal centre a rather good correlation has been found between the CO force constant and the tendency of the carbonyl ligand to react with amines. In this chapter the results of our endeavours to produce suitable thiocarbonyl cations and the subsequent investigation of the ligand reactivity of these cations with nucleophiles are reported.

The production of the dithiocarbonyl cation \([\text{Os}(\eta^2-S_2\text{CNET}_2)(\text{CS})_2(\text{PPh}_3)_2]^+\) was discussed in chapter 4. This contains only the thiocarbonyl ligand as a site for nucleophilic attack and, as an illustration of this point, reacts with sodium borohydride in ethanol to form the stable thiiformyl-containing complex \([\text{Os}(\eta^2-S_2\text{CNET}_2)(\text{CHS})(\text{CS})(\text{PPh}_3)_2]_2\), which on treatment with methyl iodide gives the carbene complex \([\text{Os}(\eta^2-S_2\text{CNET}_2)(\text{CHSMe})(\text{CS})(\text{PPh}_3)_2]_2\). I.

As depicted in Scheme 5.1, \(\text{SH}^-\) reacts with the mixed carbonyl-isocyanide-containing cation \([\text{OsCl}(\text{CO})_2(\text{CNR})(\text{PPh}_3)_2]^+\) by attacking the isocyanide ligand and gives, by loss of HCl, a \(\pi\)-bonded isothiocyanate ligand. The preparation of the carbonyl-thiocarbonyl-isocyanide-containing cation \([\text{OsCl}(\text{CO})(\text{CS})(\text{CNR})(\text{PPh}_3)_2]^+\) is depicted in Scheme 5.2. The reaction of this cation with \(\text{SH}^-\) is complicated and the products show a solvent dependence. In acetone attack occurs exclusively at the isocyanide ligand to afford \(\text{Os}(\eta^2-\text{SCNR})(\text{CO})(\text{CS})(\text{PPh}_3)_2\), but in dichloromethane-ethanol (1:1) the products are \(\text{Os}(\eta^2-\text{SCNR})(\text{CO})(\text{CS})(\text{PPh}_3)_2\) [ca. 85%] and \(\text{Os}(\eta^2-\text{CS}_2)(\text{CO})(\text{CNR})(\text{PPh}_3)_2\).
[ca. 15%] indicating attack by \( \text{SH}^- \) at both CNR and CS ligands.

The dihapto-\( p \)-tolylisothiocyanate complex is readily methylated by methyl iodide to form the dihapto-thiocarboxamido-containing cation \([\text{Os}(\eta^2-\text{SCNMe})_2(\text{CS})(\text{CO})(\text{PPh}_3)_2]^+\) and, as described in chapters 2 and 4 for the related dihapto-dithioester-containing cations, reaction with sodium borohydride opens the three-membered ring and affords a neutral hydrido-containing complex. However, this compound does not contain a \( v_\text{CS} \) band between 1200 \( \text{cm}^{-1} \) and 1400 \( \text{cm}^{-1} \) which could be attributed to the thiocarbonyl ligand. Instead a strong band at 1010 \( \text{cm}^{-1} \) in a position typically observed for a monodentate dithioester ligand [Table 2.2] is observed. Accordingly, the anticipated product I (see Scheme 5.2) was formulated as II with the monohapto-thiocarboxamido and the thiocarbonyl ligands having combined to form a four-membered metallocycle. Confirmation was obtained by an X-ray crystal structure determination\(^{103}\) (figure 5.1).

It is interesting that \( \text{OsH}(\eta^1-\text{CS}_2\text{Me})(\text{CO})(\text{CS})(\text{PPh}_3)_2 \), the dithioester analogue of I, does not show this same rearrangement. The increased nucleophilicity of the sulphur atom of a monohapto-thiocarboxamido compared with a monohapto-dithioester ligand has been noted previously.\(^{103,104}\)

The exo-sulphur atom in II is rapidly methylated by reaction with methyl iodide forming III, in which the ligand is formally a bidentate dicarbene, and reaction of this cation with borohydride produces IV where, without X-ray analysis, it is not possible to distinguish between the formulations a or b.
Figure 5.1: Structure of Os(η²-CS₂CNMeR)H(CO)(PPh₃)₂.
Scheme 5.2 (L = PPh₃;  R = p-tolyl)
EXPERIMENTAL

Os(n²-S₂CNET₂)(CHS)(CS)(PPh₃)₂.

Dihapto-diethylidithiocarbamatothioformylthiocarbonylbis(triphenylphosphine)-osmium(II).

\[ \text{Os(n²-S₂CNET₂)(CHS)(CS)(PPh₃)₂ClO}_4 \] (0.3 g) was stirred in ethanol (60 ml) containing sodium borohydride (0.2 g) for 30 min. The pink solid was collected and washed with ethanol and hexane (0.266 g, 97.8%). Recrystallisation from dichloromethane-ethanol gave pink crystals of the solvate \[ \text{Os(n²-S₂CNET₂)(CHS)(CS)(PPh₃)₂(CH₂Cl₂)} \] (CH₂Cl₂) 0.33.H N.M.R. (CDCl₃) shows τ, 4.72 [s, 0.67H, CH₂Cl₂]. M.p. 139-141°C. Anal. Found: C, 53.19; H, 4.50; N, 1.18%. C₄₃H₄₁NOS₂P₂S₄(CH₂Cl₂) 0.33 requires C, 53.08; H, 4.28; N, 1.43%.

[Os(n²-S₂CNET₂)(CHSMe)(CS)(PPh₃)₂]I.

Dihapto-diethylidithiocarbamatomethylthiolatocarbene-thiocarbonylbis-(triphenylphosphine)osmium(II)iodide.

Os(n²-S₂CNET₂)(CHS)(CS)(PPh₃)₂ (0.2 g) was stirred in methyl iodide (5 ml) for 2 min and hexane (20 ml) was added. The yellow crystals were collected and washed with hexane (0.23 g, 100%). Recrystallisation from dichloromethane-ethanol-cyclohexane gave yellow crystals. M.p. 170-174°C. Anal. Found: C, 47.91; H, 4.26; N, 1.00%.

C₄₄H₄₄INOS₂P₂S₄ requires C, 48.30; H, 4.05; N, 1.28%.
[OsCl(CO)(CS)(CNR)(PPh₃)₂]ClO₄⋅

Chlorocarbonylthiocarbonyl-p-tolylisocyanidebis(triphenylphosphine)-osmium(II)perchlorate. MW 1038.816

[OsCl(H₂O)(CS)(CNR)(PPh₃)₂]ClO₄ (1.0 g) in dichloromethane (40 ml) and ethanol (20 ml) was heated under carbon monoxide (60 p.s.i.) to 100°C for 30 min. After cooling to room temperature the dichloromethane was removed to give white needles (1.0 g, 99%). Recrystallisation from dichloromethane-ethanol-cyclohexane gave white needles. M.p. 189°C. Anal. Found: C, 53.23; H, 3.89; N, 1.16%.

C₄₆H₃₇Cl₂NO₅OsP₂S₂ requires C, 53.18; H, 3.59; N, 1.35%.

[Os(η²-SCNHR)(CO)(CS)(PPh₃)₂]ClO₄⋅

Dithapto-C₅S-N-p-tolylthiocarboxamidocarbonylthiocarbonylbis(triphenylphosphine)osmium(II)perchlorate.

[OsCl(CO)(CS)(CNR)(PPh₃)₂]ClO₄ (0.5 g) was stirred in acetone (30 ml) and sodium hydrosulphide (0.05 g) in water (1 ml) and acetone (10 ml) was added. After 15 min stirring perchloric acid (ca. 70%, 0.1 ml) was added with ethanol (20 ml) and the solvent volume was reduced to 20 ml. The cream crystalline solid was collected and washed with ethanol (0.49 g, 98.2%). Recrystallisation from dichloromethane-ethanol-cyclohexane gave cream crystals of the solvate [Os(η²-SCNHR)(CO)(CS)(PPh₃)₂]ClO₄⋅(C₆H₁₂)₀.₃₃. ¹H N.M.R. (CDCl₃/DMSO) shows τ, 8.58 [s, 4H, C₆H₁₂]. M.p. 203-205°C. Anal. Found: C, 54.25; H, 4.02; N, 1.21%. C₄₆H₃₈ClNO₅OsP₂S₂⋅(C₆H₁₂)₀.₃₃ requires C, 54.15; H, 3.98; N, 1.32%. 
OsCl₂(CS)(CNR)(PPh₃)₂

Dichlorothiocarbonyl-p-tolylisocyanidebis(triphenylphosphine)osmium(II).

OsCl₂(CS)(PPh₃)₃ (2.0 g) was suspended in dichloromethane (40 ml) and p-tolylisocyanide (0.23 g, 1.07 eq.) in dichloromethane (10 ml) was added. After 10 min stirring the solution volume was lowered to 10 ml and hexane was added to give an oily solid. The mother liquor was discarded and the oil redissolved in dichloromethane. Ethanol was added and the solvent was removed to give a voluminous solid. Hexane was added and the suspension stirred vigorously to give a finely divided white crystalline solid which was collected. The recrystallisation process was repeated to give white crystals (1.54 g, 88.8%) which were characterised by comparison with an authenticated sample.


Chloroaquothiocarbonyl-p-tolylisocyanidebis(triphenylphosphine)-osmium(II) perchlorate.

OsCl₂(CS)(CNR)(PPh₃)₂ (1.0 g) was dissolved in dichloromethane (100 ml) and silver perchlorate (0.225 g, 1.03 eq.) in ethanol (20 ml) was added. After 20 min stirring the suspension was filtered through a celite pad. Removal of dichloromethane gave white crystals (1.07 g, 98.6%). Recrystallisation from dichloromethane-ethanol gave white crystals. M.p. 196-197°C. Anal. Found: C, 52.61; H, 4.31; N, 1.27%. C₄₅H₃₉Cl₂NO₅OsP₂S requires C, 52.52; H, 3.82; N, 1.36%.
Reaction of $[\text{OsCl(CO)}(\text{CS})(\text{CNR})(\text{PPh}_{3})]_{2} \text{ClO}_{4}$ with $\text{SH}^{-}$ in Dichloromethane-Ethanol.

$[\text{OsCl(CO)}(\text{CS})(\text{CNR})(\text{PPh}_{3})]_{2} \text{ClO}_{4}$ (0.5 g) was stirred in dichloromethane (30 ml) and sodium hydrosulphide (0.15 g) in ethanol (30 ml) was added. Upon removal of dichloromethane yellow crystals separated which were collected, dissolved in dichloromethane and passed down a florisil column using dichloromethane as eluent. Two yellow bands separated on the column. The first was collected and on addition of hexane yellow crystals separated which were identified as $\text{Os(}n^{2-}\text{CS}_{2})(\text{CO})(\text{CNR})(\text{PPh}_{3})]_{2}$ by comparison of the I.R. spectrum with that of an authenticated sample ($0.065$ g, 14.4%). The second band was eluted from the column with acetone giving 50 ml of a yellow solution to which ethanol (10 ml) containing perchloric acid ($ca.$ 70%, 0.1 ml) was added. Reduction of the solvent volume gave cream crystals of $[\text{Os(}n^{2-}\text{SCNHR})(\text{CO})(\text{CS})(\text{PPh}_{3})]_{2} \text{ClO}_{4}$ (0.41 g, 82.2%). This product was compared with an authenticated sample.

$\text{Os(}n^{2-}\text{SCNR})(\text{CO})(\text{CS})(\text{PPh}_{3})]_{2}$.

*Dihapto-C,S-p-tolyliosothiocyanatecarbonylthiocarbonylbis(triphenylphosphine)-osmium(II)*.

$[\text{Os(}n^{2-}\text{SCNHR})(\text{CO})(\text{CS})(\text{PPh}_{3})]_{2} \text{ClO}_{4}$ (0.45 g) was dissolved in dichloromethane (30 ml) and sodium hydroxide (0.1 g) in ethanol (10 ml) was added. Upon removal of dichloromethane yellow crystals deposited which were collected and washed with ethanol and hexane (0.34 g, 85.5%). Recrystallisation from dichloromethane-ethanol gave yellow crystals. M.p. 183-186°C (darkens 165°C). Anal. Found: C, 59.67; H, 4.59; N, 1.37%. $C_{46}H_{37}$NOOsP$_{2}$S$_{2}$ requires C, 59.02; H, 3.98; N, 1.50%.
Chlorothiocarbonylbis(p-tolylisocyanide)bis(triphenylphosphine)-
osmium(II) perchlorate.

\[ [\text{OsCl}(\text{CS})(\text{CNR})_2(\text{PPh}_3)_2]\text{ClO}_4 \]

\[ [\text{OsCl}(\text{H}_2\text{O})(\text{CS})(\text{CNR})(\text{PPh}_3)_2]\text{ClO}_4 \] (0.25 g) was dissolved in dichloromethane (30 ml) and p-tolylisocyanide (0.03 g, 1.06 eq.) was added in dichloromethane (5 ml). The solution was stirred for 20 min and hexane was added. Removal of dichloromethane afforded cream crystals which were collected and washed with hexane (0.275 g, 100%). Recrystallisation from dichloromethane-ethanol-cyclohexane afforded white crystals of the solvate \([\text{OsCl}(\text{CS})(\text{CNR})_2(\text{PPh}_3)_2]\text{ClO}_4 \cdot (\text{C}_6\text{H}_{12})_{0.167} \cdot 1\text{H}_2\text{O}\text{M.R.} \text{ (CDCl}_3\text{ ) shows }\tau, 8.57 [\text{s}, 2\text{H}, \text{C}_6\text{H}_{12}]\text{. M.p. 217-219°C. Anal. Found: }\text{C}, 57.15; \text{H}, 4.18; \text{N}, 2.52\%\text{. C}_{53}\text{H}_{44}\text{Cl}_2\text{N}_2\text{O}_4\text{OsP}_2\text{S}_2\cdot (\text{C}_6\text{H}_{12})_{0.167}\text{ requires }\text{C}, 56.79; \text{H}, 4.06; \text{N}, 2.45\%\text{.}

\[ [\text{Os}(\eta^2-\text{SCNMeR})(\text{CO})(\text{CS})(\text{PPh}_3)_2]\text{ClO}_4 \]

Dihapto-C,S-N,N-methyl-p-tolylthiocarboxamidocarbonylthiocarbonylbis(triphenylphosphine) osmium(II) perchlorate.

\[ \text{Os}(\eta^2-\text{SCN})(\text{CO})(\text{CS})(\text{PPh}_3)_2 \] (0.3 g) was dissolved in methyl iodide (5 ml) and hexane was added to give a cream solid which was collected and washed with hexane. Recrystallisation from dichloromethane (30 ml) and ethanol (30 ml) containing perchloric acid (ca. 70%, 0.05 ml) gave cream crystals (0.335 g, 99.5%). Recrystallisation from dichloromethane-ethanol-cyclohexane gave cream crystals of the solvate \([\text{Os}(\eta^2-\text{SCNMeR})(\text{CO})(\text{CS})(\text{PPh}_3)_2]\text{ClO}_4 \cdot (\text{CH}_2\text{Cl}_2)_{0.5} \cdot (\text{C}_6\text{H}_{12})_{0.33} \]
\[ ^1 \text{H N.M.R.} (\text{CDCl}_3, \text{DMSO}) \text{ shows } \tau, \ 4.37 \ [s, \ 1H, \text{CH}_2\text{Cl}_2], \ \tau, \ 8.59 \]
\[ [s, \ 4H, \text{C}_6\text{H}_{12}]. \ \text{M.p. 176-179°C.} \ \text{Anal. Found: C, 53.49; H, 4.00; N, 1.07%.} \]
\[ \text{C}_{47}\text{H}_{40}\text{ClNO}_{5}\text{Os}_2\text{S}_2\text{.}(\text{CH}_2\text{Cl}_2)_{0.5} \ (\text{C}_6\text{H}_{12})_{0.33} \]
\[ \text{requires C, 53.03; H, 4.05; N, 1.25%.} \]

\[ \text{Os}(\eta^2-\text{CS}_2\text{CNMe}_2)\text{H}_(\text{CO})\text{(PPh}_3)_2. \]

\[ [\text{Os}(\eta^2-\text{SCNMe}_2)\text{(CO)}(\text{CS}_2\text{PPh}_3)_2]\text{ClO}_{4}\text{.}(\text{CH}_2\text{Cl}_2)_{0.5} \ (\text{C}_6\text{H}_{12})_{0.33} \ (0.25 \ g) \]
\[ \text{was dissolved in ethanol (30 ml) and sodium borohydride (0.1 g) in} \]
\[ \text{ethanol (10 ml) was added. The solution was stirred for 20 min and} \]
\[ \text{the pink crystals were collected and washed with ethanol [0.22 g, 96.5%].} \]
\[ \text{Recrystallisation from dichloromethane-ethanol gave red crystals} \]
\[ \text{containing 0.25 equivalent dichloromethane of solvation.} \]

\[ ^1 \text{H N.M.R. (CDCl}_3) \text{ shows } \tau, \ 4.77 \ [s, \ 0.5H, \text{CH}_2\text{Cl}_2]. \ \text{M.p. 179-181°C.} \ \text{Anal.} \]
\[ \text{Found: C, 58.66; H, 4.62; N, 1.32%.} \]
\[ \text{C}_{47}\text{H}_{41}\text{NO}_{5}\text{Os}_2\text{S}_2\text{.}(\text{CH}_2\text{Cl}_2)_{0.25} \]
\[ \text{requires C, 58.30; H, 4.30; N, 1.44%.} \]

\[ [\text{Os}(\eta^2-\text{C}[\text{SMe}]\text{CNMe}_2)\text{H}_(\text{CO})\text{(PPh}_3)_2]\text{I}. \]

\[ \text{Hydrido[dit}hapto-C,C'-}(\text{methylthiolato})-C,C'-\text{sulphido}(N,N'-\text{methyl-p-tolylamino})\text{dicarbene}](\text{carbonylbis(triphenylphosphine)}\text{osmium(II))iodide.} \]

\[ \text{Os}(\eta^2-\text{CS}_2\text{CNMe}_2)\text{H}_(\text{CO})\text{(PPh}_3)_2\text{.}(\text{CH}_2\text{Cl}_2)_{0.25} \ (0.2 \ g) \text{ was dissolved in} \]
\[ \text{methyl iodide and hexane was added to give yellow-orange crystals} \]
\[ \ (0.225 \ g, 100%). \ \text{Recrystallisation from dichloromethane-ethanol-} \]
\[ \text{cyclohexane gave yellow-orange platelets containing 0.125 mol cyclo-} \]
\[ \text{hexane of solvation.} \]

\[ ^1 \text{H N.M.R. (CDCl}_3) \text{ shows } \tau, \ 8.57, \ [s, \ 1.5H,} \]
\[ \text{C}_6\text{H}_{12}]. \ \text{M.p. 162-164°C.} \ \text{Anal. Found: C, 53.17; H, 4.39; N, 1.18%.} \]
\[ \text{C}_{48}\text{H}_{44}\text{NO}_{5}\text{Os}_2\text{S}_2\text{.}(\text{C}_6\text{H}_{12})_{0.125} \]
\[ \text{requires C, 53.01; H, 4.15; N, 1.27%.} \]
Reaction of $[\text{Os}(\eta^2-\text{C[SMe]SCNMe})\text{H}(\text{CO})(\text{PPh}_3)_2]\text{I}$ with Sodium Borohydride.

To $[\text{Os}(\eta^2-\text{C[SMe]SCNMe})\text{H}(\text{CO})(\text{PPh}_3)_2]\text{I} \cdot (\text{C}_6\text{H}_{12})_{0.125}$ (0.2 g) in ethanol (10 ml) was added sodium borohydride (0.05 g) in ethanol (10 ml). After 30 min stirring the lemon yellow solid was collected and washed with ethanol (0.17 g, 97%). Recrystallisation from dichloromethane-ethanol gave lemon needles. M.p. 192-193°C. Anal. Found: C, 59.88; H, 4.75; N, 1.51%. $\text{C}_{48}\text{H}_{45}\text{NOOS}_2\text{S}_2$ requires C, 59.55; H, 4.69; N, 1.45%.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{\text{CS}}$</th>
<th>$\nu_{\text{CO}}$</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os($n^2$-S$_2$CNET$_2$) (CHS) (CS)L$_2$</td>
<td>1270$^b$</td>
<td>1190w, 998m ($\nu_{\text{CHS}}$); 1490m, 1360w, 1213m, 1145w, 850w</td>
<td></td>
</tr>
<tr>
<td>[Os($n^2$-S$_2$CNET$_2$) (CHSMe) (CS)L$_2$]I</td>
<td>1290$^b$</td>
<td>1005w, 890wm$^c$ (carbene); 1510m, 1355w, 1210w, 1150w, 848w</td>
<td></td>
</tr>
<tr>
<td>OsCl$_2$ (CS) (CNR)L$_2$</td>
<td>1305</td>
<td>2150vs ($\nu_{\text{CN}}$)$^h$</td>
<td></td>
</tr>
<tr>
<td>[OsCl(H$_2$O) (CS) (CNR)L$_2$]ClO$_4$</td>
<td>1310</td>
<td>2160vs ($\nu_{\text{CN}}$); 1608w$^c$ ($\delta_{\text{OH}}$)$^d$; 1118s, 1053ms, 622m (ClO$_4^-$)</td>
<td></td>
</tr>
<tr>
<td>[OsCl(CO) (CS) (CNR)L$_2$]ClO$_4$</td>
<td>1323</td>
<td>2205vs ($\nu_{\text{CN}}$)$^e$</td>
<td></td>
</tr>
<tr>
<td>[Os($n^2$-SCNHR) (CO) (CS)L$_2$]ClO$_4$</td>
<td>1320</td>
<td>3180w$^c$ ($\nu_{\text{NH}}$); 1600w ($\delta_{\text{NH}}$); 1552m ($\nu_{\text{CN}}$); 1510m ($\nu_{\text{CC-arene}}$); 930w, 882w, 815w$^f$</td>
<td></td>
</tr>
<tr>
<td>Os($n^2$-SCNR) (CO) (CS)L$_2$</td>
<td>1285</td>
<td>1620m, 1570m ($\nu_{\text{CN}}$); 1180w$^g$</td>
<td></td>
</tr>
<tr>
<td>Os($n^2$-CS$_2$) (CO) (CNR)L$_2$</td>
<td>1095m, 1070m</td>
<td>675m ($\nu_{\text{C-S}}$)$^h$</td>
<td></td>
</tr>
<tr>
<td>[OsCl(CS)(CNR)$_2$L$_2$]ClO$_4$</td>
<td>1315</td>
<td>2160vs ($\nu_{\text{CN}}$)$^e$</td>
<td></td>
</tr>
<tr>
<td>[Os($n^2$-SCNMeR) (CO) (CS)L$_2$]ClO$_4$</td>
<td>1308</td>
<td>1540m ($\nu_{\text{CN}}$); 1505m ($\nu_{\text{CC-arene}}$); 1395w, 1245w, 885w, 820w$^e$</td>
<td></td>
</tr>
<tr>
<td>Os($n^2$-CS$_2$CNMeR) (CO)L$_2$</td>
<td>1010s</td>
<td>1520w, 1510m, 1500s, 1385w, 1310w, 1240w, 1120m, 1060m, 887w, 820w, 720w, 660w, 540w</td>
<td></td>
</tr>
<tr>
<td>[Os($n^2$-C[SMe]SCNMeR)H(CO)L$_2$]I</td>
<td>1945</td>
<td>1530m ($\nu_{\text{CN}}$); 1500m, 1380w, 1310w, 1240w, 1220w, 1152w, 1000s$^c$, 858m, 823w, 790w, 720w, 535w</td>
<td></td>
</tr>
<tr>
<td>Os($n^2$-CH[SMe]SCNMeR)H(CO)L$_2$ or</td>
<td>1895</td>
<td>1975m ($\nu_{\text{OBS}}$); 1508w, 1490w, 1410w, 1380w, 1310w, 1285w, 1240w, 1210w, 1182w, 1120w, 1062w, 970w, 942w, 908w, 845w, 825w, 778w, 720w, 682w, 543w</td>
<td></td>
</tr>
</tbody>
</table>

Footnotes: (L = Ph$_3$; R = p-tolyl) (a) very strong; (b) band also incorporates $S_2$CNET$_2$ vibration near 1270 w-m; (c) broad band; (d) $\delta_{\text{OH}}$ not discernible; (e) ClO$_4^-$ bands near 1090vs, 620s; (f) ClO$_4^-$ bands at 1105vs, 1055vs, 620s; (g) p-tolyl bands near 1500 and 820; (h) ref. 110.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (t) and Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(η²-S₂CNET₂)(CHS)(CO)L₂</td>
<td>9.48, t, 3H, NCH₂-CH₃, J(HH) = 7.1</td>
</tr>
<tr>
<td></td>
<td>9.20, t, 3H, NCH₂-CH₃, J(HH) = 7.1</td>
</tr>
<tr>
<td></td>
<td>7.69, q, 2H, N-CH₂-CH₃, J(HH) = 7.1</td>
</tr>
<tr>
<td></td>
<td>6.90, q, 2H, N-CH₂-CH₃, J(HH) = 7.1</td>
</tr>
<tr>
<td></td>
<td>2.50, m, 30H, Ph</td>
</tr>
<tr>
<td></td>
<td>-7.78, t, 1H, CHS, 3J(HP) = 2</td>
</tr>
<tr>
<td>[Os(η²-S₂CNET₂)(CHSMe)(CS)L₂]I</td>
<td>9.38, t, 3H, NCH₂-CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>9.30, t, 3H, NCH₂-CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>7.72, s, 3H, S-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.29, q, 3H, N-CH₂-CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>7.04, q, 3H, N-CH₂-CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>2.48, m, 30H, Ph</td>
</tr>
<tr>
<td></td>
<td>-5.28, m, 1H, CHSMe</td>
</tr>
<tr>
<td>[OsCl(CO)(CS)(CNR)L₂]ClO₄</td>
<td>7.60, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.10, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.33, m, 30H, Ph</td>
</tr>
<tr>
<td>[Os(η²-SCNHR)(CO)(CS)L₂]ClO₄</td>
<td>7.80, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.23, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.50, m, 30H, Ph</td>
</tr>
<tr>
<td></td>
<td>-2.62, s(br), 1H, N-H</td>
</tr>
<tr>
<td>Os(η²-SCNR)(CO)(CS)L₂</td>
<td>7.85, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.84, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.47, m, 31H, Ph</td>
</tr>
<tr>
<td>Compound</td>
<td>Chemical Shift (τ) and Coupling Constants (Hz)</td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>[OsCl(CS)(CNR)$_2$L$_2$]ClO$_4$</td>
<td>$7.64, s, 6\text{H}, \text{C}_6\text{H}_4\text{-CH}_3$</td>
</tr>
<tr>
<td></td>
<td>$3.20, m, 8\text{H}, \text{--C}_6\text{H}_4$</td>
</tr>
<tr>
<td></td>
<td>$2.38, m, 30\text{H}, \text{Ph}$</td>
</tr>
<tr>
<td>$[\text{Os}(\eta^2\text{-SCNMeR})(\text{CO})(\text{CS})L_2]ClO_4^d$</td>
<td>$7.77, s, 3\text{H}, \text{C}_6\text{H}_4\text{-CH}_3$</td>
</tr>
<tr>
<td></td>
<td>$6.53, s, 3\text{H}, \text{N-CH}_3$</td>
</tr>
<tr>
<td></td>
<td>$3.61, q, 4\text{H}, \text{--C}_6\text{H}_4$</td>
</tr>
<tr>
<td></td>
<td>$2.45, m, 31\text{H}, \text{Ph}$</td>
</tr>
<tr>
<td>$\text{Os}(\eta^2\text{-CS}_2\text{CNMeR})\text{H(CO)}L_2$</td>
<td>$19.55, t, 1\text{H}, \text{Os-H}, ^2\text{J(HP)} = 23.75$</td>
</tr>
<tr>
<td></td>
<td>$7.75, s, 3\text{H}, \text{C}_6\text{H}_4\text{-CH}_3$</td>
</tr>
<tr>
<td></td>
<td>$7.35, s, 3\text{H}, \text{N-CH}_3$</td>
</tr>
<tr>
<td></td>
<td>$3.33, q, 4\text{H}, \text{--C}_6\text{H}_4$</td>
</tr>
<tr>
<td></td>
<td>$2.43, m, 31\text{H}, \text{Ph}$</td>
</tr>
<tr>
<td>$[\text{Os}(\eta^2\text{-CS}[\text{SMe}]\text{SCNMeR})\text{H(CO)}L_2]I$</td>
<td>$17.43, t \quad 1\text{H}, \text{Os-H}, ^2\text{J(HP)} = 24$</td>
</tr>
<tr>
<td></td>
<td>$17.51, t$</td>
</tr>
<tr>
<td></td>
<td>$8.27, s, 0.75\text{H}$</td>
</tr>
<tr>
<td></td>
<td>$7.92, s, 1.5\text{H}$</td>
</tr>
<tr>
<td></td>
<td>$7.77, s, 1.5\text{H}$</td>
</tr>
<tr>
<td></td>
<td>$7.30, s, 1.5\text{H}$</td>
</tr>
<tr>
<td></td>
<td>$7.01, s, 0.75\text{H}$</td>
</tr>
<tr>
<td></td>
<td>$7.67, s\text{br}, 3\text{H}, \text{C}_6\text{H}_4\text{-CH}_3$</td>
</tr>
<tr>
<td></td>
<td>$3.58, m, 4\text{H}, \text{--C}_6\text{H}_4$</td>
</tr>
<tr>
<td></td>
<td>$2.40, m, 30\text{H}, \text{Ph}$</td>
</tr>
<tr>
<td>Compound</td>
<td>Chemical Shift (τ) and Coupling Constants (Hz)</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Os(η²-CH[SMe]SCNMeR)H(CO)L₂</td>
<td>19.97, t, 1H, Os-H, (^2)J(HP) = 22.5</td>
</tr>
<tr>
<td>or</td>
<td>7.95, s, 3H, S-CH₃</td>
</tr>
<tr>
<td>Os(η²-C[SMe]SCHNMeR)H(CO)L₂</td>
<td>7.77, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.48, s, 3H, N-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.00, t, 1H, CHSMe or CHNMeR, (^3)J(HP) = 2.5</td>
</tr>
<tr>
<td></td>
<td>3.47, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.40, m, 33H, Ph</td>
</tr>
</tbody>
</table>

Footnotes: (L = PPh₃; R = p-tolyl)

(a) [OsCl(H₂O)(CS)(CNR)L₂]ClO₄ too insoluble for \(^1\)H N.M.R.;
(b) signal disappears on addition of D₂O;
(c) restricted rotation about carbene C-S and C-N bonds produces isomers;
(d) in DMSO/CDCl₃.
CHAPTER 6

ARYL-THIOCARBONYL COMPLEXES AND REARRANGEMENT REACTIONS

In chapter 3 facile hydride transfer to the thiocarbonyl ligand to form a thioformyl ligand was reported. It was noted that while iminoformyl complexes have been similarly prepared the corresponding reaction of an hydrido-carbonyl complex to produce an isolatable formyl complex has never been observed. The transfer of alkyl or aryl ligands to isocyanide\textsuperscript{202} or carbonyl\textsuperscript{205,206} ligands has received a great deal of recent attention. Transfer of an alkyl ligand to the carbonyl ligand is believed to play a key role in the oxo (hydroformylation) process. However, no alkyl- or aryl-thiocarbonyl complexes have been reported so that the investigation of the transfer of alkyl or aryl ligands to CS has not been possible. Aryl-carbonyl and aryl-isocyanide complexes of ruthenium and osmium have been produced in this laboratory and aryl transfer to CO\textsuperscript{207,208} and CNR\textsuperscript{208,209} has been achieved. In this chapter extension of these studies to thiocarbonyl complexes is reported. Complexes containing \textit{cis} aryl and thiocarbonyl ligands have been produced and rearrangement reactions, which involve the thiocarbonyl ligand, have been clearly observed. The results indicate that bidentate thioacyl complexes are formed,

\[ \text{Os} \begin{array}{c} \text{R} \\ \text{CS} \end{array} \rightarrow \begin{array}{c} \text{C} \\ \text{R} \end{array} \text{Os} \begin{array}{c} \text{S} \end{array} \]
However, as discussed below, these latter compounds exhibit some unusual properties and, consequently, the formulations of these and subsequent derivatives are considered to be tentative until verification by X-ray crystal structure analysis is completed.

6.1 Production of Aryl-Thiocarbonyl Complexes

The studies of Roper and Wright concerning aryl transfer to CO and CNR are based on the reactions of \( \text{MHCl(CO)(PPh}_3\text{)}_3 \) \([M = \text{Ru, Os}]\) with diarylmercury compounds which afford the strongly-coloured coordinatively-unsaturated complexes \( \text{MCIR'(CO)(PPh}_3\text{)}_2 \) \([R' = p\text{-toly1, o\text{-toly1}]}\). The high yield synthesis of \( \text{OSHCl(CS)(PPh}_3\text{)}_3 \) has enabled an identical route to be employed to afford analogous thiocarbonyl complexes. Thus \( \text{OSHCl(CS)(PPh}_3\text{)}_3 \) reacts with \( \text{HgR}_2 \) \([R = p\text{-toly1}]\) in toluene under reflux to deposit \( \text{Hg} \) and afford a deep crimson solution from which crimson (near black) crystals of \( \text{OSClR(CS)(PPh}_3\text{)}_2 \) can be isolated \([\alpha. 90\%]\). If \( \text{HgClR} \) is used as a source of the aryl ligand then \( \text{OSClR(CS)(PPh}_3\text{)}_2 \) is obtained in lower yields \([\alpha. 60\%]\). \( \text{OSClPh(CS)(PPh}_3\text{)}_2 \) has been synthesised employing \( \text{HgClPh} \) only \([\alpha. 60\%]\). The possible course of these reactions has been discussed in the context of the carbonyl analogues.\(^{209}\) An X-ray crystal structure determination\(^{210}\) has shown that, as for other five-coordinate complexes of ruthenium(II) and osmium(II),\(^{211}\) \( \text{RuClR(CO)(PPh}_3\text{)}_2 \) has a square pyramidal geometry. For this compound the phosphine ligands are mutually trans and the R group is apical. A similar geometry is also likely for \( \text{OSClR(CS)(PPh}_3\text{)}_2 \), but in this complex the possibility also exists, in view of the pronounced trans-influence of the CS ligand, that CS could occupy the apical site.
Red solutions of OsCl(R)(PPh₃)₂ in dichloromethane lighten rapidly on addition of the potentially bidentate anions, diethyl-dithiocarbamate, acetate or trifluoroacetate to give the yellow six-coordinate complexes Os(η²-Y)R(CS)(PPh₃)₂ [Y = S₂CNET₂, O₂CCCH₃, O₂CCF₃]. If trifluoroacetic acid is used as a source of trifluoroacetate ion the R group is cleaved from the metal and the product obtained is Os(η¹-O₂CCF₃)₂(EtOH)(CS)(PPh₃)₂. An X-ray crystal structure analysis of the methanol-containing complex Ru(η¹-O₂CCF₃)₂(MeOH)(CO)(PPh₃)₂ has shown that methanol is coordinated to the metal and hydrogen-bonded to one trifluoroacetato ligand. Addition of silver perchlorate in ethanol to the red solution results in the rapid precipitation of silver chloride, but the anticipated product Os(η²-O₂ClO₂)R(CS)(PPh₃)₂, or a solvated cation, cannot be isolated from the yellow solution so formed and decomposes on attempted work-up. However, if NaX [X = Br, I] is added to this latter solution, rapid regeneration of the red colour is observed and OsXR(CS)(PPh₃)₂ can be obtained in high yields.

Red solutions containing the five-coordinate complexes OsXR(CS)(PPh₃)₂ [X = Cl, Br, I] are also decolourised rapidly upon reaction with acetonitrile, carbon monoxide or isocyanide to form the coordinatively saturated complexes OsXR(CS)₅(PPh₃)₂. The reaction of Os(η²-O₂CCF₃)R(CS)(PPh₃)₂ with p-chlorophenylisocyanide has also been investigated and stirring of these reactants in dichloromethane for 40 minutes affords the colourless compound Os(η¹-O₂CCF₃)R(CN-p-C₆H₄Cl)(CS)(PPh₃)₂ [Scheme 6.1].
Scheme 6.1 \( (L = \text{PPh}_3; \ R = p\text{-tolyl}; \ L' = \text{MeCN}, \text{CO}, \text{CNR}; \ X = \text{Br}, \text{I}; \ Y = S_2\text{CNET}_2', \text{CN}-p-C_6H_4\text{Cl}; \ \text{OS}^\eta_{-Y} (\text{CN}-p-C_6H_4\text{Cl})_2 (\text{CS})_2L_2, \) 

\( \text{Os}^\eta_{-Y} (\text{CS})_2L_2 \) is a solvated cation.

\( \text{OsCl}_R (\text{CS})_2L_2 \) is isolated.

\( \text{OsCl}_R (\text{CS})_2L_2 \) is isolated.

\( \text{OsCl}_R (\text{CS})_2L_2 \) is isolated.

\( \text{OsCl}_R (\text{CS})_2L_2 \) is isolated.

\( \text{OsCl}_R (\text{CS})_2L_2 \) is isolated.
6.2 **Rearrangement Reactions of Aryl-Thiocarbonyl Complexes**

When OsClR(MeCN)(CS)(PPh₃)₂ is dissolved in dichloromethane a red colour begins to develop in the solution which intensifies rapidly on heating. Isolation of the red product shows this to be a mixture of OsClR(CS)(PPh₃)₂ and OsClR(MeCN)(CS)(PPh₃)₂. If excess acetonitrile is added to the red solution the colour is discharged, indicating that acetonitrile coordination to OsClR(CS)(PPh₃)₂ is reversible, i.e. \[ \text{OsClR(CS)(PPh}_3\text{)}_2 + \text{MeCN} \rightleftharpoons \text{OsClR(MeCN)(CS)(PPh}_3\text{)}_2. \]

However, solutions of OsClR(CS)(CO)(PPh₃)₂ in dichloromethane, chloroform, benzene or toluene also rapidly turn red and the colour change is not reversed by excess carbon monoxide, even when forcing conditions are applied [100°C, 80 p.s.i., 3h]. It seems unlikely, therefore, that the red colour is caused by a five-coordinate complex. This colour change is sufficiently rapid to prevent the isolation of pure OsClR(CO)(CS)(PPh₃)₂ if the carbonylation of OsClR(CS)(PPh₃)₂ is carried out at room temperature. The bromo and iodo analogues undergo this same reaction and a qualitative comparison of the rate of colour formation suggests that the reaction occurs most rapidly for the iodo complex and least rapidly for the chloro complex. In fact OsIR(CO)(CS)(PPh₃)₂ has not been isolated, but has only been observed as an intermediate by the loss of colour that occurs when OsIR(CS)(PPh₃)₂ is treated with CO. Recrystallisation of the complexes OsXR(CO)(CS)(PPh₃)₂ results in an increased quantity of the red product, which forms sufficiently rapidly at 40°C to prevent the observation of any signals in the ^1H N.M.R. spectra,
other than those attributable to the red products. The formation of the red colour also occurs rapidly if solid samples of OsClR(CO)(CS)(PPh₃)₂ are heated to 60°C in vacuo or in an open oven.

The formation of a red complex also occurs for OsClR(CS)(CNR)(PPh₃)₂, but this reaction proceeds much more slowly at room temperature than that for the dicarbonyl analogues and, consequently, this compound can be recrystallised and a ¹H N.M.R. spectrum has been obtained. The reaction is rapid in boiling toluene and is complete, under these conditions, in less than 10 minutes. The formation of a red product occurs even more slowly for Os(η¹-O₂CCF₃)R(CN-p-C₆H₄Cl)(CS)(PPh₃)₂ where heating under reflux in boiling toluene for several hours is necessary for complete conversion. These red isocyanide-containing compounds exhibit very low (ca. 1900 cm⁻¹), very broad ν_CN bands as was found for Os(CS)(CNR)(PPh₃)₃ [Chapter 4].

All the red products have elemental analysis figures which suggest that the compositions are identical to those of the starting materials, thus suggesting that a rearrangement reaction has occurred in each case. The ¹H N.M.R. spectra indicate that the p-tolyl moiety is present in these rearranged products. However, the I.R. spectra contain some unusual features common to all the red products. The I.R. spectral changes that occur when the prototype, OsClR(CO)(CS)PPh₃)₂, undergoes this reaction will serve as an example. The ν_CO band shifts from 2055 cm⁻¹ to 1902 cm⁻¹ and the very strong ν_CS band at 1300 cm⁻¹ is replaced by a medium to strong structured band at 1310 cm⁻¹. Additional new bands
occur at 1600 cm\(^{-1}\) (m), 1178 cm\(^{-1}\) (m, sh), 975 cm\(^{-1}\) (w) and 635 cm\(^{-1}\) (w, sh). Changes also occur in the fingerprint region for the tolyl group. The band at 1600 cm\(^{-1}\) (m) is absent from the I.R. spectrum obtained for the rearranged product of OsClPh(CO)(CS)(PPh\(_3\))\(_2\) [which has been characterised only by the I.R. spectrum] indicating that the vibration responsible for this absorption is associated with the tolyl group.

It is postulated that the rearranged products contain a bidentate thioacyl ligand which is formed by transfer of the aryl ligand to CS with ring-closure. This contention is supported by an incompletely refined X-ray crystal structure analysis of OsBr(\(n^2\)-CSR)(CO)(PPh\(_3\))\(_2\) \([\text{RF} = 11\%]\) as depicted in figure 6.1.

![Figure 6.1 (bond lengths in Å)](image)

However, certain features of the I.R. spectra of these compounds are surprising. For instance, what vibration does the medium to strong band near 1300 cm\(^{-1}\) represent? Is this very conspicuous band, which is common to the phenyl derivative and all the tolyl derivatives, the \(\nu_{CS}\) vibration? If so, it occurs at a surprisingly high value since the I.R. bands associated with the monodentate thioformyl ligand are near 1200 cm\(^{-1}\) and 1000 cm\(^{-1}\) [Chapter 3], and the \(\nu_{CO}\) band for the structurally verified \(\text{dihapto-acyl ligand in}\) Cp\(_2\)Zr(\(n^2\)-COMe)Me occurs at 1545 cm\(^{-1}\), a value which is much lower.
than found for typical monohapto-acyl ligands.\textsuperscript{213} There are now several examples of bidentate acyl ligands\textsuperscript{206} and bidentate iminoacyl ligands\textsuperscript{210,214} which have been confirmed by X-ray crystal structure analyses and it is particularly noteworthy that \(\text{CpMo(CO)}_2[\eta^2-\text{C(NPh)}\text{CH}_3]\)\textsuperscript{214} exhibits a \(\nu_{\text{CN}}\) band at 1720 cm\(^{-1}\).\textsuperscript{215} This band is significantly higher than for normal monodentate iminoacyl ligands\textsuperscript{216} and it was postulated that the bidentate iminoacyl ligand resembles a \(\pi\)-bonded acetylene which could explain the higher \(\nu_{\text{CN}}\) value.\textsuperscript{213,214} Perhaps an acetylene-like bonding is also operative in these thiaoacyl complexes, but the determination of this point must await complete refinement of the crystal structure analysis.

Prolonged heating of the thiaoacyl complex in toluene does not reverse the rearrangement reaction. If \(\text{OsCl}(\eta^2-\text{CSR})(\text{CO})(\text{PPh}_3)_2\) is heated under reflux with diethyldithiocarbamate ion in a chloroform-ethanol solution no reaction has occurred after 4 hours. However, prolonged heating [15 h] in the high boiling point medium, xylene and 2-methoxyethanol, yields, by displacement of chloride and triphenylphosphine, the bidentate thiaoacyl-containing complex \(\text{Os}(\eta^2-\text{S}_2\text{CNET}_2)(\eta^2-\text{CSR})(\text{CO})(\text{PPh}_3)_2\). This result suggests that the thiaoacyl ligand has a very strong tendency to remain bidentate.

Aryl transfer to the carbonyl ligand cannot be induced to occur in \(\text{OsRCl(CO)(CNR)(PPh}_3)_2\) \([R \text{ trans to CNR}]\textsuperscript{208}\) or \(\text{OsRCl(CO)}_2(\text{PPh}_3)_2\).\textsuperscript{207} However, \(R\) migration to the isocyanide ligand occurs on heating \(\text{Os}(\eta^1-\text{O}_2\text{CCH}_3)R(\text{CO})(\text{CN})_2(\text{PPh}_3)_2\).\textsuperscript{208} For the ruthenium analogues aryl transfer to CO and CNR has been achieved and solution spectra show that the dicarbonyl complexes \(\text{RuXR(CO)}_2(\text{PPh}_3)_2\) are in
equilibrium with the monocarbonyl-acyl complexes \( \text{RuX}(\eta^2\text{-COR})(\text{CO})(\text{PPh}_3)_2 \),
which are believed to contain a bidentate acyl ligand.\(^{207}\)

The ruthenium acyl complexes do not react with acids and attempts to methylate the acyl-oxygen atom with methyl triflate or methyl iodide have been unsuccessful. The bidentate iminoacyl complexes \( \text{RuX}[\eta^2\text{-C(NR)R}](\text{CO})(\text{PPh}_3)_2 \)\(^{210}\) are protonated by acids but are inert towards alkylation by methyl triflate.\(^{209}\) The bidentate thioacyl complexes obtained in this work are not attacked by acids but do react very slowly with methyl triflate. In dry benzene this reaction affords a red oily product with \( \text{OsCl}(\eta^2\text{-CSR})(\text{CO})(\text{PPh}_3)_2 \) which is difficult to handle and has eluded characterisation. However, for \( \text{OsCl}(\eta^2\text{-CSR})\text{(CNR)}(\text{PPh}_3)_2 \) two products are obtained. The minor product is again a red oily compound which, because of handling difficulties, has eluded satisfactory characterisation. The major product is a green crystalline solid which the I.R. spectrum shows contains a trifluoromethanesulphonate ion. This ion can be exchanged for perchlorate ion to afford a perchlorate salt, but reaction with chloride ion affords a red neutral complex. The green solid is formulated as the cationic bidentate carbene complex \( [\text{OsCl}(\eta^2\text{-C(SMe)R})(\text{CNR})(\text{PPh}_3)_2]^+ \), which on reaction with chloride ion leads to the neutral monodentate carbene complex \( \text{OsCl}_2[\eta^1\text{-C(SMe)R}](\text{CNR})(\text{PPh}_3)_2 \). The former compound exhibits a medium intense band in the I.R. spectrum at 1327 \( \text{cm}^{-1} \), but the latter has no activity between 1200 \( \text{cm}^{-1} \) and 1400 \( \text{cm}^{-1} \). Both compounds exhibit a split \( v_{\text{CN}} \) band for the isocyanide ligand in the spectra obtained in nujol mulls and the splitting remains in the spectra obtained in dichloromethane [Table 6.1] suggesting that geometrical isomers are present. The intractable red oily
solid could be the neutral carbene complexes $\text{OsCl(O}_{\text{SO}_{2}}\text{CF}_{3}\text{)}[\eta^1-\text{C(SMe)R}]_2 \text{L(PPh}_{3}\text{)}_2 \ [\text{L} = \text{Cl, CNR}]$ which contain a trifluoromethanesulphonato ligand [Scheme 6.2].

\[
\text{OsXRL'}(\text{CS})\text{L}_2 \quad \rightarrow \quad \text{OsX(}\eta^2-\text{CSR})\text{L'}\text{L}_2
\]

\[
\begin{align*}
\text{MeOSO}_{2}\text{CF}_3 \\
\text{MeOSO}_{2}\text{CF}_3 \\
\text{MeOSO}_{2}\text{CF}_3
\end{align*}
\]

\[
\begin{align*}
\text{X} = \text{Cl, L'} = \text{CO} \\
\text{X} = \text{Cl} \\
\text{L'} = \text{CNR}
\end{align*}
\]

\[
\text{OsCl(O}_{\text{SO}_{2}}\text{CF}_{3}\text{)}[\eta^1-\text{C(SMe)R}]\text{L'}\text{L}_2
\]

\[
\text{OsXRL'}(\text{CS})\text{L}_2 \quad \rightarrow \quad \text{OsX(}\eta^2-\text{CSR})(\text{CO})\text{L}
\]

\[
\begin{align*}
\text{OsCl}_{2}[\eta^1-\text{C(SMe)R}]\text{(CNR)}\text{L}_2 \quad \text{Cl}^{-} \\
[\text{OsX(}\eta^2-\text{C(SMe)R})\text{(CNR)}\text{L}_2]\text{CF}_{3}\text{SO}_{3}
\end{align*}
\]

Scheme 6.2 (L = PPh$_3$; R = p-tolyl; L' = CO, X = Cl, Br, I;
L' = CNR, X = Cl; L' = CN-p-C$_6$H$_4$Cl, X = O$_2$CCF$_3$)

It is interesting that reaction of methyl triflate with $\text{Os(CO)(CS)(PPh}_3\text{)}_3$ affords an oily solid which is difficult to handle. However, treatment of this oil with chloride ion gives a yellow crystalline solid which I.R. and elemental analysis determinations indicate is not the expected product $\text{OsClMe(CO)(CS)(PPh}_3\text{)}_2$, produced by methylation of the zerovalent complex followed by displacement of phosphine by chloride ion, i.e.

\[
\text{Os(CO)(CS)L}_3 \xrightarrow{\text{Me}^+} [\text{OsMe(CO)(CS)L}_3]^+ \xrightarrow{\text{Cl}^-} \text{OsClMe(CO)(CS)L}_2
\]

(L = PPh$_3$)

Instead, the product has been tentatively identified as the carbene-containing complex $\text{OsCl}_{2}[\eta^1-\text{C(SMe)Me}](\text{CO})(\text{PPh}_3)_2$ which could be obtained as follows -
EXPERIMENTAL

Aryl-Thiocarbonyl Complexes

OsClR(CS)(PPh₃)₂⁺

Chloro-p-tolylthiocabonylbis(triphenylphosphine)osmium(II).

OsHCl(CS)(PPh₃)₃·(CH₂Cl₂)₀.₅ (1.0 g) and di-p-tolylmercury(II)
(0.5 g) were heated under reflux in degassed toluene (40 ml) for
40 min. The red solution was passed through a celite pad and the solvent
volume was reduced to 10 ml. Addition of ethanol and further
reduction of the solvent volume gave crimson (near black) crystals
which were collected and washed with boiling ethanol. Recrystallisation
from dichloromethane-ethanol gave crimson-black crystals (0.78 g, 93.9%)
containing 0.33 mol dichloromethane of solvation. ¹H N.M.R. (CDCl₃)
shows δ, 4.73 [s, 0.67H, CH₂Cl₂]. M.p. 215-217°C. Anal. Found:
C, 58.37; H, 4.25; P, 6.90%. C₄₄H₃₇ClOsP₂S·(CH₂Cl₂)₀.₃₃ requires
C, 58.27; H, 4.16; P, 6.78%.

OsClPh(CS)(PPh₃)₂⁺

Chlorophenylthiocarbonylbis(triphenylphosphine)osmium(II).

OsHCl(CS)(PPh₃)₃·(CH₂Cl₂)₀.₅ (0.3 g) and triphenylphosphine
(0.35 g) were heated under reflux in benzene (40 ml). A boiling
solution of chlorophenylmercury(II) (0.18 g) in benzene (80 ml) was
added and the solution was heated further under reflux for 40 min.
The red solution was passed through a celite pad. Ethanol was added
and the benzene was removed to give a red-brick crystalline solid which
was washed with boiling ethanol. Recrystallisation from
dichloromethane-ethanol gave red-black crystals (0.15 g, 63.1%).

M.p. 213-214°C. Anal. Found: C, 58.72; H, 4.22; P, 7.22%.

C_{43} H_{35} ClOsP_{2} S requires C, 59.27; H, 4.04; P, 7.10%.

\[ \text{Os(} \eta^2 - S_2 \text{CNET}_2 \text{)R(CS)} \text{(PPh}_3 \text{)}_2 \].

**Dihapto-diethylidithiocarbamato-p-tolylthiocarbonylbis(triphenylphosphine)osmium(II).**

\[ \text{OsClR(CS)} \text{(PPh}_3 \text{)}_2 \cdot (\text{CH}_2 \text{Cl}_2)_{0.33} (0.15 \text{ g}) \] was stirred in dichloromethane (40 ml) and sodium diethylidithiocarbamate (0.2 g) in ethanol (10 ml) was added. After 20 min stirring the yellow solution was passed through a celite pad and upon reduction of the solvent volume yellow crystals deposited which were recrystallised from dichloromethane-ethanol (0.155 g, 94.6%). M.p. 221-224°C.

Anal. Found: C, 59.21; H, 5.06; N, 1.22%. \[ \text{C}_{49} \text{H}_{47} \text{NOsP}_{2} \text{S} \] requires C, 58.95; H, 4.75; N, 1.40%.

\[ \text{Os(} \eta^2 - \text{O}_2 \text{CCH}_3 \text{)R(CS)} \text{(PPh}_3 \text{)}_2 \].

**Dihapto-acetato-p-tolylthiocarbonylbis(triphenylphosphine)osmium(II).**

\[ \text{OsClR(CS)} \text{(PPh}_3 \text{)}_2 \cdot (\text{CH}_2 \text{Cl}_2)_{0.33} (0.15 \text{ g}) \] and sodium acetate (0.2 g) were treated as above to give yellow crystals of the hemidichloromethane solvate (0.15 g, 96%). \[ ^1 \text{H N.M.R. (CDCl}_3 \text{) shows} \]

\[ \tau, 4.73 [s, 1H, \text{CH}_2 \text{Cl}_2]. \] M.p. 212-214°C. Anal. Found: C, 58.54; H, 4.44; P, 6.41%. \[ \text{C}_{46} \text{H}_{40} \text{O}_2 \text{OsP}_{2} \text{S} \cdot (\text{CH}_2 \text{Cl}_2)_{0.5} \] requires C, 58.70; H, 4.34; P, 6.51%.
Os(\(\eta^2\text{-O}_2\text{CCF}_3\))R(CS)(PPh_3)_2.

*Dihapto-trifluoroacetato- p-tolylthiocarbonylbis(triphenylphosphine)-osmium(II).*

OsClR(CS)(PPh_3)_2\cdot(CH_2Cl_2)_{0.33} (0.15 g) and triethylammonium trifluoroacetate (ca. 0.2 g) were treated as above to give yellow crystals which were too insoluble for \(^1H\) N.M.R. measurements but which analysis indicates contain 0.33 mol dichloromethane of solvation (0.16 g, 98.3%). M.p. 210-215°C. Anal. Found: C, 56.01; H, 4.06; P, 6.49%. C\(_{46}\)H\(_{37}\)F\(_2\)O\(_2\)OsP\(_2\)S.(CH\(_2\)Cl\(_2\))\(_{0.33}\) requires C, 56.14; H, 3.83; P, 6.25%.

Os(\(\eta^2\text{-O}_2\text{CCF}_3\))\(_2\)(EtOH)(CS)(PPh_3)_2.

**Bis(monohapto-trifluoroacetato)ethanolthiocarbonylbis(triphenylphosphine)-osmium(II).**

OsClR(CS)(PPh_3)_2\cdot(CH_2Cl_2)_{0.33} (0.15 g) and trifluoroacetic acid (0.2 ml) were stirred in dichloromethane (30 ml) for 5 min. Ethanol was added and reduction of the solvent volume gave yellow crystals which were collected and recrystallised from dichloromethane-ethanol (0.16 g, 94.5%). M.p. 180-183°C. Anal. Found: C, 50.43; H, 3.92; P, 6.72%. C\(_{43}\)H\(_{36}\)F\(_2\)O\(_2\)OsP\(_2\)S requires C, 50.09; H, 3.52; P, 6.01%.

OsBrR(CS)(PPh_3)_2.

**Bromo-p-tolylthiocarbonylbis(triphenylphosphine)osmium(II).**

OsClR(CS)(PPh_3)_2\cdot(CH_2Cl_2)_{0.33} (0.15 g) was dissolved in dichloromethane (30 ml) and silver perchlorate (0.04 g, 1.18 eq.) in ethanol (10 ml) was added. The yellow solution was passed through a pad of
celite and sodium bromide (0.2 g) in ethanol-water (5 ml, 1:1) was rapidly added. The solvent volume was reduced to give crimson-black crystals which were redissolved in dichloromethane and passed down a florisil column using dichloromethane as eluent. The crimson band was collected, ethanol was added and reduction of the solvent volume gave crimson-black crystals (0.13 g, 85.2%). M.p. 210-214°C. Anal. Found: C, 56.69; H, 4.33; P, 6.43%.

\( \text{C}_{44}\text{H}_{37}\text{BrOsP}_{2}\text{S} \) requires C, 56.83; H, 4.01; P, 6.66%.

**OsIR(CS)(PPh}_3)_2**.

**Iodo-p-tolylthiocarbonylbis(triphenylphosphine)osmium(II).**

\[ \text{OsClR(CS)(PPh}_3)_2 \cdot \text{(CH}_2\text{Cl}_2)_{0.33} \] silver perchlorate (0.04 g, 1.18 eq) and sodium iodide (0.2 g) were treated as above to give crimson-black crystals (0.135 g, 84.2%). M.p. 217-219°C.

Anal. Found: C, 54.15; H, 4.06; P, 5.97%. \( \text{C}_{44}\text{H}_{37}\text{IOsP}_{2}\text{S} \) requires C, 54.10; H, 3.82; P, 6.34%.

**OsClR(MeCN)(CS)(PPh}_3)_2**.

**Chloro-p-tolylacetonitrilethiocarbonylbis(triphenylphosphine)osmium(II).**

\[ \text{OsClR(CS)(PPh}_3)_2 \cdot \text{(CH}_2\text{Cl}_2)_{0.33} \] (0.1 g) was dissolved in dichloromethane (20 ml) and acetonitrile (1 ml) was added. The solvent volume was reduced to 5 ml and ethanol was added to give white crystals containing 0.25 mol dichloromethane of solvation (0.104 g, 100%). \( ^1\text{H N.M.R. (CDCl}_3 \) shows \( \tau, 4.70 \) [s, 0.5H, CH\text{Cl}_2].

M.p. 161-163°C. Anal. Found: C, 58.73; H, 4.50; P, 7.43%.

\( \text{C}_{46}\text{H}_{40}\text{ClNOsP}_{2}\text{S.(CH}_2\text{Cl}_2)_{0.25} \) requires C, 58.61; H, 4.31; P, 6.54%. 
OsClR(CO)(CS)(PPh\textsubscript{3})\textsubscript{2}.

Chloro-p-tolylcarbonylthiocarbonylbis(triphenylphosphine)osmium(II).

OsClR(CO)(CS)(PPh\textsubscript{3})\textsubscript{2}.(CH\textsubscript{2}Cl\textsubscript{2})\textsubscript{0.33} (0.15 g) was stirred in the minimum quantity of dichloromethane to effect complete dissolution and the solution was cooled to 0°C. Carbon monoxide was passed through the solution for 10 s and hexane at 0°C was added. The solvent volume was reduced, without application of heat, to afford white crystals (0.15 g, 100%). M.p. 220-222°C (turns red 145-150°C). Anal. Found: C, 59.26; H, 4.38; P, 6.77%. C\textsubscript{45}H\textsubscript{37}ClO0S\textsubscript{2}P\textsubscript{2}S requires C, 59.16; H, 4.08; P, 6.78%.

OsBrR(CO)(CS)(PPh\textsubscript{3})\textsubscript{2}.

Bromo-p-tolylcarbonylthiocarbonylbis(triphenylphosphine)osmium(II).

OsBrR(CO)(CS)(PPh\textsubscript{3})\textsubscript{2} (0.15 g) was treated with carbon monoxide as above to afford white crystals (0.15 g, 97.1%). M.p. 139-144°C (turns red 135-140°C). Anal. Found: C, 56.78; H, 4.40; P, 6.65%. C\textsubscript{45}H\textsubscript{37}BrO0S\textsubscript{2}P\textsubscript{2}S requires C, 56.42; H, 3.89; P, 6.47%.

OsClR(CS)(CNR)(PPh\textsubscript{3})\textsubscript{2}.

Chloro-p-tolylthiocarbonyl-p-tolylisocyanidebis(triphenylphosphine)-osmium(II).

OsClR(CS)(PPh\textsubscript{3})\textsubscript{2}.(CH\textsubscript{2}Cl\textsubscript{2})\textsubscript{0.33} (0.3 g) was dissolved in dichloromethane (40 ml) and the solution was cooled to 10°C. A dichloromethane solution (10 ml) of p-tolylisocyanide (0.05 g, 1.3 eq.) was added followed by hexane (40 ml). Upon reduction of the solvent volume white crystals were deposited (0.33 g, 100%). Recrystallisation from dichloromethane-ethanol, without application of heat, gave white
crystals. M.p. 170-172°C (turns red above 140°C). Anal. Found: C, 62.61; H, 4.77; N, 1.19%. C_{52}H_{44}ClNOS_{2} requires C, 62.29; H, 4.42; N, 1.40%.

Monohapto-trifluoroacetato-p-tolyl-p-chlorophenylisocyanidethiocarbonylbis-(triphenylphosphine)osmium(II).

Os(η²-O₂CCF₃)R(CN-p-C₆H₄Cl)(CS)(PPh₃)₂ (0.15 g) and p-chlorophenylisocyanide were stirred in dichloromethane (30 ml) for 40 min. The solvent volume was reduced to 5 ml and ethanol was added to give a cream floccular solid (0.17 g, 99.2%). Recrystallisation from dichloromethane-ethanol gave large colourless crystals containing 0.25 mol dichloromethane of solvation. ¹H N.M.R. (CDCl₃) shows τ, 4.72 [s, 0.5H, CH₂Cl₂]. M.p. 177-179°C (turns red above 160°C). Anal. Found: C, 57.16; H, 4.28; N, 1.36%. C_{33}H_{41}ClF₃NO₂OsP₂S(CH₂Cl₂)0.25 requires C, 57.01; H, 3.73; N, 1.25%.

Bidentate Thioacetyl Complexes

OsCl(η²-CSR)(CO)(PPh₃)₂.

Chloro-dihapto-p-methylthiobenzoylcarbonylbis(triphenylphosphine)osmium(II).

OsClR(CO)(CS)(PPh₃)₂ (0.15 g) was dissolved in dichloromethane (30 ml) and the solution was heated under reflux for 5 min. Ethanol was added and reduction of the solvent volume gave scarlet crystals (0.15 g, 100%). M.p. 251-254°C. Anal. Found: C, 59.42; H, 4.72; P, 6.62%. C_{45}H_{37}ClOOS_{2}S requires C, 59.17; H, 4.08; P, 6.78%.
Bromo-dihapto-p-methylthiobenzoylcarbonylbis(triphenylphosphine)osmium(II).

OsBrR(CO)(CS)(PPh₃)₂ (0.15 g) was treated as above to give crimson crystals containing 0.125 mol dichloromethane of solvation (0.15 g, 98.9%). ¹H N.M.R. (CDCl₃) shows τ, 4.72 [s, 0.25H, CH₂Cl₂]. M.p. 260-263°C. Anal. Found: C, 55.66; H, 4.33; P, 6.12%.

₄₅C₁₇H₃₇BrO₂S₂(C₄H₂Cl₂)₀.₁₂₅ requires C, 55.96; H, 3.88; P, 6.40%.

OsI(n²-CSR)(CO)(PPh₃)₂.

Iodo-di hapto-p-methylthiobenzoylcarbonylbis(triphenylphosphine)osmium(II).

OsIR(CS)(PPh₃)₂ (0.15 g) was treated as above to give sienna crystals which were recrystallised from chloroform-ethanol to give a mixture of sienna platelets and burnt umber crystals (0.15 g, 100%). M.p. 253-255°C. Anal. Found: C, 53.81; H, 4.13; P, 5.99%.

₄₅C₁₇H₃₇IO₂S₂ requires C, 53.78; H, 3.71; P, 6.16%.

OsCl(n²-CSR)(CNR)(PPh₃)₂.

Chloro-di hapto-p-methylthiobenzoyl-p-tolylisocyanidebis(triphenylphosphine)osmium(II).

OsClR(CS)(CNR)(PPh₃)₂ (0.3 g) was heated under reflux in toluene (30 ml) for 20 min. Ethanol was added and reduction of the solvent volume gave red crystals which were recrystallised from dichloromethane-ethanol (0.3 g, 100%). M.p. 225°C. Anal. Found: C, 62.54; H, 4.77; N, 1.29%. C₅₂H₄₄ClNO₂S₂ requires C, 62.29; H, 4.42; N, 1.40%.
Os\((\eta^1-O_2CCF_3)(\eta^2-CSR)(CN-p-C_6H_4Cl)(PPh_3)_2\).

**Monohapto-trifluoroacetato-dihapto-p-methylthiobenzoyl-p-chlorophenylisocyanidebis(triphenylphosphine)osmium(II).**

Os\((\eta^1-O_2CCF_3)R(CN-p-C_6H_4Cl)(CS)(PPh_3)_2(CH_2Cl_2)_{0.25}(0.15\ g)\)
was heated under reflux in toluene (25 ml) for 3 h. Ethanol was
added and reduction of the solvent volume gave maroon crystals
which were recrystallised from dichloromethane-ethanol to give
large maroon crystals (0.147 g, 100%). M.p. 208-212°C. Anal.
Found: C, 58.40; H, 4.35; N, 1.50%. C\(_{53}^{\ H_{41}}\)Cl\(_3\)NO\(_2\)OsP\(_2\)S requires
C, 57.84; H, 3.76; N, 1.27%.

OsCl\((\eta^2-CSPh)(CO)(PPh_3)_2\).

**Chloro-dihapto-thiobenzoylcarbonylbis(triphenylphosphine)osmium(II).**

OsClPh(CS)(PPh\(_3\)_2 (0.15 g) was dissolved in dichloromethane
(30 ml) and carbon monoxide was passed through the solution for
several seconds. The solution was heated under reflux for 5 min
and ethanol was added. Reduction of the solvent volume gave red
crystals (0.14 g, 93.3%) which have been characterised by the I.R.
spectrum.

Os\((\eta^2-S_2CNET_2)(\eta^2-CSR)(CO)(PPh_3)_2\).

**Dihapto-diethylidithiocarbamato-dihapto-p-methylthiobenzoylcarbonyl-
triphenylphosphineosmium(II).**

OsCl\((\eta^2-CSR)(CO)(PPh_3)_2 (0.15 g) and sodium diethylidithiocarbamate
(0.1 g) were heated under reflux in xylene (20 ml) and 2-methoxyethanol
(20 ml) for 15 h. Upon reduction of the solvent volume crimson
crystals deposited which were recrystallised from dichloromethane-
ethanol to give burgundy platelets (0.115 g, 91.7%). M.p. 235-240°C. Anal. Found: C, 50.81; H, 4.94; N, 1.69%.

C₃₂H₃₂NOOS₃ requires C, 50.31; H, 4.22; N, 1.83%.

\[
\text{[OsCl(}\eta^2-\text{C(SMe)}\text{)}\text{R}(\text{CN})\text{(PPh}_3\text{)}\text{)}_2\text{ClO}_4\text{].}
\]

Chloro-dihapto-C₅S-methylthiolato-p-tolylcarbene-p-tolylisocyanide-bis(triphenylphosphine)osmium(II) perchlorate.

OsCl(\eta^2-CSR)(CN)(PPh₃)₂ (0.3 g) was stirred in dry benzene with methyl triflate (0.2 ml) for 3 h. The lime green needles were collected and recrystallised from dichloromethane (20 ml) and ethanol (20 ml) containing sodium perchlorate (0.2 g) to give lime green crystals (0.17 g, 50.9%). M.p. 134-136°C. Anal. Found: C, 56.60; H, 4.47; N, 1.12%. C₅₃H₄₇Cl₂NO₄OsP₂S requires C, 56.98; H, 4.24; N, 1.25%.

OsCl₂[\eta¹-C(SMe)R(CNR)(PPh₃)]₂.

Dichloro-monohapto-methylthiolato-p-tolylcarbene-p-tolylisocyanide-bis(triphenylphosphine)osmium(II).

[OsCl(\eta²-C(SMe)R)(CN)(PPh₃)]₂ClO₄ (0.1 g) and lithium chloride (0.1 g) were heated under reflux in ethanol (10 ml) for 10 min. The red crystals were recrystallised from dichloromethane-ethanol to give red crystals (0.09 g, 95.5%). M.p. 158-161°C. Anal. Found: C, 60.41; H, 5.31; N, 1.20%. C₅₃H₄₇Cl₂NO₄S requires C, 60.45; H, 4.50; N, 1.33%.
OsCl₂ [η¹-C(SMe)Me] (CO)(PPh₃)₂²⁺

Dichloro-monohapto-methylmethylthiolatocarbene-carbonybis(triphenylphosphine)osmium(II).

Os(CO)(CS)(PPh₃)₃ (0.3 g) was stirred in a solution of methyl triflate (0.2 ml) in dry benzene (20 ml) for 5 min. Hexane was added and the solvent was decanted from the brown oil which was heated under reflux in ethanol (20 ml) with lithium chloride (0.2 g). The yellow crystals were collected and recrystallised from dichloromethane-ethanol (0.21 g, 82.7%). M.p. 198-200°C.

Anal. Found: C, 53.92; H, 4.57; P, 7.40%. C₄₀H₃₆Cl₂O₀S₂P₂S requires C, 54.11; H, 4.09; P, 6.98%.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{\text{CS}}$</th>
<th>$\nu_{\text{CO}}$</th>
<th>$\nu_{\text{CN}}$</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsCl$_2$(CS)$_2$</td>
<td>1290</td>
<td></td>
<td></td>
<td>1190, 1051, 1012, 800 (sh) (toly1)</td>
</tr>
<tr>
<td>OsCl$_2$(CS)$_2$</td>
<td>1288</td>
<td>1490</td>
<td></td>
<td>1565, 1075, 1021 (phenyl)</td>
</tr>
<tr>
<td>Os(η$^2$-S$_2$CNEt$_2$)R(CS)$_2$</td>
<td>1270$^b$</td>
<td></td>
<td></td>
<td>1048, 1015, 790, 1355, 1216, 1146, 920, 850</td>
</tr>
<tr>
<td>Os(η$^2$-O$_2$CMe)R(CS)$_2$</td>
<td>1282</td>
<td></td>
<td></td>
<td>1520, 1463 ($\nu_{\text{CO}_2}$), 1052, 1015, 802 (toly1), 950</td>
</tr>
<tr>
<td>Os(η$^2$-O$_2$CCF$_3$)R(CS)$_2$</td>
<td>1290</td>
<td></td>
<td></td>
<td>1603, 130, 1162, 870, 791, 737 (CF$_3$CO$_2$), 1255, 1215, 804 (toly1)</td>
</tr>
<tr>
<td>Os(η$^1$-O$_2$CCF$_3$)$_2$(EtOH)(CS)$_2$</td>
<td>1303$^d$</td>
<td></td>
<td></td>
<td>3560, 1600 (br) ($\delta_{\text{OH}}$), 1665 (br) ($\nu_{\text{C=O}}$), 1199, 1150, 877, 785, 730 (CF$_3$CO$_2$)</td>
</tr>
<tr>
<td>OsBrR(CS)$_2$</td>
<td>1285</td>
<td></td>
<td></td>
<td>1188, 1050, 1011, 799 (toly1)</td>
</tr>
<tr>
<td>OsIR(CS)$_2$</td>
<td>1281</td>
<td></td>
<td></td>
<td>1188, 1052, 1010, 798 (toly1)</td>
</tr>
<tr>
<td>OsClR(MeCN)(CS)$_2$</td>
<td>1282</td>
<td></td>
<td></td>
<td>1190, 1058, 1020, 812 (toly1)</td>
</tr>
<tr>
<td>OsClR(CO)(CS)$_2$</td>
<td>1300</td>
<td>2055</td>
<td></td>
<td>1175, 1015, 835, 802 (toly1)</td>
</tr>
<tr>
<td>OsBrR(CO)(CS)$_2$</td>
<td>1292</td>
<td>2030</td>
<td></td>
<td>1190, 1015, 805 (toly1)</td>
</tr>
<tr>
<td>OsClR(CS)(CNR)$_2$</td>
<td>1290</td>
<td>2142</td>
<td></td>
<td>1688, 1312, 1195, 1141, 790, 727 (CF$_3$CO$_2$), 1017 (toly1), 832, 805 (toly1)</td>
</tr>
<tr>
<td>Os(η$^1$-O$_2$CCF$_3$)R(CN-p-C$_6$H$_4$I)(CS)$_2$</td>
<td>1291</td>
<td>2130</td>
<td></td>
<td>1600, 1315, 1300, 1293, 1178, 975, 830, 818, 789 (sh), 635 (CSR)</td>
</tr>
<tr>
<td>OsCl(η$^3$-CSR)(CO)L$_2$</td>
<td>1902</td>
<td></td>
<td></td>
<td>1599, 1310, 1300, 1287, 1175, 972, 830, 815, 789, 635 (CSR)</td>
</tr>
<tr>
<td>OsBr(η$^3$-CSR)(CO)L$_2$</td>
<td>1897</td>
<td></td>
<td></td>
<td>1599, 1311, 1300, 1285, 1175, 972, 838, 830, 818, 789, 633 (CSR)</td>
</tr>
<tr>
<td>OsI(η$^3$-CSR)(CO)L$_2$</td>
<td>1897</td>
<td></td>
<td></td>
<td>1600, 1308, 1295, 1172 (sh), 972, 789 (sh), 635 (sh)</td>
</tr>
<tr>
<td>OsCl(η$^3$-CSR)(CNR)L$_2$</td>
<td>1940$^G$, 1870 vs$^G$</td>
<td></td>
<td></td>
<td>1600, 1308, 1295, 1172 (sh), 972, 789 (sh), 635 (sh)</td>
</tr>
</tbody>
</table>

---

$^a$ wavenumbers in cm$^{-1}$.

$^b$ Refs. 27, 29 and 31.

$^c$ Refs. 25, 26 and 28.

$^d$ Refs. 24, 26 and 29.

$^e$ Refs. 24 and 26.

$^f$ Refs. 24 and 26.

$^g$ Ref. 27.
Table 6.1  (cont.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν&lt;sub&gt;CS&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ν&lt;sub&gt;CO&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ν&lt;sub&gt;CN&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Other Bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os(η¹-O₂CCF₃)(η²-CSR)(CN-p-C₆H₄Cl)₂</td>
<td>1950&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1890&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1705wm; 1684vs (ν&lt;sub&gt;C=O&lt;/sub&gt;); 1599wm, 1310wm, 1302m (sh), 1293s, 1172s (sh), 1012w (sh), 980w, 790s (sh), 635w (sh); 1196vs, 1132s, 737s (sh) (CF₃CO₂); 1412s (C₆H₄Cl); 844s&lt;sup&gt;3&lt;/sup&gt; 823s&lt;sup&gt;3&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>OsCl(η²-CSPh)(CO)₂&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1915&lt;sup&gt;c&lt;/sup&gt; 1895&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1499s&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1312w, 1295s, 1172w, 972w, 829s, 771w, 655w (sh) (CSPh)</td>
<td></td>
</tr>
<tr>
<td>Os(η²-S₂CNEt₂)(η²-CSR)(CO)L</td>
<td>1893</td>
<td></td>
<td>1599m, 1310s, 1302s, 1172s (sh), 975w, 832s, 821m, 788m, 635w (sh) (CSR); 1360w, 1275s, 1211wm, 1147w, 911w</td>
<td></td>
</tr>
<tr>
<td>[OsCl(η²-C[SMe]R)(CNR)L₂]ClO₄</td>
<td>2100&lt;sup&gt;k&lt;/sup&gt;, 2060s&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td>1599m, 1327m, 1190w, 1298w, 1182w, 820wm&lt;sup&gt;ε&lt;/sup&gt; (C[SMe]R); 1093vs, 625m (ClO₄)</td>
<td></td>
</tr>
<tr>
<td>OsCl₂(η²-C[SMe]R)(CNR)L₂</td>
<td>2095&lt;sup&gt;k&lt;/sup&gt;, 2060&lt;sup&gt;k&lt;/sup&gt;</td>
<td></td>
<td>1603w, 1190w, 890w, 865m, 845w (C[SMe]R); 820m, 809s&lt;sup&gt;ε&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

Footnotes:  (L = PPh₃;  R = p-toly1)  
(a) very strong band  
(b) band also incorporates S₂CNEt₂ vibration near 1270w-m;  
(c) compound characterised by I.R. spectrum only;  
(d) band also incorporates CF₃CO₂ band near 1300m;  
(e) band overlaps phosphine associated band at 1190w;  
(f) band due to both tolyl groups;  
(g) very broad band;  
(h) band could derive from a CF₃CO₂ vibration;  
(i) band includes CSR and CF₃CO₂ vibrations;  
(j) band due to C₆H₄Cl and tolyl groups;  
(k) same two bands observed in spectrum obtained in CH₂Cl₂;  
(l) solid state splitting gives multiple bands.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (τ) and Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OsClR(CS)L₂</td>
<td>7.83, s, 3H, C₆H₄⁻CH₃</td>
</tr>
<tr>
<td></td>
<td>3.72, s, ⁴H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.58, m, 3OH, Ph</td>
</tr>
<tr>
<td>OsClPh(CS)L₂</td>
<td>3.53, s, ⁴H, Os-C₆H₅</td>
</tr>
<tr>
<td></td>
<td>2.55, m, 3OH, Ph</td>
</tr>
<tr>
<td>Os(n²-S₂CNET₂)R(CS)L₂</td>
<td>9.36, t, 3H, NCH₂⁻CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>9.15, t, 3H, NCH₂⁻CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>7.90, s, 3H, C₆H₄⁻CH₃</td>
</tr>
<tr>
<td></td>
<td>7.26, q, 2H, N-CH₂⁻CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>6.88, q, 2H, N-CH₂⁻CH₃, J(HH) = 7.2</td>
</tr>
<tr>
<td></td>
<td>3.43, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.62, m, 3OH, Ph</td>
</tr>
<tr>
<td>Os(n²-O₂CMe)R(CS)L₂</td>
<td>9.40, s, 3H, O₂CCH₃</td>
</tr>
<tr>
<td></td>
<td>7.94, s, 3H, C₆H₄⁻CH₃</td>
</tr>
<tr>
<td></td>
<td>3.43, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.62, m, 3OH, Ph</td>
</tr>
<tr>
<td>Os(n²-O₂CCF₃)R(CS)L₂</td>
<td>b</td>
</tr>
<tr>
<td>Os(n¹-O₂CCF₃)₂(ETOH)(CS)L₂</td>
<td>9.92, t, ⁴H, HOCH₂⁻CH₃, J(HH) = 5.5</td>
</tr>
<tr>
<td></td>
<td>6.50, s, ²H, HO-CH₂⁻CH₃</td>
</tr>
<tr>
<td></td>
<td>2.41, m, 33H, Ph</td>
</tr>
<tr>
<td>OsBrR(CS)L₂</td>
<td>7.83, s, 3H, C₆H₄⁻CH₃</td>
</tr>
<tr>
<td></td>
<td>3.80, q, 4H, -C₆H₄⁻</td>
</tr>
<tr>
<td></td>
<td>2.55, m, 3OH, Ph</td>
</tr>
<tr>
<td>OsIR(CS)L₂</td>
<td>b</td>
</tr>
<tr>
<td>Compound</td>
<td>Chemical Shift ((\tau)) and Coupling Constants (Hz)</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>OsClR(MeCN)(CS)L₂</td>
<td>8.37, s, 3H, NC-CH₃</td>
</tr>
<tr>
<td></td>
<td>7.78, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.36, q, 4H, -C₆H₄-</td>
</tr>
<tr>
<td></td>
<td>2.60, m, 30H, Ph</td>
</tr>
<tr>
<td>OsClR(CO)(CS)L₂</td>
<td>e</td>
</tr>
<tr>
<td>OsBrR(CO)(CS)L₂</td>
<td>e</td>
</tr>
<tr>
<td>OsClR(CS)(CNR)L₂</td>
<td>7.77, s, 3H</td>
</tr>
<tr>
<td></td>
<td>{ C₆H₄-CH₃ }</td>
</tr>
<tr>
<td></td>
<td>7.70, s, 3H</td>
</tr>
<tr>
<td></td>
<td>3.49, m, 8H, -C₆H₄-</td>
</tr>
<tr>
<td></td>
<td>2.65, m, 30H, Ph</td>
</tr>
<tr>
<td>Os((\eta^1)-O₂,CCF₃)R(CN-p-C₆H₄Cl)(CS)L₂</td>
<td>7.80, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.00, 38H, -C₆H₄- + Ph</td>
</tr>
<tr>
<td>OsCl((\eta^2)-CSR)(CO)L₂</td>
<td>7.90, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.17, q, 4H, -C₆H₄-</td>
</tr>
<tr>
<td></td>
<td>2.60, m, 31H, Ph</td>
</tr>
<tr>
<td>OsBr((\eta^2)-CSR)(CO)L₂</td>
<td>7.87, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.14, q, 4H, -C₆H₄-</td>
</tr>
<tr>
<td></td>
<td>2.57, m, 30H, Ph</td>
</tr>
<tr>
<td>OsI((\eta^2)-CSR)(CO)L₂</td>
<td>7.90, s, 3H, C₆H₄-CH₃</td>
</tr>
<tr>
<td></td>
<td>3.08, q, 4H, -C₆H₄-</td>
</tr>
<tr>
<td></td>
<td>2.60, m, 30H, Ph</td>
</tr>
<tr>
<td>OsCl((\eta^2)-CSR)(CNR)L₂</td>
<td>7.95, s, 3H</td>
</tr>
<tr>
<td></td>
<td>{ C₆H₄-CH₃ }</td>
</tr>
<tr>
<td></td>
<td>7.72, s, 3H</td>
</tr>
<tr>
<td></td>
<td>3.02, m, 39H, -C₆H₄- + Ph</td>
</tr>
<tr>
<td>Compound</td>
<td>Chemical Shift (τ) and Coupling Constants (Hz)</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------------------</td>
</tr>
</tbody>
</table>
| Os($^{1-2}$-CCF$_3$)($^{2}$-CSR)($^{2}$-CSR)($^{2}$-CSR)($^{2}$-CSR)Cl$_2$ | 7.85, s, 3H, C$_6$H$_4$-CH$_3$
3.10, m, 40H, -C$_6$H$_4$- + Ph |
| Os($^{2}$-S$_2$CNET$_2$)($^{2}$-CSR)($^{2}$-CSR)(CO)L | 8.76, t, 3H, NCH$_2$-CH$_3$, J(HH) = 7.3
8.67, t, 3H, NCH$_2$-CH$_3$, J(HH) = 7.3
7.73, s, 3H, C$_6$H$_4$-CH$_3$
6.33, m, 4H, N-CH$_2$-CH$_3$
2.55, m, 18H, Ph |
| [Os($^{2}$-C([SMe]R)Cl(CNR)L$_2$]ClO$_4$ | 8.20, s, 3H, S-CH$_3$
7.88, s, 3H
7.64, s, 3H
3.15, m, 39H, -C$_6$H$_4$- + Ph |
| OsCl$_2$[$^{1}$-C(SMe)R](CNR)L$_2$ | 8.64, s, 3H, S-CH$_3$
7.67, s, 6H, C$_6$H$_4$-CH$_3$
3.84, m, 8H, -C$_6$H$_4$-
2.52, m, 32H, Ph |
| OsCl$_2$[$^{1}$-C(SMe)Me](CO)L$_2$ | b |

Footnotes: (L = PPh$_3$; R = p-tolyl) (a) singlet resonance remains unchanged at -90°C;
(b) too insoluble for $^1$H N.M.R.;
(c) very broad resonance;
(d) very broad resonance, no coupling observed;
(e) migration reaction too fast at 40°C to allow for $^1$H N.M.R. [section 6.2].
REFERENCES


11. continued

G.R. Bird, Phys.Rev., 1955, 98, 1837; S. Gustafson and


1967, 2037.


1968, 2198.


17. M. Baird, G. Hartwell, Jr., R. Mason, A.I.M. Rae and
G. Wilkinson, Chem.Comm., 1967, 92; R. Mason and A.I.M. Rae,

18. G.R. Clark, T.J. Collins, S.M. James, W.R. Roper and K.G. Town,


1977, 133, 93.

491.

23. T.A. Stephenson and E.S. Switkes, Inorg.Nuclear Chem.Letters,


73, C33.


38. (a) G. Jaouen, Tetrahedron Letters, 1973, 5159;


(b) J.S. Field and P.J. Wheatley, J.C.S.Dalton, 1972, 2269.


114. R.O. Harris and W.R. Roper, personal communication.


(b) J.P. Collman, Accounts Chem.Res., 1968, 1, 136;
(c) R. Ugo, Co-ordination Chem.Rev., 1968, 3, 319;
    (b) M.C. Baird, J.Organometallic Chem., 1974, 64, 289.


149. I.S. Kolomnikov, T.S. Lobekva and M.E. Vol'pin, Izvest.

150. Y. Inoue, Y. Sasaki and H. Hashimoto, J.C.S.Chem.Comm., 1975,
    718.

151. Y. Inoue, H. Izumida, Y. Sasaki and H. Hashimoto, Chem.Letters,
    1976, 863.

152.(a)M.A. Vannice, Catalysis Rev., 1976, 14, 153;
    (b)H. Storch, N. Columbic and R. Anderson, "The Fischer-Tropsch
    and Related Syntheses", Wiley, New York, 1951;
    (c)Y.T. Eidus, Russ.Chem.Rev., 1967, 36, 338;

    1976, 15, 136.


    1976, 98, 1296.

    99, 2796.


159. J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw,

160. J.C. Huffman, J.G. Stone, W.C. Krussel and K.G. Caulton,

162. (a) E.L. Muettterties, Science, 1977, 196, 839;  
    (b) A.L. Robinson, Science, 1976, 194, 1150.  
164. (a) H. Kölbel and D. Hanus, Chem.-Ing.-Tech., 1974, 46, 1042,  
    and references therein;  
    (b) A. Deluzarche, R. Kieffer and A. Muth, Tetrahedron Letters,  
        1977, 3357;  
    (c) A. Deluzarche, J.P. Hindermann, R. Kieffer, A. Muth,  
        M. Papadopoulos and C. Tanielian, Tetrahedron Letters,  
        1977, 797;  
    (d) H. Kölbel and H. Roberg, Ber.Bunsengesellschaft Phys.Chem.,  
        1977, 81, 634, and references therein.  
166. (a) J.P. Collman and S.R. Winter, J.Amer.Chem.Soc., 1973, 95,  
    4089;  
    (b) C.P. Casey and S.M. Neumann, J.Amer.Chem.Soc., 1976, 98,  
        5395;  
    (c) S.R. Winter, G.W. Cornett and E.A. Thompson, J.Organometallic  
168. W. Van Der Veer and F. Jellinek, Rec.Trav.chim., 1966, 85,  
    842.  
    1965, 7, 115.  
171. A.P. Ginsberg, Transition Metal Chem., 1965, 1, 111.  
172. N. Ahmad, S.D. Robinson and M.F. Uttley, J.C.S.Dalton,  
    1972, 843.


   (b) E.O. Fischer, Pure Appl.Chem., 1970, 24, 407;
   (c) C.G. Kreiter and E.O. Fischer, Boston I.U.P.A.C. 1971, Butterworths, Vol.6, p. 151;
   (d) E.O. Fischer, Pure Appl.Chem., 1972, 30, 353;


(b) A. Berry and T.L. Brown, *J.Organometallic Chem.*, 1971, 33, C67;


ACKNOWLEDGEMENTS

I have enjoyed being a research student in the Chemistry Department of the University of Auckland. It was my extreme good fortune that I was given the opportunity to mix and work with my colleagues and friends in the Chemistry Department and I am pleased that an opportunity such as this exists to say thank you.

To Warren Roper, who has supervised this work, I owe very special thanks. Thank you Warren for your continuing encouragement, for your enthusiastic, intelligent guidance, and for leading me into this area of chemistry, which I have found so rewarding.

To Christine Headford and James Wright, thank you for your generosity in spending so many hours proof-reading this thesis.

And further to Christine (who kicks like a mule), James (the group gourmet), Keith Town (may his shroud be of brown corduroy), Simon Hoskins and Robin Ramage, tea and coffee drinkers, plaque printers and interior decorators extraordinaire - thank you for the many happy times.

To Al Walker and his family of Canada and Kevin Grundy for their friendship, and to Al Aspell for his friendship (and for the discussions?, debates?, and occasional agreements?) thanks.

Thank you George Clark, Sue Boniface and Joyce Waters for sharing in this work and for permission to reprint the structural diagrams. I also wish to thank the technical and academic staff for their contribution and aid to my learning and the University Grants Committee for granting me financial support.
Most especially, thank you to my wife, Maureen.

And, as you type this final line, thank you Dorothy Chaffe for the excellent job you have done typing this thesis.