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THIOCARBONYL COMPLEXES OF
RUTHENIUM AND OSMIUM

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ABSTRACT

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 $[\text{Os}-\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{S} \end{array}]$ results from the transfer of one hydrido ligand to CS and subsequent reactions, which are also probably hydride transfers, produce the thioformaldehyde

$[\text{Os} \begin{array}{l} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{S} \end{array}]$ and methylthiolato $[\text{Os}-\text{SCH}_3]$ 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 $[\text{Os}-\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{NMe} \end{array}]$ and $[\text{Os}-\text{C} \begin{array}{l} \text{H} \\ \diagup \\ \text{O} \end{array}]$ is demonstrated.

The review in chapter 1 also recounts how observation has shown that strong σ -donor and strong π -acceptor properties of the CS ligand exert a profound effect upon the reactivity of CS complexes. In particular, strong π -acceptor properties mark the CS ligand as an ideal candidate for stabilising very electron-rich metal centres

such as d^8 ruthenium(O) or osmium(O). 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 $[\text{Os} \begin{array}{c} \text{C-R} \\ \diagup \quad \diagdown \\ \text{S} \end{array}]$ 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

	Page
<u>ABSTRACT</u>	i
List of Tables	viii
List of Important Figures	ix
List of Abbreviations	x
<u>CHAPTER 1: INTRODUCTION</u>	
<u>THIOCARBONYL AND SELENOCARBONYL COMPLEXES OF TRANSITION METALS</u>	1
(I) SYNTHESIS:	1
(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:	21
(i) X-Ray Crystallography;	22
(ii) Infrared and Raman Spectroscopy;	26
(iii) Theoretical Studies and Photoelectron Spectroscopy;	33
(iv) ^{13}C N.M.R. Spectroscopy;	35 ⁶
(v) Mass Spectrometry;	36 ⁷
(vi) Mössbauer Spectroscopy.	39
(III) CHEMICAL REACTIVITY	40
A. Reactions at the Metal Centre.	40
(i) Substitution Reactions;	40
(ii) Oxidative Addition and Redox Reactions.	53

B, Ligand Reactions.	57
(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
<u>CHAPTER 2</u>	
<u>THIOCARBONYL COMPLEXES FROM CARBON DISULPHIDE ADDUCTS</u>	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
<u>CHAPTER 3</u>	
<u>REDUCTION OF THE THIOCARBONYL LIGAND</u>	116
3.1 $\text{OsCl}_2(\text{CS})(\text{PPh}_3)_3$;	120
3.2 Hydrido-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	141
<u>CHAPTER 4</u>	
<u>ZEROVALENT THIOCARBONYL COMPLEXES OF OSMIUM</u>	168
4.1 Synthesis and Reactions of Zerovalent Complexes;	169
4.2 Synthesis of Dithiocarbonyl Complexes.	174
EXPERIMENTAL	179

<u>CHAPTER 5</u>	
<u>NUCLEOPHILIC ATTACK AT THE THIOCARBONYL LIGAND</u>	194
EXPERIMENTAL	200
<u>CHAPTER 6</u>	
<u>ARYL-THIOCARBONYL COMPLEXES AND REARRANGEMENT REACTIONS</u>	211
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

	Page
<u>CHAPTER 1</u>	
1. Representations of CS and CSe Complex Structures	25
2. I.R. Data for CSe Complexes and CS Analogues.	312
3. ^{13}C N.M.R. Data for Thiocarbonyl Complexes	38
<u>CHAPTER 2</u>	
2.1 I.R. Data for Thiocarbonyl Complexes	110
2.2 I.R. Data for Thioester and Related Complexes	111
2.3 I.R. Data for Other Complexes	112
2.4 ^1H N.M.R. Data	113
<u>CHAPTER 3</u>	
3.1 I.R. Data for Hydrido-Thiocarbonyl Complexes	160
3.2 ^1H N.M.R. Data for Hydrido-Thiocarbonyl Complexes	161
3.3 I.R. Data for Thioformyl and Derived Complexes	163
3.4 ^1H N.M.R. Data for Thioformyl and Derived Complexes	165
3.5 I.R. and ^1H N.M.R. Data for Related Adducts of $\text{Os}(\text{CO})_2(\text{PPh}_3)_2$	141
<u>CHAPTER 4</u>	
4.1 I.R. Data for Thiocarbonyl Complexes	191
4.2 ^1H N.M.R. Data for Thiocarbonyl Complexes	192
<u>CHAPTER 5</u>	
5.1 I.R. Data for New Complexes	207
5.2 ^1H N.M.R. Data for New Complexes	208
<u>CHAPTER 6</u>	
6.1 I.R. Data for New Compounds	232
6.2 ^1H N.M.R. Data for New Complexes	234

LIST OF IMPORTANT FIGURES

	Page
<u>CHAPTER 2</u>	
2.2 Structure of $[\text{Ru}(\eta^2\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2]^+$.	80
2.3 (a) The Inner Coordination Sphere of $\text{OsH}(\eta^1\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2$ with some distances presented.	86
(b) A stereoview of $\text{OsH}(\eta^1\text{-CS}_2\text{Me})(\text{CO})_2(\text{PPh}_3)_2$.	86
2.5 Structure of $[\text{RuH}(\text{H}_2\text{O})(\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4$.	91
<u>CHAPTER 5</u>	
5.1 Structure of $\text{Os}(\eta^1\text{-CS}_2\text{CNMeR})\text{H}(\text{CO})(\text{PPh}_3)_2$.	198
<u>CHAPTER 6</u>	
6.1 Preliminary Results of X-Ray Crystal Structure Analysis of $\text{OsBr}(\eta^2\text{-CSR})(\text{CO})(\text{PPh}_3)_2$.	217

LIST OF ABBREVIATIONS

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