UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

STRUCTURE AND REACTIVITY OF THIOCARBONYL COMPLEXES

A thesis submitted by

RAINER RALF PILLE

in partial fulfilment of the
requirements for the degree of

MASTER OF SCIENCE

in inorganic chemistry

in the faculty of
Science and Mathematics
of the

UNIVERSITY OF PRETORIA

PRETORIA

December 1985

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

ACKNOWLEDGEMENTS

My sincerest gratitude to Professor dr S Lotz for his enthusiasm, encouragement and constant assistance.

I gratefully thank Mr E Palmer for determining PMR spectra; Dr P H van Rooyen for the X-ray structure determination, Mr R Muir for much needed glassware and Miss E Albertse for typing the manuscript.

Finally I would like to thank my colleagues including my "organic" colleagues for contributing to the pleasant laboratory and social conditions and family and friends for their encouragement and support.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

SUMMARY

This study was undertaken to investigate the synthesis, reactivity and structural aspects of new chromium(0) thiocarbonyl complexes.

The preparation of π-arene thiocarbonyl chromium(0) complexes and the subsequent synthesis and X-ray structure analysis of the end-to-end bridged $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ complex is discussed.

Furthermore the reactivity of π-arene thiocarbonyl chromium(0) and pentacarbonyl thiocarbonyl chromium(0) with regard to substitution reactions, and modifaction of the thiocarbonyl ligand was investigated.

OPSOMMING

Hierdie studie behels die bereiding, reaktiwiteit en strukturele aspekte van nuwe chroom(0) tiokarboniel komplekse.

Die bereiding van π-areen tiokarboniel chroom(0) komplekse en die daaropvolgende sintese en X-straal struktuurbepaling van die gebrugde $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ kompleks, word bespreek.

Verder is die reaktiwiteit van π-areen tiokarboniel chroom(0) en pentakarboniel tiokarboniel chroom(0) met betrekking tot substitusie reaksies, en tiokarboniel modifisering bestudeer.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CONTENTS

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

INTRODUCTION

The discovery of a metal carbon bond in 1827 by the Danish chemist Zeiss[1] in the compound $K[Pt(C_2H_4)Cl_3]$ and the isolation of the first carbonyl complex, $[Pt(CO)Cl_2]_2$, in 1868 by Schutzenberger[2] could be considered to be the birth of organometallic chemistry. At that stage the coordination and the bonding properties of the organic ligand to the central inorganic nucleus was not understood.

In 1951 Orgel, Pauling and Zeiss[3] postulated π-backbonding from transition metals to the carbonyl ligand and this led to some understanding of the nature of the metal-carbon interaction and prompted widespread interest in this field.

The growth and nature of organometallic chemistry led to some specialized techniques i.e. the use of an inert atmosphere to prevent oxidation of the central metal atom which is normally in a low oxidation state. Ligand modifications and manipulations sometimes require low temperatures (up to -100°C), and a lot of patience.

Since the end of the nineteenth century, carbon monoxide has been known to bond to transition metals in low oxidation states to form metal carbonyls[4]. Other Group VI A carbonyls, namely CS and CSe have only been extensively investigated over the past 15 years. This late development can be ascribed to the instability and greater reactivity of CS and CSe compared to the stable CO. Metal complexes containing molecules that are unstable in the free state, such as CX, CH_2X, CH_2CX and CH_3CHX (X=S,Se,Te) can now be investigated owing to the stabilizing effect on coordination to a transition metal[5].

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

From the time that the first thiocarbonyl complexes, namely trans-$RhX(CS)(PPh_3)_2$ X = Cl,Br were synthesized by Baird and Wilkinson[6] in 1966, it has become evident that CS can be stabilized by coordination to many transition metals. Since then well over a hundred metal thiocarbonyl complexes have been synthesized using mainly carbon disulphide as a source of CS.

Structural studies of metal carbonyls and thiocarbonyls rely mainly on Infrared spectroscopy, and NMR studies are essential for the characterization of organic ligands. The use of advanced computer programmes for X-ray diffraction can determine useful information regarding structures, ligand and bonding properties, ring conformation and inter- and intramolecular interaction.

It has been found that many metal carbonyls can be used in organic syntheses as homogenous catalysts in industrial processes[7] and it is anticipated that similar uses may be found in metal-, thio- and selenocarbonyls. Several arene chromium thiocarbonyl derivatives have shown selective homogenous catalytic activity for the isomerization of dienes[8].

Current interest in the field of thiocarbonyls and the possibility that metal thiocarbonyls may be stepping stones to simple thicketones, thioketenes and thioaldehydes led to this study.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CHAPTER 1

SYNTHESIS AND REACTIVITY OF Π-ARENE THIOCARBONYL COMPLEXES OF CHROMIUM(0)

Introduction

Sections 1.1 to 1.4 deal mainly with the known literature methods, the reactivity and the effect of ligands on the complexes. In order to prepare the thiocarbonyl complexes it was necessary to obtain the precursors, namely the tricarbonyl complexes and the experimental details are discussed in section 1.6.

1.1 Synthesis of π-arene chromium(0) tricarbonyl complexes

This study deals with π-arene chromium(0) thiocarbonyl complexes and it is therefore appropriate to look at the interactions between Group VI metals and ligands. The precursor of π-arene chromium(0) thiocarbonyl complexes are the corresponding π-arene chromium(0) tricarbonyl complexes. The π-arene chromium(0) tricarbonyl complexes were prepared by the thermal displacement of CO from chromium(0) hexacarbonyl[9]. This formation is indicated in equation 1.

$$Cr(CO)_6 + ArH \xrightarrow{reflux} (\pi\text{-}ArH)Cr(CO)_3 + 3CO \quad (1)$$

Further displacement of CO from a $(\pi\text{-}ArH)Cr(CO)_3$ complex is accomplished photochemically as shown in equation 2.

$$(\pi\text{-}ArH)Cr(CO)_3 + L \xrightarrow{hv,\ Solv.} (\pi\text{-}ArH)Cr(CO)_2L + CO \quad (2)$$

L = PR_3[10], C_8H_{14}[10], THF[11], CS[10], CNR[12], $S(R^1)R^2$ [13].

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

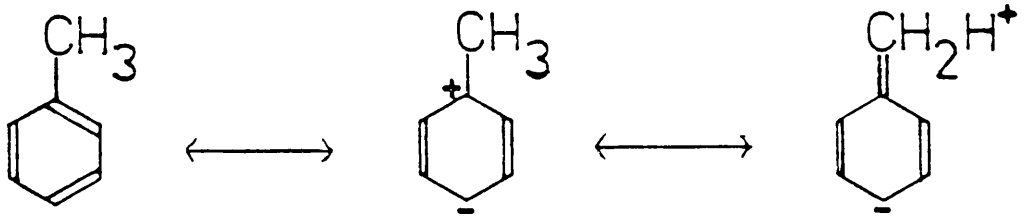
Although thermal reaction conditions generally favour π-arene displacement, the thermal labilization of a carbonyl in Cr(π-arene) $(CO)_3$ by means of catalyst mixtures was recently reported[14].

It is known that the substituent on an aromatic ring has an important effect on the properties, stability and thus reactivity of the three remaining ligands in a π-arene complex. These properties and the preparation of some complexes will be discussed briefly to point out important aspects to be considered in the synthesis of π-arene thiocarbonyl complexes.

1.2 The benzene ring and the effect of its substituents[15]

There are two mechanisms by which a group may withdraw or donate electrons from or to the attached benzene ring, namely the inductive and resonance effect.

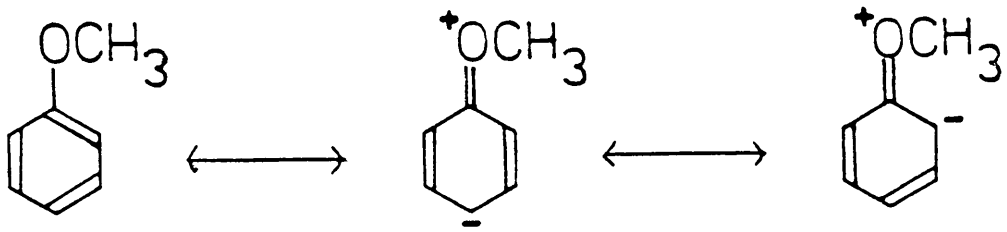
Toluene (1), anisole (2) and 1,2,3-trimethoxybenzene (3) would be expected to have a different reactivity than benzene by virtue of the inductive effect of the substituents methyl, methoxy and 1,2,3-trimethoxy respectively. The inductive effect can be shown by means of the following resonance forms.



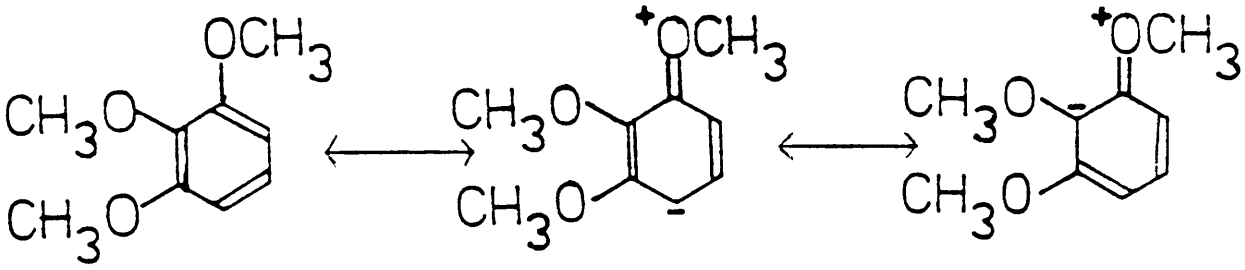
1

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

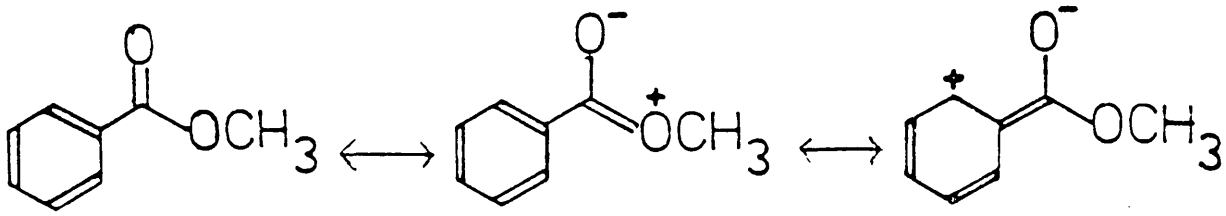


2

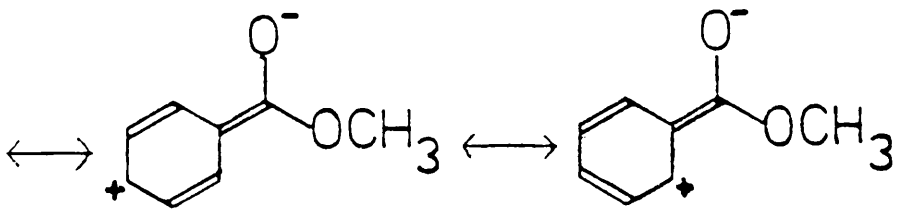


3

The carbo-methoxy group in methyl benzoate (4) on the other hand shows a resonance effect which indicates electron withdrawal from the benzene ring.



4



Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

In view of this the following π-arene chromium(0) tricarbonyl complexes (precursors to the corresponding π-arene chromium(0) thiocarbonyl complexes) were prepared:

(a) benzene chromium(0) tricarbonyl

(b) toluene chromium(0) tricarbonyl

(c) methyl benzoate chromium(0) tricarbonyl

(d) mesitylene chromium(0) tricarbonyl

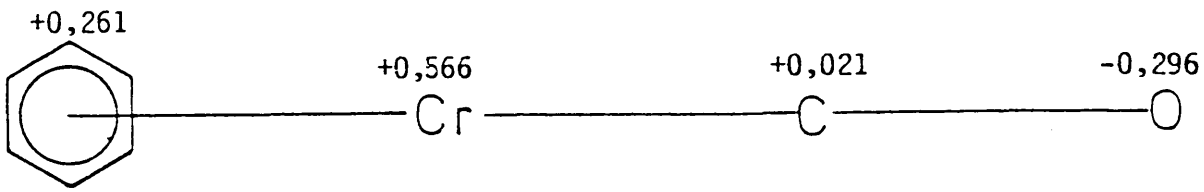
(e) anisole chromium(0) tricarbonyl

(f) 1,2,3-trimethoxybenzene chromium(0) tricarbonyl

1.3 Electronic effects in π-arene complexes of chromium(0)

Molecular orbital energy calculations predict a net charge transfer from the π-coordinated arene ring to the transition metal[16]. This high electron density on the transition metal is in turn relieved by the strong π-acceptor capabilities of the carbonyl ligands, which thus enhances the stability of the complex. The calculations show a positive character on the π-arene ligand whereas the carbonyl carbon shows a less positive character in the case of the π-arene complex compared to hexacarbonyl chromium(0). This charge characterization is depicted below.

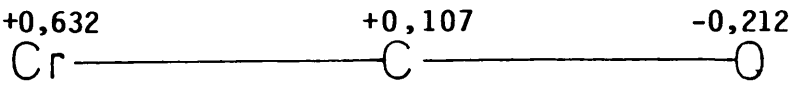
$Cr(\eta^6\text{-}C_6H_6)(CO)_3$



Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

$Cr(CO)_6$



The conclusions drawn from the molecular orbital energy calculations are confirmed by the relative stability of π-arene complexes compared to chromium hexacarbonyl, as well as spectroscopic characterization (NMR and Infrared)[17,18].

The dipole of Cr $(\eta^6\text{-}C_6H_5R)(CO)_3$ complexes varies between 4 and 6 D, where the π-arene part of the complex is considered to be the positive pole and the carbonyl oxygen the negative pole[19].

The bonding properties of other ligands, L, other than carbonyl are also of importance in so far as stability of $Cr(\pi\text{-arene})L_3$ complexes is concerned. If L has π-acceptor capabilities which are comparable to the π-acceptor capabilties of the carbonyl ligand, then stable $Cr(\pi\text{-arene})L_3$ complexes can be expected. In contrast ligands with weak π-acceptor capabilities will lead to relatively unstable complexes. Thus, the nature of R and L in $Cr(\eta^6\text{-}C_6H_5R)(CO)_2L$ type complexes are of importance for a stable electronic balance in these complexes. Owing to the better π-acceptor capabilities of the CS ligand (Chapter 2) it can be expected that π-arene thiocarbonyl complexes are more stable than the π-arene tricarbonyl analogues.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

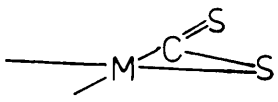
1.4 Preparation of thiocarbonyl complexes

Many thiocarbonyl complexes of Groups VI to Groups VIII transition metals have been synthesized[60] since Baird and Wilkinson[6] reported the first thiocarbonyl complexes in 1966. Very few complexes containing more than one thiocarbonyl ligand have yet been reported and are restricted to manganese(I) cyclopentadienyl complexes, $Mn(\eta^5\text{-}C_5H_5)(CO)_{3-n}(CS)_n$, n = 1,2,3[20].

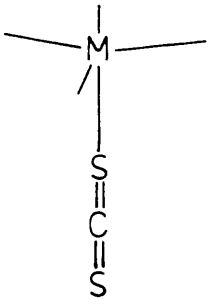
Various methods have been employed in the preparation of metal thiocarbonyls utilizing reagents such as carbon disulphide (CS_2), thiophosgene (Cl_2CS) and alkoxy derivatives of thiophosgene (ClC(S)OR, R=Me, Et) as a source of CS[8] and details of these are given below.

1.4.1 Preparation using carbon disulphide

Transition metal complexes reacting with carbon disulphide give rise to a number of differently coordinated CS_2 complexes. The complexes may contain π-bonded CS_2 as found in the complex $Pt(PPh_3)_2CS_2$[21] 5, sulphur bonded CS_2 as found in $Pt(Me)I(PPh_3)_2CS_2$[22] 6, bridged CS_2 in $K_6[(CN)_5CoCS_2Co(CN)_5]$[23] 7 as well as metal thiocarbonyls found in the reaction of trans-$IrCl(N_2)(PPh_3)_2$ 8 with CS_2[24].



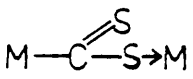
5



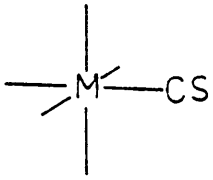
6

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA



7



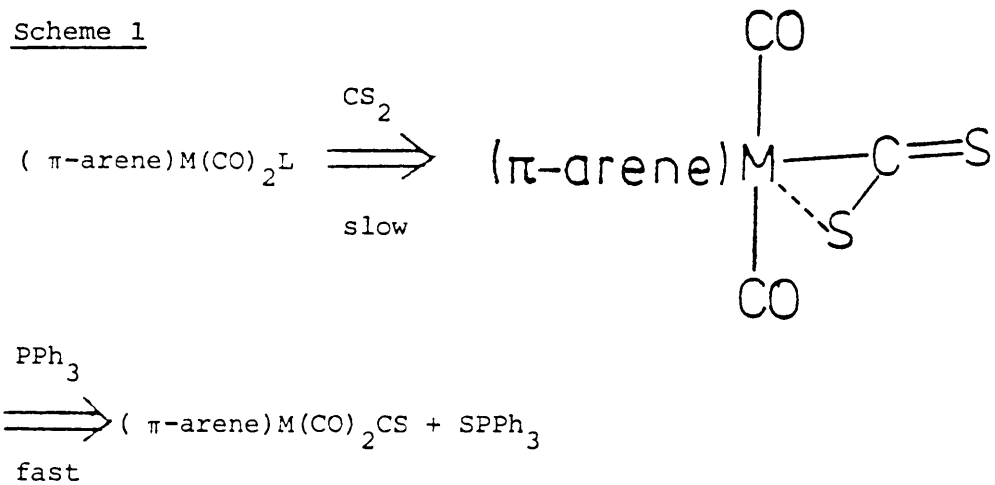
8

The π-bonded CS_2 complexes are often precursors to metal thiocarbonyls provided a suitable sulphur acceptor is present. Even though metal thiocarbonyls are also formed without a suitable sulphur acceptor, the fate of the sulphur atom is not known and the metal thiocarbonyl complexes are obtained in low yields.

1.4.2 Preparation using carbon disulphide/triphenylphosphine

Since the presence of a suitable sulphur acceptor tends to produce high yields of certain metal thiocarbonyls, it has been found that triphenyl= phosphine produces the best results[25]. In this kind of π-arene metal thiocarbonyl preparation a bulky labile ligand such as cyclooctene (C_8H_{14})[10] or THF[11] is displaced by carbon disulphide. In the next step the abstraction of a sulphur atom by triphenylposphine, which is aided by its coordination to the transition metal, occurs. This process is depicted in Scheme 1.

Scheme 1



Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

where (a) π-arene = η^5-C_5H_5, η^5-C_5H_4Me etc. and M=Mn[26]

(b) π-arene = η^6-C_6H_6, η^6-C_6H_5COOMe etc. and M=Cr[11]

1.4.3 Preparation using thiophosgene

This method involves the reduction of $M(CO)_6$ M=W,Cr in THF with sodium amalgam (this generates the $[M_2(CO)_{10}]^{2-}$ anion [27]) and the reaction of the resulting solution with thiophosgene to give the $M(CO)_5CS$ complex.

There are two distinct disadvantages to this method, namely low yield of the thiocarbonyl complex (<10%) and a long and involved purification process. The corresponding selenocarbonyl complexes $M(CO)_5CSe$ could not be prepared in this manner owing to the nonexistence of Cl_2CSe.

1.4.4 Preparation using alkoxy derivatives of thiophosgene

Reation of $[Fe(Cp)(CO)_2]$ with ClC(S)OR (R=Me,Et) yields the thiocarbonyl derivative $Fe(Cp)(CO_2)C(S)OR$ and addition of hydrochloric acid to this product gives $[Fe(Cp)(CO)_2CS]Cl$[28].

1.5 Reactivity of π-arene thiocarbonyl complexes investigated in this study

The photochemical substitution of a carbonyl ligand with Group XV ligands in π-arene thiocarbonyl complexes has already been reported[10]. In this reaction two optically active diastereoisomeres were found in equal quantities which were separated by chromatography.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

In this work the photochemical substitution reaction of $Cr(\eta^6\text{-}C_6H_5Me)(CO)_2CS$ with PPh_2Me yielded two diastereoisomeres which could not be separated by chromatography and the separation was accomplished by recrystallization.

Only one product was isolated from the photochemical reaction of $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$ with 1,3-dithiane.

The reactivity of π-arene thiocarbonyl complexes towards nucleophiles has not been reported. It was attempted under varying conditions to bring about nucleophilic attack on the thiocarbonyl carbon by reagents such as (+)-1-Phenylethylamine and dimethylamine but these attempts proved to be fruitless.

More promising results were obtained in the reaction of $Cr(\eta^6\text{-}C_6H_5R)(CO)_2CS$ (R=H,Me) with PhLi at -70°C. A red unstable salt, presumably $Li[Cr(\eta^6\text{-}C_6H_5R)(CO)_2(C(S)Ph)]$ was observed but attempted alkylation of the salt with MeI or $CF_3SO_3CH_3$ resulted in total decomposition.

1.6 Synthesis of π-arene tri- and thiocarbonyl chromium(0) complexes

General Procedures

All reactions and manipulations were carried out under an atmosphere of nitrogen and the solvents were dried in the usual manner. Reagent grade chemicals were used without further purification. The irradiation experiments were carried out in a Pyrex flask with a water cooled jacket, using a Philips medium pressure mercury lamp. Column chromatography was performed on 2 x 40cm columns at -20°C (SiO_2; 0,063 -0,200mm). Melting points were recorded on a Kofler hot-stage apparatus and are reported uncorrected.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Infrared spectra were recorded on a Beckman IR4250 or Beckman Acculab 2 spectrometer, calibrated against polystyrene. PMR spectra were recorded on a Brücker WP 80 MHz spectrometer using tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on a Perkin Elmer RMU-6H instrument operating at 70eV. Microanalyses were performed by F Pascher and E Pascher, Microanalytical Laboratories, Bonn.

These procedures were applied in the syntheses and reactions discussed in the chapters that follows.

1.6.1 Preparation of π-arene chromium(0) tricarbonyl complexes

The complexes $Cr(\eta^6\text{-}C_6H_6)(CO)_3$, $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_3$ and $Cr(C_6H_5COOMe)(CO)_3$ were prepared following the C A L Mahaffy and P L Pauson[55] method while $Cr(\eta^6\text{-}C_6H_5Me)(CO)_3$ and $Cr(\eta^6\text{-}C_6H_3Me_3)(CO)_3$ were prepared following the method of B Nicholls and M C Whiting[9].

1.6.2 Synthesis of 1,2,3-trimethoxybenzene chromium(0) tricarbonyl

A solution of $Cr(CO)_6$ (2,20g, 10,00mmol) and 1,2,3-trimethoxybenzene (5,04g, 30,00mmol) in dibutylether ($100cm^3$) was refluxed under nitrogen for 12 hours. The solvent was removed under reduced pressure and the yellow residue was purified by column chromatography (hexane: ether::1:1) to give the product (83%) as fine yellow crystals; m.p. 34-35°C; $^m/_e$ 304 (M^+).

1.6.3 Preparation of π-arene chromium(0) thiocarbonyl complexes

The π-arene chromium(0) thiocarbonyl complexes were all prepared according to the method of G Jaouen and G Simmoneaux[10], whereby one of the three carbonyls was replaced by cyclooctene by means of photolysis

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

and treatment of the unstable π-arene dicarbonyl olefin complex with CS_2/PPh_3 (Scheme 1). This method proved to give constant good yields of all the desired thiocarbonyl complexes with readily available reagents.

1.6.4 Synthesis of carbonyl (1,3-dithiane) methylbenzoate thiocarbonyl chromium(0)

A solution of dicarbonyl methylbenzoate thiocarbonyl chromium(0) (0,29g, 1,00mmol) and 1,3-dithiane (0,12g, 1,00mmol) in benzene ($80cm^3$) was irradiated at room temperature for 1,5 hours during which extensive decomposition occured. After filtration the crude product was purified by column chromatography (hexane:ether::3:1) to give the pure compound (19%) as red crystals; mp 67°C decomposition; $^m/_e$ 380 (M^+).

1.6.5 Synthesis of carbonyl (methyldiphenylphosphine) thiocarbonyl toluene chromium(0)

A mixture of dicarbonyl thiocarbonyl toluene chromium(0) (0,25g, 1,00mmol) and methyldiphenylphosphine (1,60g, 8,00mmol) in benzene ($80cm^3$) was irradiated at room temperature for 2 hours. The yellow solution gradually turned orange and some decomposition was observed. After filtration the two diastereoisomers were purified by column chromatography (hexane:ether::1:1). The orange diastereoisomer I was obtained after recrystallization from ether/hexane while the yellow diastereoisomer II remained in the solution and was crystallized afterwards (hexane:ether::5:1). Diastereoisomer I: mp 123-125°C; $^m/_e$ 416(M^+). Diastereoisomer II: mp 102-104°C; $^m/_e$ 416(M^+).

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

General method

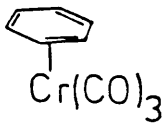
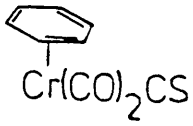
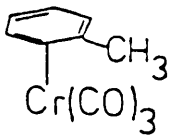
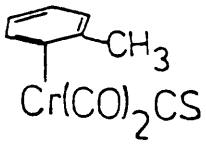
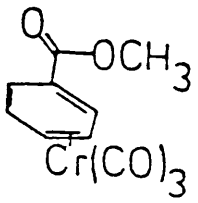
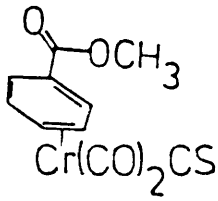
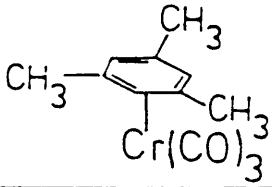
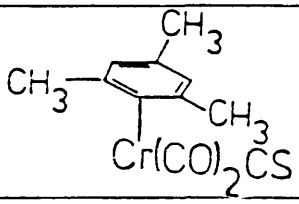
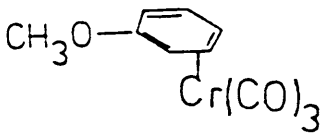
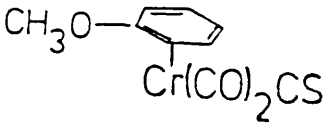
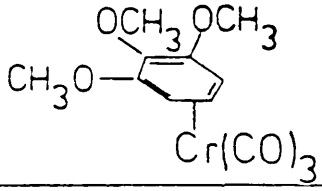
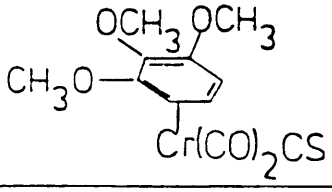
The π-arene chromium(O) tricarbonyl complex (8mmol), cyclooctene (0,15mol) and benzene (100cm^3) were placed in the irradiation vessel. The irradiation was carried out at room temperature whilst bubbling a stream of nitrogen through the solution. The yellow solution gradually turned orange and constant monitoring of the disappearance of the π-arene tricarbonyl complex by means of thin layer chromatography ensured maximum π-arene dicarbonyl olefin complex generation, and therefore complete formation of π-arene chromium(O) thiocarbonyl. After the optimum irradiation time, the dark orange solution was added to a mixture of triphenylphosphine (1,95g, 8,00mmol) and carbon disulphide (60cm^3) and stirred overnight. After filtration and removal of the solvent under reduced pressure, the crude product was purified by column chromatography (hexane:ether::4:1). The first yellow fraction obtained was unreacted π-arene tricarbonyl complex and the second darker yellow fraction was the desired π-arene chromium(O) thiocarbonyl complex. Results regarding irradiation time, percentage yield and melting points for individual π-arene chromium(O) thiocarbonyl complexes are summarized in Table 1. Elemental analyses of new π-arene thiocarbonyls are given in Table 2.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 1

Reaction conditions and results in the preparation of individual π-arene chromium(0) thiocarbonyl complexes

Tricarbonyl complex (starting material)	Irradiation time (hrs)	Product	Yield (%)	mp (°C) [lit]
	2,0		63	124* [125[11]]
	2,5		59	42 - 43
	1,5		69	80 - 81 [79[10]]
	2,5		79	126 - 128
	2,25		52	82 - 83 [84[56]]
	2,5		75	78 - 80*

* decomposition

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 2

Elemental analyses of new π-arene chromium(0) thiocarbonyl complexes

Complex	Analytically calculated (%)			Found (%)		
	C	H	S	C	H	S
$(\eta^6\text{-}C_6H_5OMe)Cr(CO)_2CS$	46,15	3,08	12,31	46,11	2,07	12,28
$(\eta^6\text{-}C_6H_3Me_3)Cr(CO)_2CS$	52,94	4,41	11,76	52,92	4,44	11,68
$(\eta^6\text{-}C_6H_3(OMe))_3Cr(CO)_2CS$	45,00	3,75	10,00	44,96	3,70	10,08
$(\eta^6\text{-}C_6H_5Me)Cr(CO)(CS)PPh_2Me^-$	63,46	5,05	7,69	63,59	5,11	7,61
$(\eta^6\text{-}C_6H_5COOMe)Cr(CO)(CS)[\overline{S(CH_2)_3SCH_2}]$	44,21	4,21	25,26	44,31	4,27	25,19

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CHAPTER 2

STRUCTURAL AND SPECTROSCOPIC ASPECTS OF METAL THIOCARBONYLS

Introduction

Structural studies of organometallic complexes rely on Infrared spectroscopy (metal carbonyls) while NMR determinations are essential for the structure determination of organic ligands. X-ray or neutron diffraction studies are commonly used today in order to understand ligand properties, arene ring conformations and indirectly chemical reactivity. Each of these will be discussed shortly (2.1 and 2.2) as well as the use of these techniques in the structure determination of new compounds (2.3).

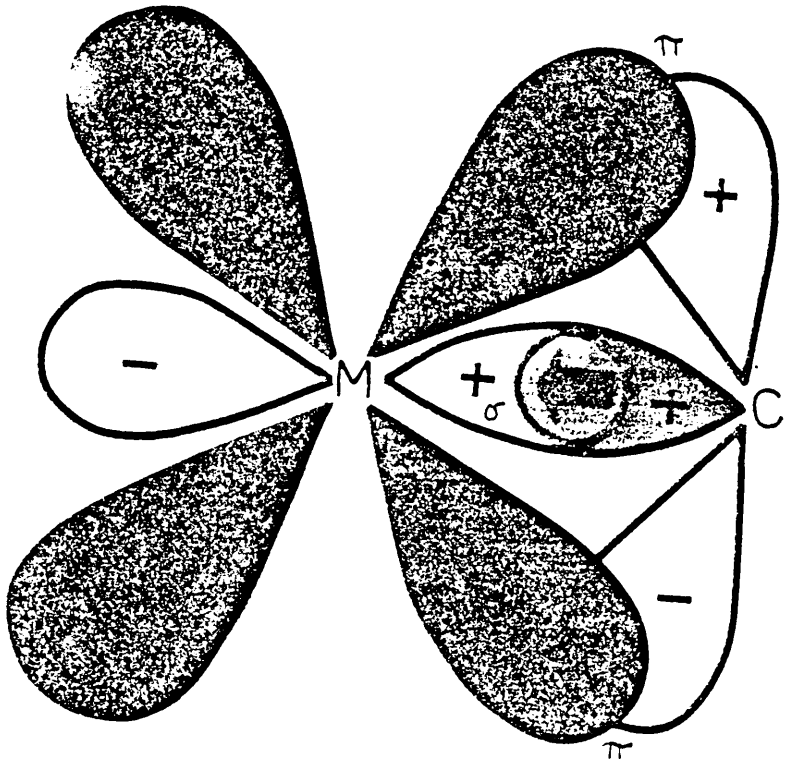
2.1 Spectroscopy of metal carbonyls

An Infrared spectrum of a transition metal carbonyl complex supplies useful structural information regarding bonding properties of the carbonyl ligands as well as the other ligands in a complex. The absorption position gives an indication of the C-O bond order and it follows that a high C-O bond order implies a low M-C bond order and vice versa. The number of bands is a useful guideline in deducing the structure of the complex. The bond interaction between CX and transition metal can be indicated by the following resonance structures:

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The C-X bond order will therefore vary depending on the degree of π-backbonding to the CX ligand as well as the σ-bonding to the metal as indicated below.



In the PMR spectrum some protons are shielded or deshielded depending on the electronic environment. The resonances of a shielded proton occur upfield (low chemical shift) and those of a deshielded proton are expected more downfield (higher chemical shift). Chemical shifts are expressed in δ- values relative to the internal standard TMS.

X-ray diffraction gives an indication of the spatial arrangement of the atoms relative to each other. The determined bond distances and angles indirectly supply information regarding the electronic structure from which conclusions can be drawn about chemical bonding.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

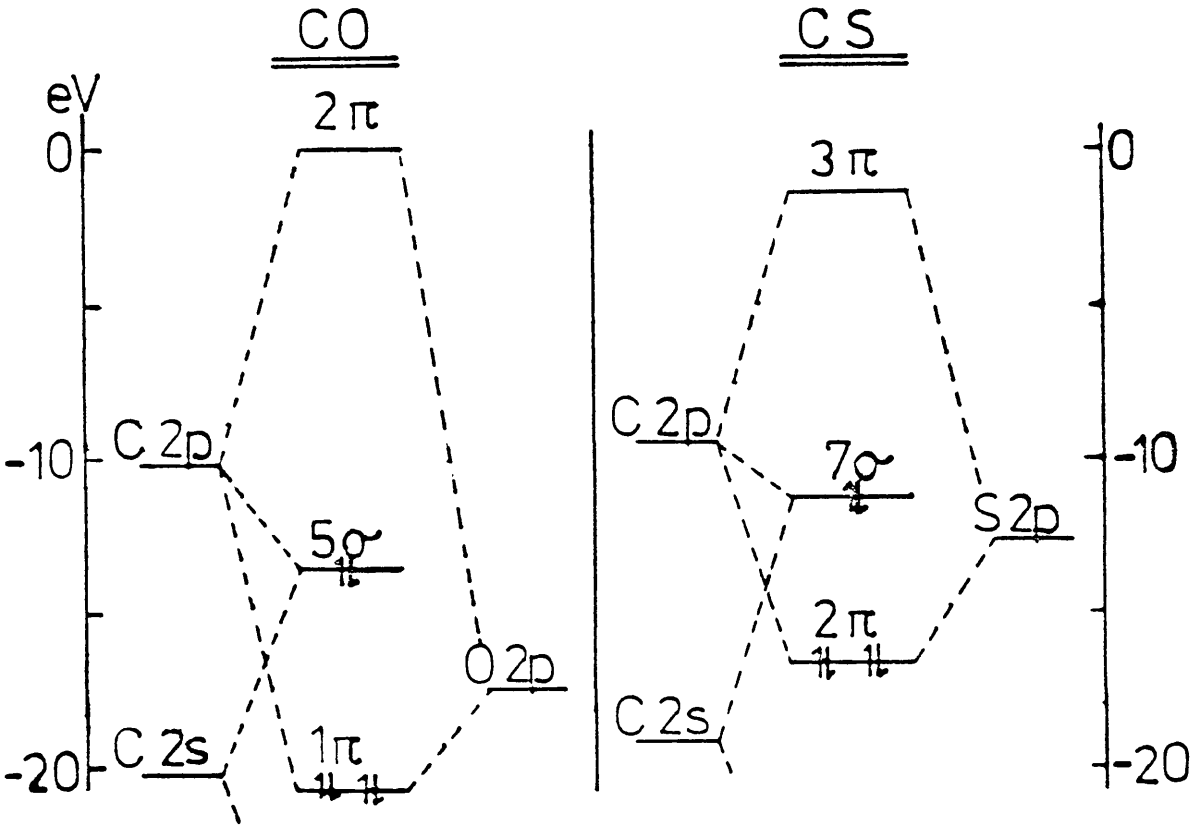
UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

2.2 Structural aspects of metal carbonyls

In order to understand spectroscopic measurements of metal-, carbonyl, thio- and selenocarbonyls it is appropriate to look at the electronic differences between these ligands.

Even though oxygen, sulphur and selenium are all Group VI A elements, the corresponding carbonyls CX, X=O,S,Se differ markedly in stability, bonding properties to metals and reactivity.

It has been found that CS is a better σ-donor and π-acceptor ligand than CO[29]. This can be seen from the molecular orbital diagrams of CO and CS[30] given below.



From this molecular orbital diagram it is clear that the 7σ (bonding) orbital of CS, which acts as σ-donor orbital to the transition metal, occurs at a higher energy level than the 5σ (bonding) donor orbital of

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CO, whereas the 3 π(antibonding) acceptor level of CS, which acts as π-acceptor orbital from the transition metal, occurs at a lower energy level than the 2 π(antibonding) acceptor level of CO.

The lower electronegativity of the sulphur function contributes additional charge to the carbon centre which in turn destabilizes the carbon function and the 7 σ-orbital. The interaction between the carbon and the sulphur p π-orbitals is also reduced, resulting in a low antibonding orbital, the 3 π-orbital. The CS 3 π-orbital is still associated predominantly with the carbon centre (although it does contain an appreciable sulphur contribution) and does have increased capability for accepting electrons from the transition metal[29].

It can therefore be expected that the M-CS bond is stronger than the M-CO bond and in effect the M-CS distance is shorter than the M-CO distance.

Infrared and ^{13}C NMR studies by D Cozak and I S Butler[31] on the complexes $Mn(\eta^5-C_5H_4R)(CO)_2CX$, X=O,S,Se and R=H, Me and $Re(\eta^5-C_5H_5)(CO)_2CX$, X=O,S,Se showed that CSe is a better net electron withdrawing group (σ-donor and π-acceptor) than both CO and CS. In addition to this the order of net electron ability appears to be CSe > CS > CO. The three types of complexes M-CO, M-CS and M-CSe all give rise to strong, sharp Infrared absorptions attributable to ν(CX) decreasing in energy in the order X=O ≫ S > Se.

S S Woodard[32] et al reported an excellent correlation between thiocarbonyl absorption frequencies and C-S bond distances in a number of thiocarbonyl complexes. Those complexes with the least available

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

metal π-orbital electron density have the shortest C-S distances while more electron rich metal complexes have longer C-S distances (see 2.3.3).

2.3 Spectroscopic measurements of π-arene mixed carbonyl chromium complexes

2.3.1 Infrared frequencies of π-arene tricarbonyl chromium(0) complexes

The Infrared spectra of (π-arene) tricarbonyl complexes reveal two interesting aspects, namely the number and the positions of the absorption bands.

The more intense absorption, the E band, appears at a larger wavelength while the second absorption is the A' band, assigned to symmetrical CO stretch vibrations.

The Infrared CO vibrations of (π-arene) tricarbonyl complexes which were prepared for this study are listed in Table 3.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 3 Infrared carbonyl vibrations of π-arene tricarbonyl complexes

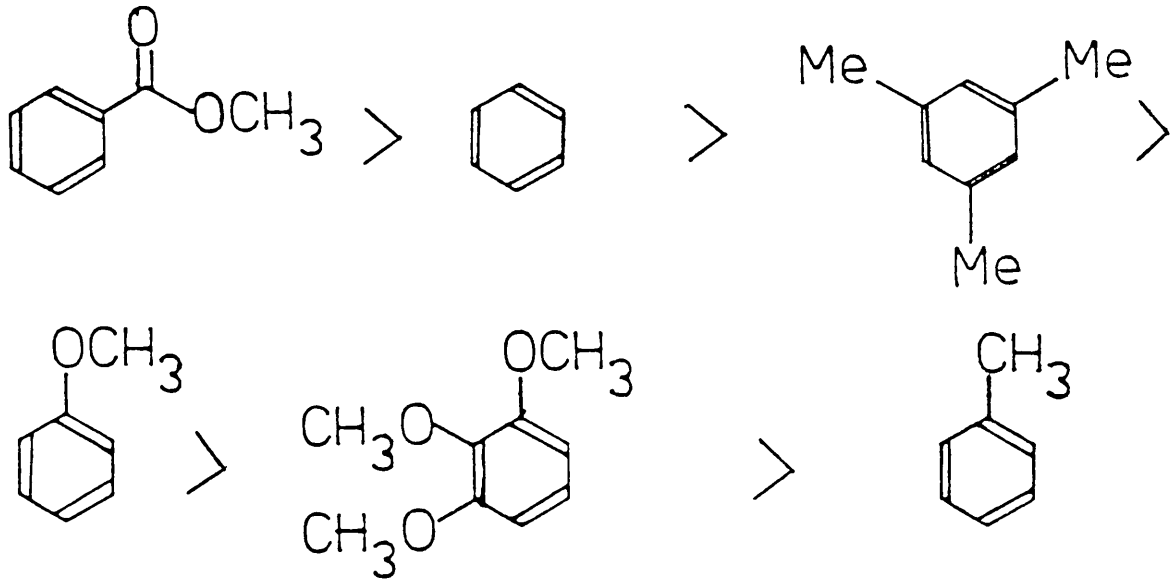
Complex	ν(CO) (cm^{-1})	
	E peak	$A^{'}$ peak
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$	1910	1976
$(\eta^6\text{-}C_6H_5Me)Cr(CO)_3$	1882	1959
$(\eta^6\text{-}C_6H_5COOMe)Cr(CO)_3$	1925	1986
$(\eta^6\text{-}C_6H_5OMe)Cr(CO)_3$	1900	1970
$(\eta^6\text{-}C_6H_3Me_3)Cr(CO)_3$	1898	1962
$(\eta^6\text{-}C_6H_3(OMe)_3)Cr(CO)_3$	1890	1961

The carbonyl absorption in hexacarbonyl chromium(0) appears at a higher frequency (1992 cm^{-1}) than the absorption of the π-arene tricarbonyl chromium(0) complexes which indicates more π-backbonding to the CO ligand in the π-arene tricarbonyl chromium(0) complexes than in $Cr(CO)_6$. From this follows that the tridentate π-arene ligand has

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

weaker π-backbonding capabilities than three carbonyl ligands have together. It is also evident that the different substituents on the benzene ring have an influence on the wavelength of the carbonyl frequencies. It appears that toluene has weaker π-backbonding capabilities than methyl benzoate and the substituted benzene rings can be arranged in order of decreasing π-backbonding capabilities as shown below.



2.3.2 Infrared frequencies of π-arene thiocarbonyl chromium(0) complexes

Owing to the better σ-donor and π-acceptor capabilities of the thiocarbonyl ligand as described in section 2.2 it is expected that the carbonyl absorptions shift to a higher frequency than those of the corresponding π-arene tricarbonyl complexes. The increased interaction between transition metal and thiocarbonyl ligand decreases the interaction between transition metal and carbonyl ligand and therefore increases the C-O interaction. This is evident from the carbonyl and thiocarbonyl freqencies observed for the $Cr(\eta^6\text{-}C_6H_5R)(CO)_2(CS)L$ R=Me, L=$PMePh_2$ and R=COOMe, L=1,3-dithiane complexes. Both ligands, L, are

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

good σ-donor and weak π-acceptor ligands and place additional electron density on the chromium centre. It can therefore be expected that both ν(CO) and ν(CS) frequencies are lowered owing to the increased interaction between M-C(X) X=O,S. The thiocarbonyl ligand lowers the symmetry of the complex and this may lead to a split in the E absorption band as observed in some of the complexes. Infrared frequencies of some thiocarbonyl complexes are given in Table 4.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 4 Infrared frequencies of π-arene thiocarbonyl chromium(0) complexes

Complex		ν(CO) (cm^{-1}) [lit][11]	ν(CS) (cm^{-1}) [lit][11]
$Cr(\eta^6\text{-}C_6H_6)(CO)_2CS$	(a)	1913, 1931, 1980 [1922, 1967]	1230 [1220]
$Cr(\eta^6\text{-}C_6H_5Me)(CO)_2CS$	(a)	1937, 1986	1229
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$	(a)	1942, 1980 [1940, 1980]	1232 [1224]
$Cr(\eta^6\text{-}C_6H_5OMe)(CO)_2CS$	(a)	1921, 1964	1221
$Cr(\eta^6\text{-}C_6H_3Me_3)(CO)_2CS$	(a)	1900, 1919, 1961	1218
$Cr(\eta^6\text{-}C_6H_3)(OMe)_3)(CO)_2CS$	(a)	1910, 1954	1214
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)(CS)\ S(CH_2)_3SCH_2$	(b)	1911	1192
$Cr(\eta^6\text{-}C_6H_5Me)(CO)(CS)(PPh_2Me)$	(c)	1902	1187

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

(a) Measured in hexane

(b) Measured in carbon disulphide

(c) The same Infrared frequencies were obtained for both diastereoisomers.

2.3.2 PMR measurements of π-arene chromium(0) complexes

The chemical shifts of the protons of the free aromatic ligand are shifted downfield on coordination to the metal. This phenomenon can be ascribed to the reduction of ring current owing to the π-electron withdrawal by the $Cr(CO)_3$ and $Cr(CO)_2CS$ moeity. The total effect is thus a shift to a lower field of the coordinated aromatic ring protons and to a lesser extent that of alkyl substituents. Owing to the better π-backbondig and σ-bonding properties of the thiocarbonyl ligand relative to the carbonyl ligand it is expected that the π-arene proton signal will be expected slightly further downfield for the thiocarbonyl complexes compared to the corresponding tricarbonyl complexes as can be seen by inspection of Table 5 and 6.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 5 Chemical shifts[a] of π-arene tricarbonyl and π-arene thiocarbonyl complexes

Complex	π-arene protons	subst. protons
$Cr(\eta^6\text{-}C_6H_6)(CO)_3$	5,17 - 5,60 (m)	-
$Cr(\eta^6\text{-}C_6H_5Me)(CO)_3$	5,13 - 5,51 (m)	2,19 (s)
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_3$	5,20 - 6,09 (m)	3,84 (s)
$Cr(\eta^6\text{-}C_6H_5OMe)(CO)_3$	5,01 - 5,78 (m)	3,79 (s)
$Cr(\eta^6\text{-}C_6H_3Me_3)(CO)_3$	4,97 - 5,61 (m)	2,20 (s)
$Cr(\eta^6\text{-}C_6H_3(OMe)_3)(CO)_3$	4,67 - 5,44 (m)	3,83 (s) 3,85 (s) 3,86 (s)

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 5 (Continued)

Complex	π-arene proton [lit][11]	subst. protons
$Cr(\eta^6\text{-}C_6H_6)(CO)_2CS$	5,32 - 5,62 (m) [5,4(s)]	-
$Cr(\eta^6\text{-}C_6H_5Me)(CO)_2CS$	5,35 - 5,71 (m)	2,24 (S)
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$	5,42 - 6,31 (m) [5,4(m), 6,0(d)]	3,95 (s) [3,8(s)]
$Cr(\eta^6\text{-}C_6H_5OMe)(CO)_2CS$	5,31 - 5,82 (m)	3,99 (s)
$Cr(\eta^6\text{-}C_6H_3Me_3)(CO)_2CS$	5,09 - 5,76 (m)	2,22 (s)
$Cr(\eta^6\text{-}C_6H_3(OMe)_3)(CO)_2CS$	4,73 - 5,42 (m)	3,86 (s) 3,87 (s) 3,89 (s)

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 6 Chemical shifts[(a)] of $Cr(\eta^6\text{-}C_6H_5R)(CO)(CS)L$ complexes

Complex		π-arene protons	substituent R	ligand L
R	L			
Me	PPh_2Me	4,98-5,56(m)	2,16(s)	7,09-7,57(m,10H,$P\underline{Ph}_2$)
				1,62(d,3 H,J 4,4 Hz, $P\underline{Me}$)
COOMe	$S(CH_2)_3SCH_2$	4,79-6,16(m)	3,90(s)	3,62-3,89(m,2H,$SC\underline{H}_2S$)
				2,84(m,4H,$S\text{-}C\underline{H}_2\text{-}CH_2\text{-}C\underline{H}_2\text{-}S$)
				2,13(m,2H,$S\text{-}CH_2\text{-}C\underline{H}_2\text{-}CH_2\text{-}S$)

(a) Measured in $CDCl_3$ relative to internal standard TMS.

(b) An interesting feature in the spectra of both methyl benzoate complexes is the distinct split in the π-arene protons. The two protons on the π-arene ring ortho to the carbo-methoxy group are situated more downfield than the remaining three π-arene protons. This occurence is due to the strong electron withdrawing capabilities of the carbo-methoxy group which reduces the electron density around these two ortho protons and chemical shifts are found further downfield relative to the remaining three protons.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

2.3.3 Structural aspects of metal carbonyl, thiocarbonyl and selenocarbonyl complexes determined by X-ray crystallography

From X-ray studies it was determined that the bonding of terminal CX, X=S, Se is similar to that in analogous metal carbonyls, namely near linear M-C-X linkages. Important structural aspects of metal-, thio- and selenocarbonyl complexes are given in Table 7.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 7 Bond distances and analyses of some mixed carbonyl complexes

Complex	M-C-O angle (°)	M-C-X angle (°)	C-O (Å)	C-X (Å)
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_3$ [58]	178,8	-	1,16	-
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$ [38]	176,9	178,0(15)	1,16	1,57(2)
$RuCl_2(CO)(CSe)(PPh_3)_2$ [57]	178,0(2)	174(1)	1,21(3)	1,67(2)
$Cr(CO)_2(CS)[(CH_3O)_3P]_3$ [39]	178,9	176,4(3)	1,15	1,59(9)
$[Ir(CO)_2(CS)(PPh_3)_2]PF_6$ [37]	174,4	178,2	1,24	1,51

From the values provided it is clear that the M-C-X, X=O,S,Se bond angles are near linear which implies that π-backbonding takes place to two perpendicular π-antibonding carbon orbitals (perpendicular to M-C-X linkage).

The C-X distances are in agreement with current bonding theories concerning CX, X=O,S,Se ligands[29].

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

2.4 Stability of carbonyl, thiocarbonyl and selenocarbonyl complexes

Theoretically it is expected that thio- and selenocarbonyl complexes are more stable than carbonyl complexes. This follows directly from the better π-acceptor and σ-bonding properties of CS and CSe (2.2) which provides a relatively even electronic balance in a complex. I S Butler[33] et al reported a range of chromium(0), manganese(I) and rhenium(I) selenocarbonyl complexes and found these complexes to be moisture and air stable. It was found however, that the complexes gradually decomposed in solution especially if they were not protected from light. C R Clark[11] et al also found that the mixed carbonyl-, selenocarbonyl complex $RuCl_2(CO)(CSe)(PPh_3)_2$ was quite stable in air and moisture.

In this study it was observed on developed thin layer chromatography plates that the π-arene thiocarbonyl complexes were more stable in air and moisture than their corresponding π-arene tricarbonyl complexes.

Taking this information into consideration no definite generalization concerning the moisture and air stability of carbonyl, thiocarbonyl and selenocarbonyl complexes can be made. It appears however, that selenocarbonyl complexes are more stable than thiocarbonyl complexes which in turn are more stable than the carbonyl complexes.

This deduction coincides with theoretical trends concerning these three types of complexes[30].

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

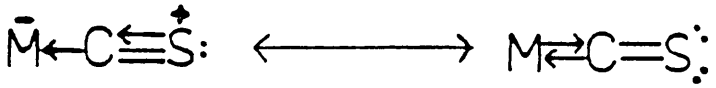
UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CHAPTER 3

SYNTHESIS OF END-TO-END BRIDGED THIOCARBONYL COMPLEXES

Introduction

In an attempt to synthesize an end-to-end bridged dinulear thiocarbonyl complex, it was reasoned that the best way to accomplish this was to expose a terminal thiocarbonyl with a sulphur atom of relatively high nucleophilicity to an effective 16 electron complex. Besides electronic effects around the thiocarbonyl ligand, steric limitations have to be taken into account. The electronic effect around the thiocarbonyl ligand can to some extent be regulated by choosing ligands which would place a high electron density on the metal centre. By choosing ligands with strong σ-donor and weak π-backbonding properties, a high electron density can be placed on the metal. This in turn would increase bond interaction between the metal and thiocarbonyl carbon and would thus place a relatively high electron density on the thiocarbonyl sulphur (Chapter 2) as indicated below.



The increased electron density on the thiocarbonyl sulphur makes the sulphur a centre of high nucleophilicity and thus a strong Lewis base. Evidence of this phenomenon can be found in the work of B D Dombek and R J Angelici[34] who, by replacing CO with DPE (ethylene bis (diphenylpho= sphine)) a strong σ-donor, weak π-backbonding ligand) were able to lower the ν(CS) absorption frequency in $W(CO)_5CS$ at 1258 to 1161cm^{-1} in the $W(DPE)_2(CO)CS$ complex.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The thiocarbonyl ligand in this $W(DPE)_2(CO)CS$ complex readily reacted with electrophiles, whereas the $W(CO)_5CS$ complex was unreactive towards similar electrophiles.

The correlation between bond order in C-S and electron density on the sulphur atom make Infrared ν(CS) absorption frequencies a valuable guideline for the monitoring of electronic effects around the thiocarbonyl ligand. Of the initial three π-arene thiocarbonyl complexes prepared (π-arene = C_6H_6, C_6H_5COOMe, C_6H_5Me) the sulphur atom of the $Cr(\eta^6\text{-}C_6H_5Me)(CO)_2CS$ complex was expected to have the highest nucleophilicity owing to the electron donating methyl group on the arene ring and a ν(CS) absorption at $1229cm^{-1}$.

Contrary to the findings of B D Dombek and R J Angelici[35] who reported that only tungsten thiocarbonyl complexes with ν(CS) absorption frequencies below $1200cm^{-1}$ would be reactive towards electrophiles, we found that a number of π-arene thiocarbonyl chromium(0) complexes with ν(CS) frequencies well above $1200cm^{-1}$ reacted with the $Cr(CO)_5THF$ electrophile.

Besides the electronic effect in the thiocarbonyl ligand we found that a number of factors, mainly relating to reaction conditions, had to be taken into account for the formation of end-to-end bridged thiocarbonyl complexes.

Since R J Angelici and B D Dombek[36] reported the first bridged thiocarbonyl complex in 1975, no further end-to-end bridged complexes have been reported. Spectroscopic results of these compounds were poor and it was decided to synthesize more of these complexes and study them structurally.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The bridged thiocarbonyl complex holds interesting future prospects owing to the activation of the thiocarbonyl ligand in this end-to-end bridged mode. Attempts in bringing about a nucleophilic attack on the thiocarbonyl carbon have so far been unsuccessful.

This chapter will deal with the synthesis of a number of end-to-end bridged thiocarbonyl complexes (3.1) and the finer experimental techniques employed in isolating these complexes (3.2)

3.1 The first end-to-end bridged thiocarbonyl complexes

B D Dombek and R J Angelici[36] reported the synthesis of first end-to-end bridged thiocarbonyl complexes. They found when $W(CO)(CS)(DPE)_2$ having the lowest $\nu(CS)$ stretching frequency ($1161cm^{-1}$) yet reported for a terminal thiocarbonyl complex, was exposed to $W(CO)_5(acetone)$[27] in dichloromethane, the orange complex $(DPE)_2(CO)WCSW(CO)_5$ was formed (yield >80%) which was recrystallized from dichloromethane/hexane or carbon disulphide. Similarly when equimolar amounts of $W(CO)(CS)(DPE)_2$ and $HgCl_2$ or HgI_2 were reacted in dichloromethane, orange or red crystals respectively were obtained in good yield (>80%) (Equation 3).

$$W(CO)(CS)(DPE)_2 + HgX_2 \longrightarrow (DPE)_2(CO)WCSHgX_2 \quad X=Cl,I \quad (3)$$

An ionic diamagnetic complex was formed in yields above 80% when $W(CO)(CS)(DPE)_2$ was stirred with 0,5 equivalents of $AgBF_4$ in dichloromethane or acetone. This complex was identified as $[(DPE)_2(CO)WCSAgSCW(CO)(DPE)_2]\ BF_4$ and like the previous two end-to-end bridged thiocarbonyl complexes was found to be stable in solid state yet decomposed within minutes in acetone.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Unfortunately none of the above metioned complexes were suitable for spectroscopic studies. The ν(CS) absorption frequencies were to some extent obscured by strong DPE absorption which placed some uncertainty on the exact location of the ν(CS) absorption band.

Uncertainty also surrounds the exact nature of CS bonding in the unstable complex $\left[(\eta^5\text{-}C_5H_5)Mn(CO)_2\right]_2CS$ prepared by I S Butler[11] et al. The low ν(CS) mode of 1048cm^{-1} was thought to be in accord with a CS end-to-end bridged structure.

3.2 Synthesis of (π-arene)(CO)$_2$CrCSCr(CO)$_5$ complexes

3.2.1 Preparation of end-to-end bridged thiocarbonyl complexes

Addition of saturated solutions of $(\eta^6\text{-}C_5H_5R)Cr(CO)_2CS$ and $Cr(CO)_5THF$ led to the displacement of the weakly coordinated THF (this in effect is a 16 electron complex). The end on linked dinuclear complex precipitated in near quantitative yields as shown in equation 4.

$$(\pi\text{-arene})Cr(CO)_2CS + Cr(CO)_5THF \xrightarrow{\text{hexane}} (\pi\text{-arene})(CO)_2CrCSCr(CO)_5 + THF \quad (4)$$

The poorer solubility of the product compared to the solubility of the parent thiocarbonyl complex in hexane, conveniently ensured a product of high purity. Three factors were found to be significant in the formation of these end-to-end bridged thiocarbonyls, which will be discussed in turn.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

3.2.2 Factors influencing the formation of (π-arene)$(CO)_2$CrCSCr$(CO)_5$

Stable red crystals (see equation 4) were obtained after recrystal= lization from dichloromethane/hexane. It was found however that the linkage is weak and is easily broken in polar solvents with coordinating properties. The recrystallization was best accomplished by passing a stream of nitrogen over the dichloromethane/hexane mixture thereby removing the more volatile dichloromethane. In contrast, when recrystallization was attempted in an ether/hexane mixture decomposition of the complex occured immediately. The nature of the solvent is therefore critical not only in the formation of the complex but also for the isolation thereof.

Another aspect of importance is the electron density on the sulphur of the thiocarbonyl ligand. Complexes with low ν(CS) Infrared absorption frequencies are expected to form the best suited Lewis bases. The unsuccessful attempt to link Mn(Cp)$(CO)_2$CS and Cr$(CO)_5$THF can be explained in terms of the high ν(CS) absorption of Mn(Cp)$(CO)_2$CS at 1266cm^{-1}. B D Dombek and R J Angelici[34] found in their tungsten thiocarbonyl complexes that a ν(CS) absorption lower than 1200cm^{-1} was required for the formation of stable end-to-end adducts. In this study however, it was shown that ν(CS) absorption values of 1230cm^{-1} for the parent thiocarbonyl were not too high for the formation of stable end-to-end adducts. Nevertheless, the use of ν(CS) absorption as a general guideline for electronic effects was found to be useful.

The third aspect which seemed to be of importance in the formation of end-to-end adducts was the conformation and symmetry of the arene ring[59]. Although the formation of end-to-end adducts was observed, difficulties were experienced in isolating them as stable complexes.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The subtituent in the arene ring is important both with regard to electronic effects in the thiocarbonyl ligand and the conformation of the final complex. An attempt to prepare the complexes (η^6-C_6H_6)$(CO)_2CrCSCr(CO)_5$ and (η^6-C_6H_5COOMe)$(CO)_2CrCSCr(CO)_5$ was made but owing to the low electron density on the sulphur atom of the parent thiocarbonyl these complexes could not be isolated.

3.2.3 Synthesis of (η^6-C_6H_5Me)$(CO)_2CrCSCr(CO)_5$

The reaction was performed by reacting two solutions together as described below.

Solution A consisted of Cr(η^6-C_6H_5Me)$(CO)_2CS$ (0,25g, 1,00mmol) dissolved in a minimum volume of hexane at room temperature.

Solution B consisting of $Cr(CO)_6$ (0,22g, 1,00mmol), THF ($4cm^3$) and hexane ($150cm^3$), was irradiated for 0,5 hours at room temperature, whereafter the total volume of solvent was reduced by half under reduced pressure.

Whilst stirring, Solution B was added to Solution A and within two minutes a red product started to precipitate. After five minutes the remaining pale yellow solution was decanted and the precipitate was washed with hexane ($3x20cm^3$). The final product was recrystallized and obtained in an 80 % yield from dichloromethane/hexane, mp 84-86°C; $^m/_e$ 436 (M^+); Anal. calc. for $Cr_2C_{15}H_8O_7S$: C 41,29%; H 1,85%; S 7,35%, Found C 41,83%; H 2,11%, S 7,98%.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

3.2.4 Synthesis of $(\eta^6\text{-}C_6H_5OMe)(CO)_2CrCSCr(CO)_5$

Solution A contained $Cr(\eta^6\text{-}C_6H_5OMe)(CO)_2CS$ (0,26g, 1,00mmol) dissolved in a minimum volume of hexane.

Solution B consisting of $Cr(CO)_6$ (0,22g, 1,00mmol) and THF ($4cm^3$) in hexane ($150cm^3$), was irradiated for 0,5 hours at room temperature.

Whilst stirring, Solution B was added to Solution A whereafter the solvent was slowly removed under reduced pressure. If the solvent removal rate was too high, it was found that the orange solution turned yellow and that $Cr(CO)_6$ precipitated out of the mixture. The desired orange product precipitated when approximately 80% of the solvent was removed. The remaining solvent was decanted and the product was washed with hexane ($3x20cm^3$). By decanting the remaining solvent it was ensured that the formed adduct was clean of any excess parent thiocarbonyl or $Cr(CO)_5THF$.

The final product was recrystallized from dichloromethane/hexane and obtained in an 83% yield, mp 98°C decomposition; $^m/_e$ 452 (M^+) ; Anal. calcd. for $Cr_2C_{15}H_8O_8S$: C 39,83%, H 1,78%, S 7,09%, Found: C 40,27%, H 2,08%, S 7,74%.

3.2.5 Synthesis of $(\eta^6\text{-}C_6H_3Me_3)(CO)_2CrCSCr(CO)_5$

The same method as described in section 3.2.4 was followed and the product was obtained in a 79% yield, mp decomposition; $^m/_e$ 464 (M^+); Anal. calcd. for $Cr_2C_{17}H_{12}O_7S$: C 43,97%, H 2,62%, S 6,90%, Found: C 44,47%, H 3,14%, S 7,52%.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

3.2.6 Synthesis of $(\eta^6\text{-}C_6H_3(OMe)_3)(CO)_2CrCSCr(CO)_5$

The same method as described in section 3.2.4 was followed and the product was obtained in a 76% yield, mp decomposition; $^m/_e$ 512 (M^+); Anal. calcd. for $Cr_2C_{17}H_{12}O_{10}S$: C 39,84%, H 2,34%, S 6,25%, Found: C 40,35%, H 2,90%, S 6,72%.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CHAPTER 4

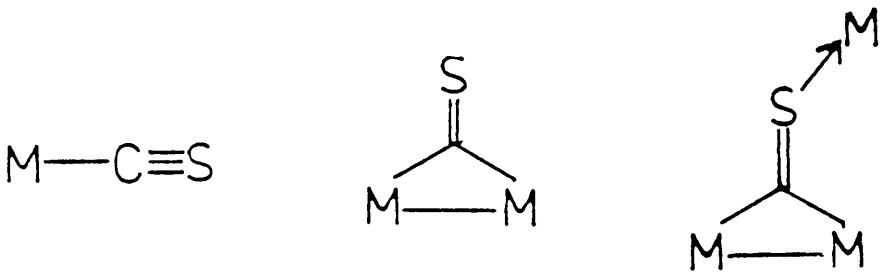
STRUCTURAL ASPECTS OF THIOCARBONYL COMPLEXES

Introduction

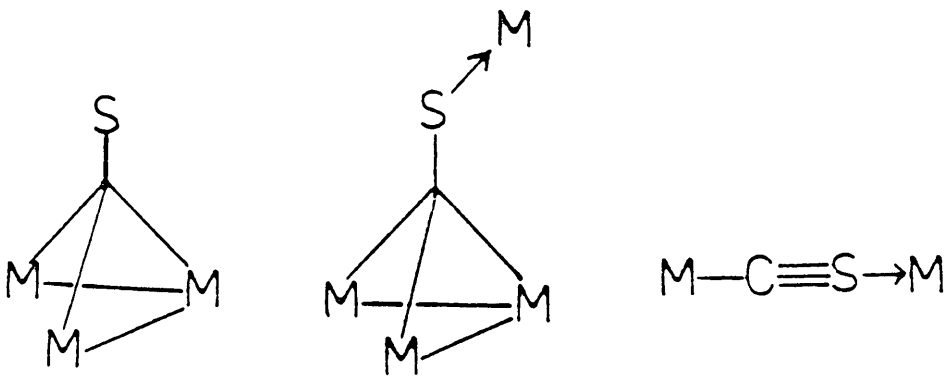
The coordination of carbon disulphide with a wide variety of transition metals has extensively been investigated and reported. In contrast, structural studies on the thiocarbonyl ligand are limited and in many cases absent. The known literature methods are given and a novel contribution from our laboratories is discussed.

4.1 Literature

Thiocarbonyl ligands have been known to coordinate to transition metals in a variety of different ways. The possible arrangements are shown below.



A B C



D E F

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

This chapter deals with the different modes of coordination, spectroscopic data and important structural aspects such as bond lengths and bond angles of metal thiocarbonyl complexes.

Each of the above mentioned modes of coordination will be discussed in turn.

Terminal thiocarbonyl (A)

The most commonly coordinated thiocarbonyl is the terminal CS (A) of which a large number have been prepared. X-ray studies on four of these complexes have been carried out and a summary of the important structural aspects are shown in Table 8.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 8 Structural measurements of terminal thiocarbonyl complexes

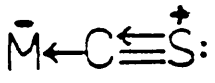
Compound	M-C-S angle (Deg.)	M-CS dist. (Å)	M-CO dist. (Å)	C-S dist. (Å)	C-O dist. (Å)
trans-$W(CO)_4(CS)(CNC_6H_{11})$ [32]	179,0(1.2)	1,94 (19)	2,06	1,56	min. 1,10 max. 1,15
$[Ir(PPh_3)_2(CO)_2CS]PF_6$ [37]	178,6(16) 177,8(15)	1,86 (27) 1,87 (24)	1,92 1,94	1,51 (26) 1,50 (24)	min. 1,15 max. 1,21
$Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$ [38]	178,0(15)	1,79 (2)	1,84	1,57 (2)	min. 1,15 max. 1,16
$Cr(CO)_2(CS)[(CH_3O)_3P]_3$ [39]	176,4(6)	1,78 (9)	1,83	1,58 (9)	min. 1,14 max. 1,15

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

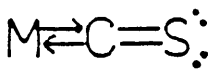
UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Taking experimental error into consideration it can be said that the M-C-S angles are linear, which is indicative of sp hydridization of the carbon and sulphur atoms. Deviations from linearity can be ascribed to unequal π-backbonding to one π^*-acceptor orbital.

From the values in Table 8, it is also observed that those complexes with the least π-orbital electron density (the Ir(1) complex) have the shortest C-S distance while more electron rich metal complexes have longer C-S distances. Thus, there seems to be a direct correlation between electron density on a metal and C-S bond distances and hence ν(CS) frequencies. The more backbonding between the d orbitals of the metal and the empty antibonding orbitals of the carbon i.e. the more interaction between metal and carbon, the stronger the metal-carbon bond (2) appears to be and thus follows a correspondingly weaker carbon-sulphur bond. This trend can be schematically presented as follows:



(1)



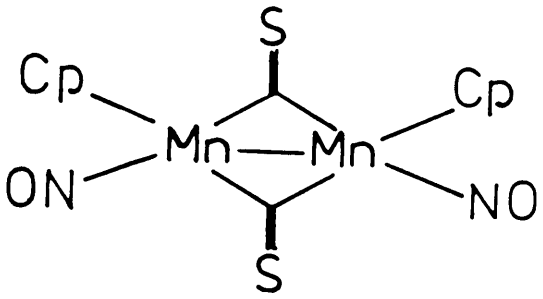
(2)

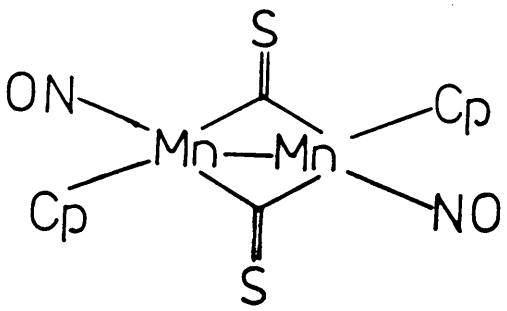
Bridged thiocarbonyl (B)

The dimeric complex $[Mn(\eta^5\text{-}C_5H_5)(CS)(NO)]_2$ was prepared in 20 % yield by R Arneri[40] et al and showed a low thiocarbonyl frequency of 1150(sh) and 1118 (vs) cm^{-1} which suggests a bridged thiocarbonyl ligand. The H^1 NMR spectrum showed two singlets at (benzene) 4,72 and 4,53 for the cis and trans isomers of cyclopentadienyl shown below.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA





An analogous bridged thiocarbonyl complex, $[Fe(\eta^5-C_5H_5)(CO)(CS)]_2$ was reported by R J Angelici[41] et al and again the cis and trans isomers were formed which could be separated by column chromatography. The Infrared spectrum of the trans isomer showed a thiocarbonyl frequency at 1131cm^{-1}, and a single carbonyl frequency at 1979cm^{-1}, while the cis isomer showed a thiocarbonyl frequency at 1124cm^{-1} and carbonyl frequencies at 2011 and 1982cm^{-1}.

The X-ray structure carried out on the cis isomer revealed an average C-S bond distance of 1,59 Å which is slightly longer than the C-S bond distance of terminal thiocarbonyls (between 1,51 and 1,57 Å) and an average Fe-CS bond distance of 1,91 Å.

The average Fe-C-S angle recorded was 139,4° which as expected, differs greatly from linearity.

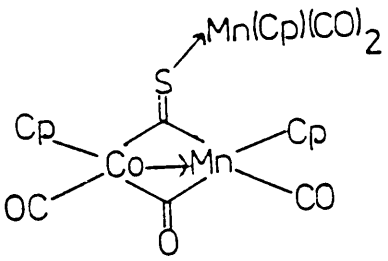
Doubly bridged sulphur coordinated thiocarbonyl (C)

A doubly bridged thiocarbonyl with additional coordination through the

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

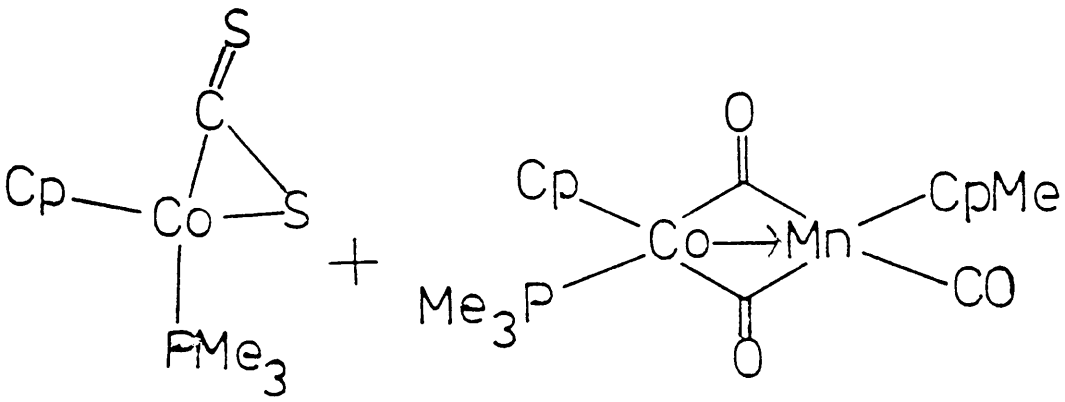
sulphur atom has been reported by O Kolb and H Werner[42].



Although no X-ray structure determination has been carried out on this complex the following spectroscopic data should be mentioned. The carbonyl frequencies (terminal and bridged) were recorded at 1950, 1913, 1855 and 1800cm^{-1} and the thiocarbonyl frequency at 1050cm^{-1} which is approximately 70cm^{-1} lower than the doubly bridged thiocarbonyl.

Triply bridged thiocarbonyl (D)

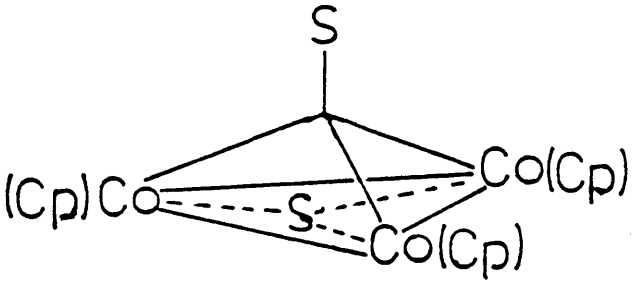
H Werner[43] et al found that when Co(Cp)(μ^2-CS_2)(PMe_3) (9) was reacted with (Cp)(PMe_3)Co(μ-CO)$_2$Mn(CO)(C_5H_4Me) (10), the triply bridged trinuclear complex [(Cp)Co]$_3$(μ^3-S) (CS) (11) formed and not the expected [(Cp)(PMe_3)Co]$_2$ (CS_2) complex.



9 10

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

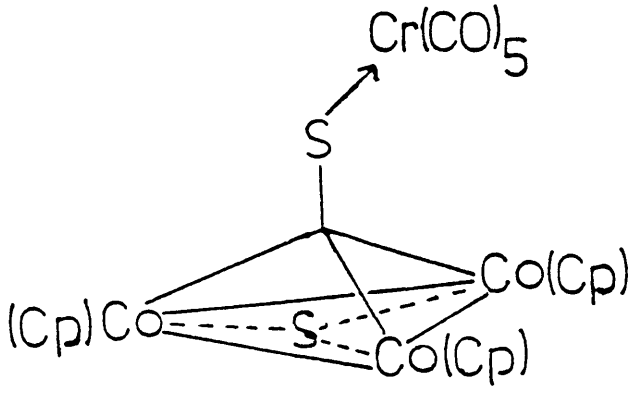


11

In complexes with terminal CS, bond lengths of between 1,51 and 1,57 Å are indicative of a bond order of between two and three whereas complex (11), the first reported triply bridged thiocarbonyl, shows a C-S distance of 1,70 Å which is remarkably near to a C-S single bond length. Consequently the thiocarbonyl sulphur atom could be expected to be a centre of high nucleophilicity.

Triply bridged sulphur coordinated thiocarbonyl (E)

H Werner[43] et al subsequently found that complex (11) readily reacted with RI (R=Me, Et, i-Pr) to give $[((Cp)Co)_3(S)CSR]I$ (12) and with $Cr(CO)_5THF$ to give the triply bridged thiocarbonyl sulphur coordinated complex $[(Cp)Co]_3(S)CSCr(CO)_5$ (13).



13

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The X-ray structure of (12) showed a C-S distance of 1,68 Å which is nearly the same as for complex (11) and a S-Cr distance of 2,49 Å which is comparable with the S-Cr distance of 2,38 Å in the complex $Cr(CO)_5(SCR_2)$[44].

End-to-End bridged thiocarbonyl (F)

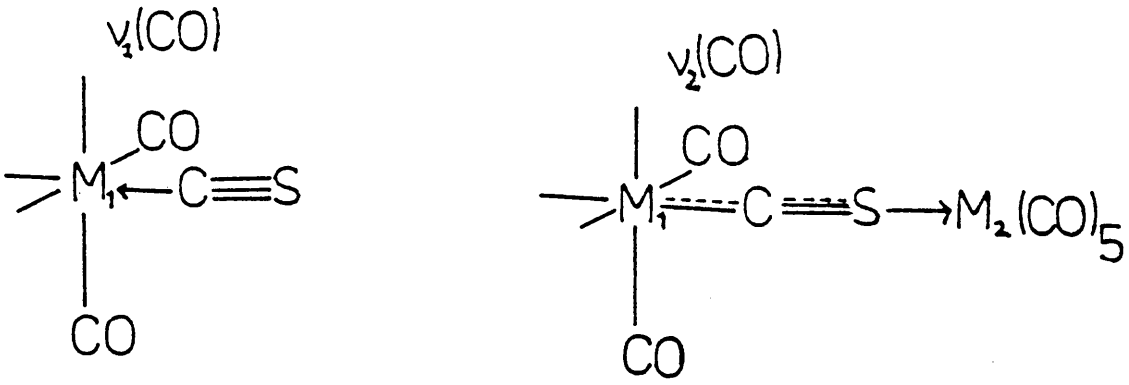
A study of the literature showed that only three of these end-to-end bridged thiocarbonyls have been reported so far, namely $(DPE)_2(CO)WCSW(CO)_5$, $(DPE)_2(CO)WCSHgX_2$ and $[(DPE)_2(CO)WCSAgSCW(CO)(DPE)_2]BF_4$ by B D Dombek and R J Angelici[36]. No X-ray crystal structure determination has been done on any of these complexes and very limited spectroscopic data is available. What is significant however is that the ν(CS) frequency of $[W(CO)(DPE)_2CS]_2Ag$ was believed to be at 1106cm^{-1} and the ν(CS) frequency of the parent complex $W(CO)(DPE)_2CS$ at 1161cm^{-1}.

The exact location of the thiocarbonyl absorption in the bridged complex was obscured by DPE bands. The CS frequencies would indicate a relatively long C-S bond in the end-to-end bridged thiocarbonyl compared to the parent complex.

The lowest carbonyl frequency of the $W(CO)_5$ moiety was believed to overlap the CO absorption of the $W(CO)(CS)(DPE)_2$ fragment. This carbonyl has therefore shifted to a higher frequency (40cm^{-1}) compared to its position in the starting complex and would indicate less W-C interaction in the starting complex due to a flow of electrons from the M-C-S part through to the $M(CO)_5$ fragment as shown below.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA



The flow of electron density from M_1 to M_2 reduces the initial charge on M_1 and reduces the M_1 - C(O) interaction. This increases the C-O interaction and hence results in a higher ν_2(CO) frequency.

After the work of B D Dombek and R J Angelici[36] on bridged thiocarbonyls, a contribution was made by these laboratories on the synthesis of a number of end-to-end bridged thiocarbonyls (Chapter 3) and the X-ray structure determination of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ is discussed in section 4.2.

4.2 Structure determination of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$

4.2.1 PMR and Infrared

Chemical shifts and Infrared carbonyl and thiocarbonyl stretching frequencies of the arene thiocarbonyl complexes and end-to-end bridged adducts are given in Table 9.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 9

PMR data and Infrared frequencies in the ν(CO) and ν(CS) regions of $Cr(\eta^6\text{-}C_6H_3R_3)(CO)_2(CS)$ and $(\eta^6\text{-}C_6H_3R_3)(CO)_2CrCSCr(CO)_5$

Compound[a]			^{1}H NMR (ppm)[b]		IR[c] (cm^{-1})	
R	R	R	π-arene	Me	ν(CO)	ν(CS)
H	H	Me	5,35-5,71(m)	2,24(s)	2070,1973 1908,1878	1156
			5,35-5,71(m)	2,24(s)	1986,1947	1230
H	H	OMe	5,01-5,79(m)	2,17(s)	2040,1980 1933,1880	1140
			5,01-5,79(m)	2,17(s)	1960,1920	1218
Me	Me	Me	5,09-5,44(m)	2,22(s)	2062,1945 1905,1873	1160
			5,09-5,44(m)	2,22(s)	1960,1919	1220

(a) Values for the parent thiocarbonyl complexes are given below those of the corresponding end-to-end bridged thiocarbonyl complexes.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

(b) Measured in $CDCl_3$ relative to the internal standard TMS. The number of protons established by integration are given in accord with the given structures.

(c) Measured in hexane for parent thiocarbonyl complexes and in KBr discs for the end-to-end thiocarbonyl complexes.

A shift to a higher frequency of the ν(CO) absorption was observed for $(DPE)_2(CO)WCSHgX_2$[36]. This result points to less π-interaction between the chromium and carbonyl carbons on account of a lowering of electron density on the chromium due to the end-on coordination of the sulphur. These shifts are of great enough magnitude that it should be reflected in M-CO bond lengths. Unfortunately no conclusive evidence to this effect followed from the Cr-CO bond distances in G and additional structural studies are needed. Nevertheless, ignoring possible electronic effects due to ring substituents, bond lengthening due to end-on coordination seems probable as the Cr-CO distances of 1,886 and 1,852 Å in G are a little longer on average than the corresponding values of 1,850 and 1,847 Å in J. The effect of replacing an electron withdrawing substituent on the arene ring (COOMe) by an electron donating substituent (Me), led to a shortening of the Cr-CO distances as was found for $Cr(\eta^6\text{-}C_6H_5R)(CO)_3$(R=Me,COOMe).

A feature relating to the geometry of G is the eclipsed position of the tripod $Cr[CSCr(CO)_5](CO)_2$ in relation to the arene carbon atoms. The bridging thiocarbonyl is found directly opposite the methyl substituent. A large number of studies relating to different conformations found due to variations in arene ring substituents, have been reported[45]. By contrast very little has been done by way of looking at positions taken up by ligands other than carbonyls with regard to arene ring substituents.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

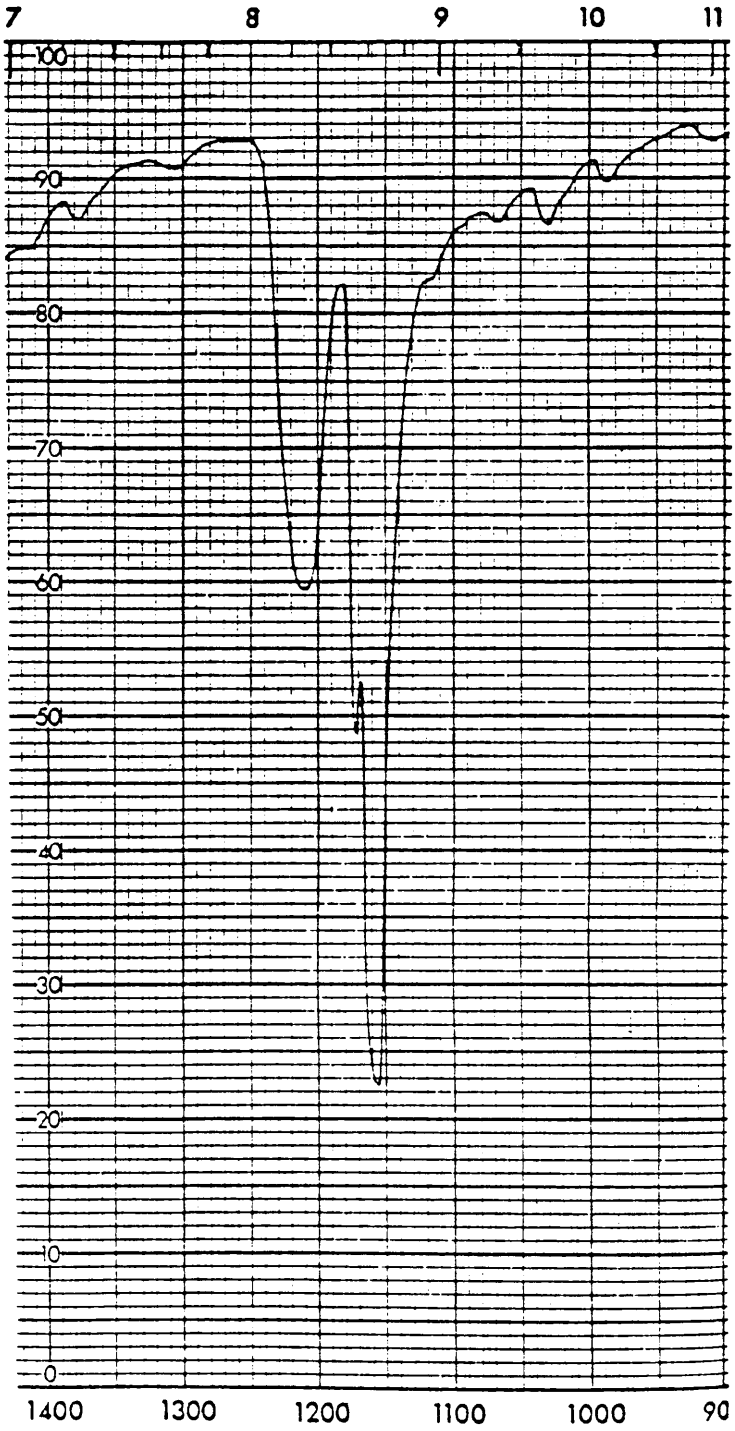
The chemical shift of the π-arene ring protons as well as the protons of the π-arene ring substituents differed very little from those of the parent thiocarbonyl complexes. This would imply that the end-on coordination of the thiocarbonyl ligand has little or no effect on the bonding properties of the π-arene ligand.

Unfortunately the carbonyl absorption bands in the Infrared spectra are broad and it is therefore impossible to assign values to the (π-arene) $Cr(CO)_2$ part of the molecule as a result of overlapping with the more intense absorptions of the $Cr(CO)_5$ moiety. It is anticipated that the carbonyl frequency of the parent thiocarbonyl has moved to a higher frequency in the end-on bridged complex.

End-on coordination of thiocarbonyl ligands lowered the ν(CS) absorption bands by more than $70cm^{-1}$ compared to the parent thiocarbonyl. The ν(CS) band was clearly seen in the spectrum shown on the following page.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA



These values are in good agreement and also support conclusions drawn of the estimated position of thiocarbonyl bands obscured by DPE ligand absorption for the complex $(DPE)_2(CO)WCSHgX_2$[36]. The lowering of the CS bond order on coordination to another metal is also supported by the lengthening of the C-S bond distance.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

4.2.2 Crystal and molecular structure of $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (G)

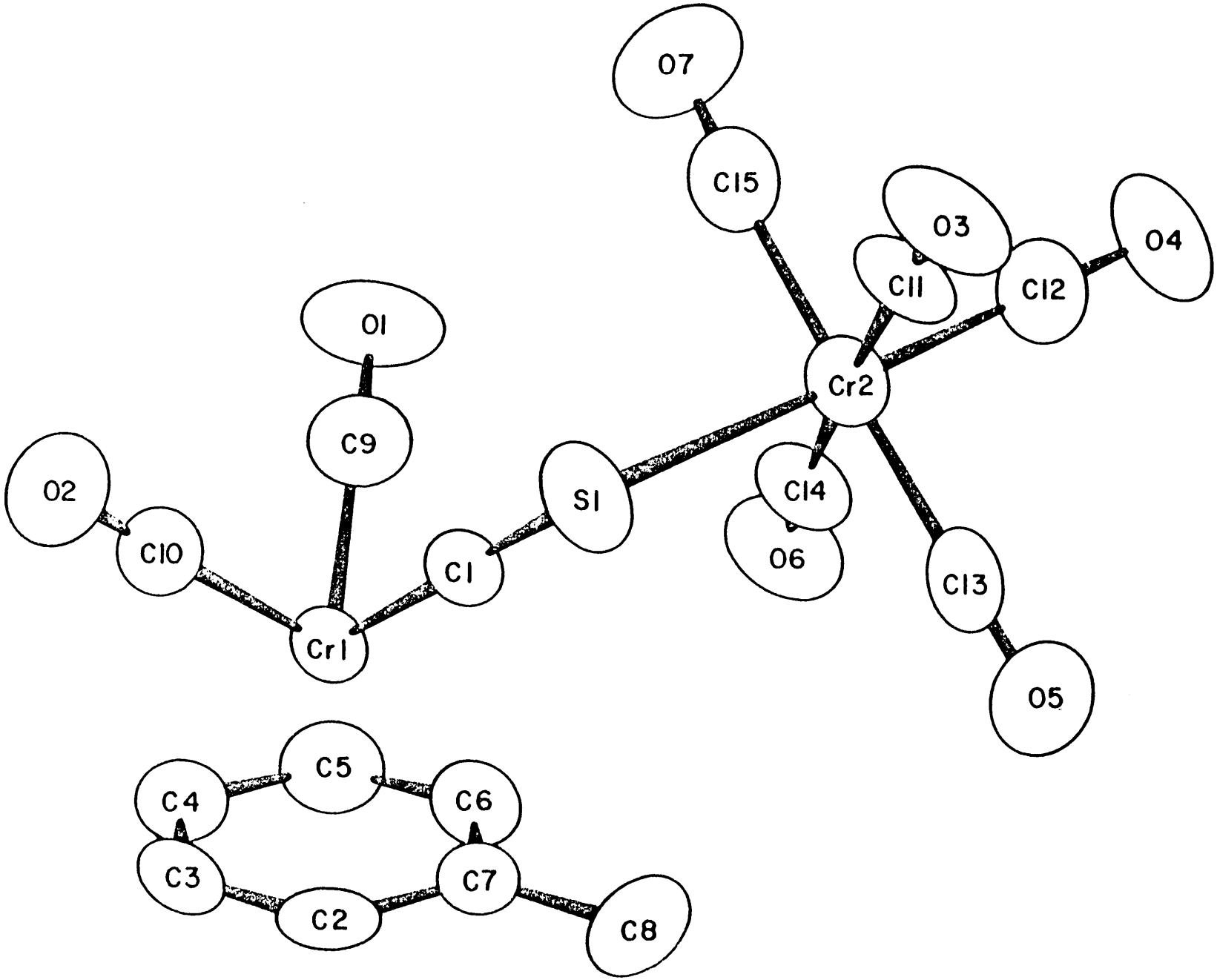
The molecule (G) shown in Figures 1 and 2 along with the atomic numbering scheme used, consists of discrete entities except for the possible interaction between O(5) and H(3) of another molecule, as their separation of 2,39 Å indicates the possible existence of intermolecular hydrogen bonding.

This interaction however does not effect the geometry of the complex with regard to bond distances and angles.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

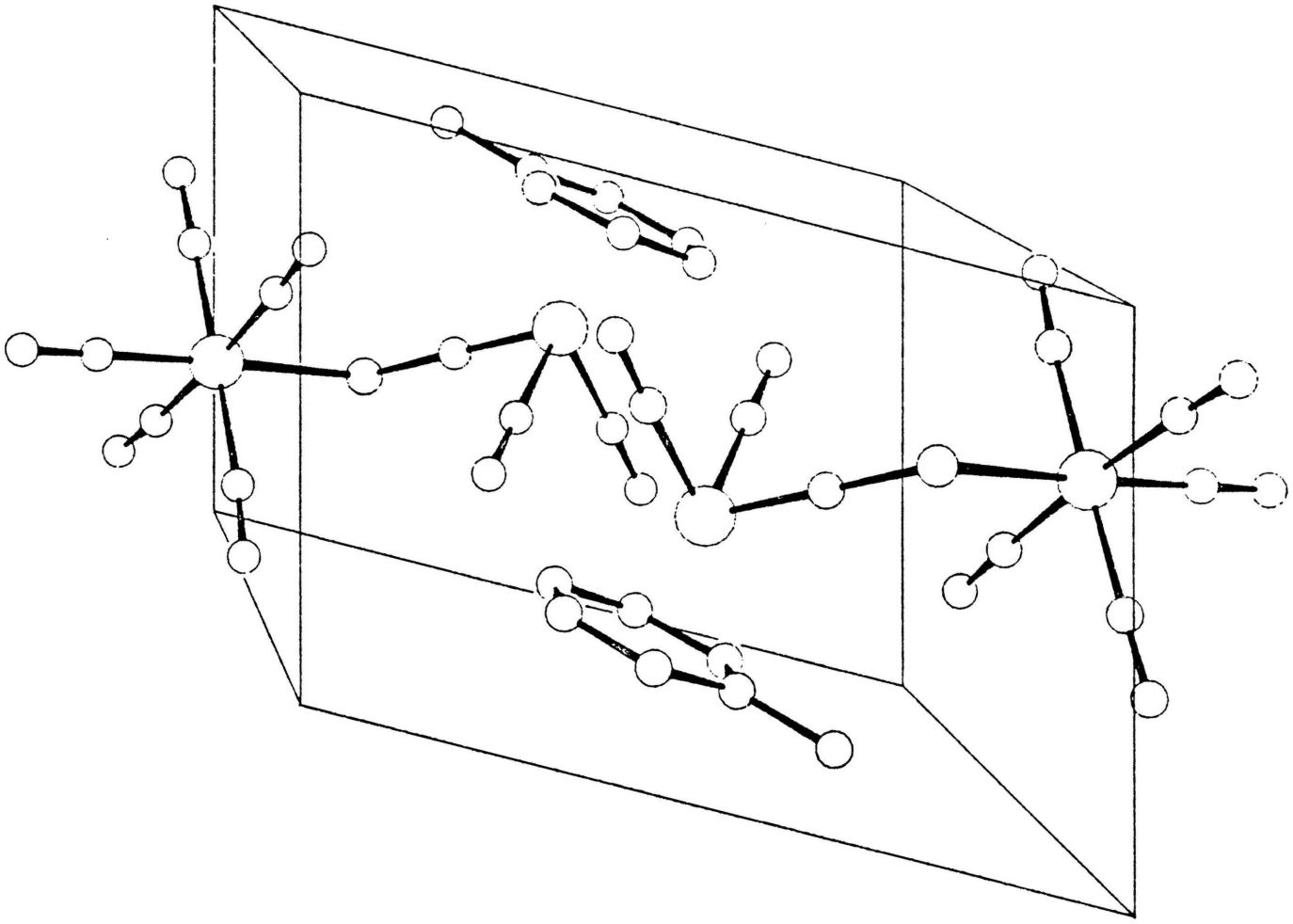
FIGURE 1 The molecular structure of G showing the atomic numbering scheme used



Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

FIGURE 2 Complex G: Packing diagram of G



Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The coordination of the sulphur atom to the second chromium centre leads to a lengthening of the C-S distance. The value of 1,60(5)Å is significantly longer than the expected distances of 1,51 - 1,57 Å for terminal thiocarbonyl ligands (Table 8). This distance is comparable to the 1,62(8) Å in Cr $SCMe_2$ $(CO)_5$ and with 1,592(8) and 1,587(7) Å of the bridged thiocarbonyl of $[Fe(Cp)(CO)(CS)]_2$.

Compensation for the long C-S bond in G was found in a short Cr(1)-C(1) distance. The value of 1,75(5) Å is significantly shorter than the corresponding distance of 1,80 Å in $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$ (Table 8) indicating a considerable degree of π-interaction between the chromium and the thiocarbonyl carbon. Although significant differences exist in the Cr-C and C-S bond distances of G and $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$ the Cr---S distances are almost identical at 3,35 Å and 3,37 Å respectively.

This indicates a more even charge distribution in the bridged complex between the metal centres.

Tables 10 and 11 give bond distances and bond angles respectively of compound G.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 10 Bond lengths (Å) (involving non-H atoms) for G

Cr(1)-C(1)	1.747(5)	Cr(1)-C(2)	2.256(6)
Cr(1)-C(3)	2.241(5)	Cr(1)-C(4)	2.274(6)
Cr(1)-C(5)	2.267(5)	Cr(1)-C(6)	2.249(5)
Cr(1)-C(7)	2.256(6)	Cr(1)-C(9)	1.886(6)
Cr(1)-C(10)	1.852(6)	Cr(2)-S(1)	2.486(2)
Cr(2)-C(11)	1.910(6)	Cr(2)-C(12)	1.844(6)
Cr(2)-C(13)	1.892(7)	Cr(2)-C(14)	1.923(6)
Cr(2)-C(15)	1.937(8)	S(1)-C(1)	1.604(5)
C(2)-C(3)	1.395(10)	C(2)-C(7)	1.404(8)
C(3)-C(4)	1.425(10)	C(4)-C(5)	1.401(9)
C(5)-C(6)	1.399(10)	C(6)-C(7)	1.396(9)
C(7)-C(8)	1.490(11)	C(9)-O(1)	1.109(7)
C(10)-O(2)	1.133(7)	C(11)-O(3)	1.123(7)
C(12)-O(4)	1.149(7)	C(13)-O(5)	1.132(9)
C(14)-O(6)	1.127(7)	C(15)-O(7)	1.112(10)

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 11 Bond angles (°) (involving non-H-atoms) for G

Cr(1)-C(2)-C(7)	71.9(3)	C(3)-C(2)-C(7)	120.7(6)
Cr(1)-C(3)-C(2)	72.5(3)	C(1)-C(3)-C(4)	72.9(3)
C(2)-C(3)-C(4)	121.1(5)	Cr(1)-C(4)-C(3)	70.4(3)
Cr(1)-C(4)-C(5)	71.7(3)	C(3)-C(4)-C(5)	117.1(6)
Cr(1)-C(5)-C(4)	72.3(3)	Cr(1)-C(5)-C(6)	71.3(3)
C(4)-C(5)-C(6)	121.7(6)	Cr(1)-C(6)-C(5)	72.6(3)
Cr(1)-C(6)-C(7)	72.2(3)	C(5)-C(6)-C(7)	120.8(5)
Cr(1)-C(7)-C(2)	71.9(3)	Cr(1)-C(7)-C(6)	71.7(4)
C(2)-C(7)-C(6)	118.6(6)	Cr(1)-C(7)-C(8)	129.5(4)
C(2)-C(7)-C(8)	120.2(6)	C(6)-C(7)-C(8)	121.2(5)
Cr(1)-C(9)-O(1)	177.2(5)	Cr(1)-C(10)-O(2)	177.9(5)
Cr(2)-C(11)-O(3)	177.2(6)	Cr(2)-C(12)-O(4)	179.1(5)
Cr(2)-C(13)-O(5)	177.5(5)	Cr(2)C(14)-O(6)	177.7(6)
C(1)-Cr(1)-C(9)	86.6(2)	C(1)-Cr(1)-C(10)	86.4(3)
C(9)-Cr(1)-C(10)	89.0(3)	S(1)-Cr(2)-C(11)	87.2(2)
S(1)-Cr(2)-C(12)	175.9(2)	C(11)-Cr(2)-C(12)	88.7(2)
S(1)-Cr(2)-C(13)	89.7(2)	C(11)-Cr(2)-C(13)	88.8(3)
C(12)-Cr(2)-C(13)	90.1(3)	S(1)-Cr(2)-C(14)	93.8(2)
C(11)-Cr(2)-C(14)	176.5(3)	C(12)-Cr(2)-C(14)	90.3(2)
C(13)-Cr(2)-C(14)	87.9(3)	S(1)-Cr(2)-C(15)	91.8(2)
C(11)-Cr(2)-C(15)	92.0(3)	C(12)-Cr(2)-Cr(15)	88.4(3)
C(13)-Cr(2)-C(15)	178.3(3)	C(14)-Cr(2)-C(15)	91.3(3)
Cr(2)-S(1)-C(1)	110.4(2)	C(1)-C(1)-S(1)	177.3(3)
C(3)-C(2)-C(7)	120.7(6)	C(2)-C(3)-C(4)	121.1(5)
C(3)-C(4)-C(5)	117.1(6)	C(4)-C(5)-C(6)	121.7(6)
C(5)-C(6)-C(7)	120.8(5)	C(2)-C(7)-C(6)	118.6(6)
Cr(1)-C(7)-C(8)	129.5(4)	C(2)-C(7)-C(8)	120.2(6)
C(6)-C(7)-C(8)	121.2(5)	Cr(1)-C(9)-O(1)	177.2(5)
Cr(1)-C(10)-O(2)	177.9(5)	Cr(2)-C(11)-O(3)	177.2(6)

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

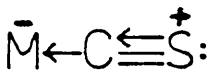
TABLE 11 /cont.

Cr(2)-C(12)-O(4)	179.1(5)	Cr(2)-C(13)-O(5)	177.5(5)
Cr(2)-C(14)-O(6)	177.7(6)	Cr(2)-C(15)-O(7)	175.4(6)
C(1)-Cr(1)-C(2)	100.8(2)	C(1)-Cr(1)-C(3)	131.6(2)
C(2)-Cr(1)-C(3)	36.1(3)	C(1)-Cr(1)-C(4)	166.3(3)
C(2)-Cr(1)-C(4)	65.7(2)	C(3)-Cr(1)-C(4)	36.8(2)
C(1)-Cr(1)-C(5)	142.4(3)	C(2)-Cr(1)-C(5)	76.0(2)
C(3)-Cr(1)-C(5)	64.7(2)	C(4)-Cr(1)-C(5)	36.0(2)
C(1)-Cr(1)-C(6)	108.2(2)	C(2)-Cr(1)-C(6)	64.6(2)
C(3)-Cr(1)-C(6)	76.7(2)	C(4)-Cr(1)-C(6)	65.4(2)
C(5)-Cr(1)-C(6)	36.1(3)	C(1)-Cr(1)-C(7)	90.8(2)
C(2)-Cr(1)-C(7)	36.3(2)	C(3)-Cr(1)-C(7)	65.5(2)
C(4)-Cr(1)-C(7)	77.9(2)	C(5)-Cr(1)-C(7)	65.0(2)
C(6)-Cr(1)-C(7)	36.1(2)	C(1)-Cr(1)-C(9)	86.6(2)
C(2)-Cr(1)-C(9)	163.9(2)	C(3)-Cr(1)-C(9)	141.3(3)
C(4)-Cr(1)-C(9)	106.1(2)	C(5)-Cr(1)-C(9)	89.4(2)
C(6)-Cr(1)-C(9)	99.6(2)	C(7)-Cr(1)-C(9)	130.6(2)
C(1)-Cr(1)-C(10)	86.4(3)	C(2)-Cr(1)-C(10)	105.7(2)
C(3)-Cr(1)-C(10)	87.8(2)	C(4)-Cr(1)-C(10)	98.6(2)
C(5)-Cr(1)-C(10)	130.9(3)	C(6)-Cr(1)-C(10)	163.4(2)
C(7)-Cr(1)-C(10)	140.0(3)	C(9)-Cr(1)-C(10)	89.0(3)
S(1)-Cr(2)-C(11)	87.2(2)	S(1)-Cr(2)-C(12)	175.9(2)
C(11)-Cr(2)-C(12)	88.7(2)	S(1)-Cr(2)-C(13)	89.7(2)
C(11)-Cr(2)-C(13)	88.8(3)	C(12)-Cr(2)-C(13)	90.1(3)
S(1)-Cr(2)-C(14)	93.8(2)	C(11)-Cr(2)-C(14)	176.5(3)
C(12)-Cr(2)-C(14)	90.3(2)	C(13)-Cr(2)-C(14)	87.9(3)
S(1)-Cr(2)-C(15)	91.8(2)	C(11)-Cr(2)-C(15)	92.0(3)
C(12)-Cr(2)-C(15)	88.4(3)	C(13)-Cr(2)-C(15)	178.3(3)
C(14)-Cr(2)-C(15)	91.3(39	C(2)-S(1)-C(1)	110.4(2)
Cr(1)-C(1)-S(1)	177.3(3)	Cr(1)-C(2)-C(3)	71.3(3)

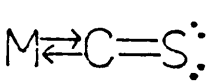
Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The most striking features of the crystal structure determination of compound G is found in the bond angles in the CSCr unit. The Cr(2)-S(1)-C(1) angle of 110.4(2)° in G indicates a significant change in hybridization of the sulphur atom on coordination to the second chromium atom and cannot be rationalized in terms of canonical forms I or II.



I



II

In contrast the Cr-C-S angle in $Cr[S(Et)CH_2Ph](CO)_5$ of 112.0° and 120.3° in $Cr[SCMe_2](CO)_5$ with sp^3 and sp^2 hybridized sulphur atoms respectively, closely correlated with the ideal angle values of 109,4° and 120°. The Cr(1)-C(1)-S(1) arrangement is practically linear (177,3°), comparing well with end-on thiocarbonyls.

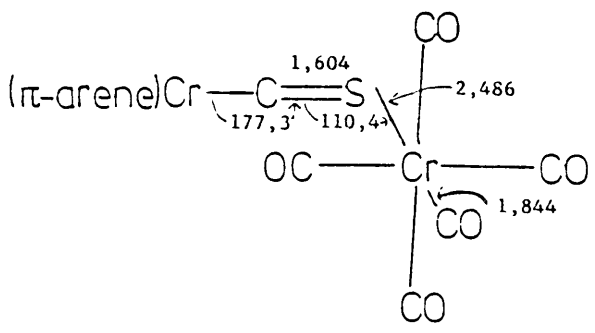
Structures related to G for comparison of relevant bond lengths (Å) and angles (deg)

G $(\eta^6\text{-}C_6H_5Me)(CO)_2CrCSCr(CO)_5$ (this work);

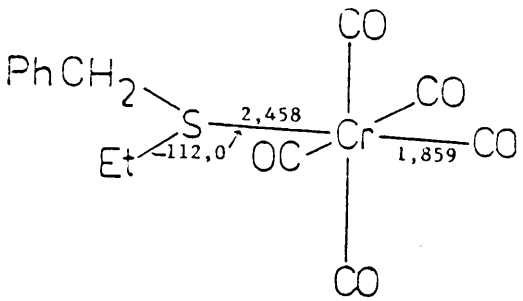
H $Cr[S(Et)CH_2Ph](CO)_5$ [46];

I $Cr[SCMe_2](CO)_5$ [44];

J $Cr(\eta^6\text{-}C_6H_5COOMe)(CO)_2CS$ [38]



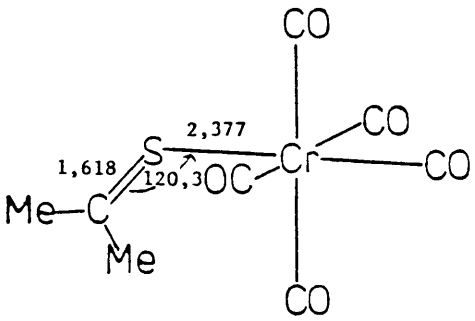
G



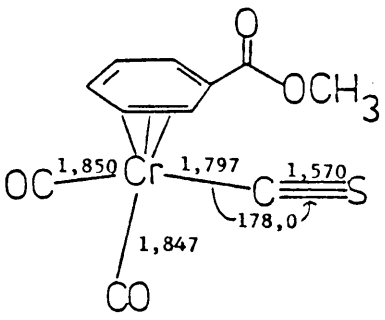
H

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA



I



J

4.2.3 X-ray Analysis

Crystals of G were triclinic, space group $P\bar{1}$ with Z = 2, a = 7,395(1), b = 10,372(3), c = 12,057(1)A, α = 77,72(2), β = 79,91 (1) and γ = 75,69(2)°, D_c = 1,502gcm^{-3} ($MoK_{\alpha 2}$) = 15 cm^{-1}. A total of 5 053 reflections were measured in the ω-mode with $3° < \Theta < 25°$ on a Enraf Nonius CAD4 diffractometer, of which 1127 were regarded as unobserved ($I < 2\sigma < I$). The structure was solved and refined by blocked matrix least squares techiniques using SHELX. The position of all the hydrogen atoms were obtained from a difference Fourier synthesis and these were refined isotropically. Convergene using 2520 reflection for 253 parameters and $\sigma^{-2}(F)$ weights, was reached at R = 0,083 and R_w = 0,035. The maximum noise level of the final difference Fourier was 0,52eÅ^{-3}.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 12 Fractional coordinates ($x10^4$, $x18^3$ for H) and equivalent isotropic temperature factors (A , $x10^3$,) for G

	x/a	y/b	z/c	U(eq)
Cr(1)	8826(1)	5437(1)	7491(1)	43(1)
Cr(2)	3492(1)	10205(1)	7674(1)	47(1)
S(1)	3658(2)	7950(1)	8924(1)	52(1)
C(1)	4699(7)	6773(5)	8210(4)	40(3)
C(2)	8407(7)	4591(6)	8394(5)	50(4)
C(3)	7984(8)	3552(5)	7986(6)	55(4)
C(4)	7850(8)	3663(6)	6804(6)	53(4)
C(5)	8155(8)	4856(7)	6075(5)	53(4)
C(6)	8521(7)	5913(6)	6492(5)	49(4)
C(7)	8648(7)	5796(6)	7652(6)	50(4)
C(8)	9094(9)	6900(7)	8099(6)	79(5)
C(9)	4179(8)	6244(6)	6383(5)	61(4)
O(1)	3154(6)	6725(5)	5765(3)	85(3)
C(10)	4007(8)	4539(6)	8322(5)	54(4)
O(2)	2860(6)	4027(4)	8836(4)	79(3)
C(11)	1781(8)	10938(5)	8881(5)	49(4)
O(3)	815(6)	11408(4)	9585(4)	68(3)
C(12)	3254(9)	11938(6)	6829(5)	57(4)
O(4)	3114(7)	12997(4)	6290(4)	77(3)
C(13)	5499(9)	10451(6)	8329(5)	55(4)
O(5)	6717(7)	10629(5)	8686(4)	83(3)
C(14)	5327(9)	9513(6)	6482(5)	52(4)
O(6)	6425(6)	9147(4)	5777(3)	71(3)
C(15)	1457(10)	9990(7)	6961(5)	66(4)
O(7)	275(7)	9955(6)	6520(5)	103(4)

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

TABLE 12 /cont.

H(2)	859(6)	452(4)	929(4)	93(7)*
H(3)	760(7)	271(5)	864(4)	93(7)*
H(4)	751(7)	283(5)	639(4)	93(7)*
H(5)	788(6)	484(5)	522(4)	93(7)*
H(6)	885(7)	684(4)	591(4)	93(7)*
H(8A)	858(7)	690(5)	908(4)	93(7)*
H(8B)	849(7)	765(5)	798(4)	93(7)*
H(8C)	1016(7)	680(5)	823(4)	93(7)*

* isotropic temperature factor.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CHAPTER 5

PREPARATION AND REACTIVITY OF $M(CO)_5CS$ COMPLEXES

Introduction

The reactivity of $W(CO)_5CS$ has been extensively studied[47,48] but the corresponding chromium complex has been neglected. This chapter will deal with a comprehensive literature survey (5.1) and reactions carried out in this study (5.2 and 5.3).

5.1 Literature

5.1.1 Preparation of $M(CO)_5CS$ complexes

B D Dombek and R J Angelici[27] reported the preparation of $M(CO)_5CS$ M = W,Cr which involved the reduction of $M(CO)_6$ in THF with sodium amalgam and the subsequent treatment of the resulting solution with thiophosgene. The thiocarbonyl complex was obtained in low yield (<10%) and required separation from the hexacarbonyl starting material. This separation was accomplished by treating the mixture with tetrabutylammonium iodide which selectively reacts with the thiocarbonyl complex to form tetrabutylammonium trans-tetracarbonyliodo (thiocarbonyl) tungstate for M = W. $Ag(CF_3SO_3)$ was added to the solution under carbon monoxide pressure to give the thiocarbonyl complex, silver iodide and $[Bu_4N][CF_3SO_3]$.

A M English[49] et al reported an improved method in the preparation of $Cr(CO)_5CX$ X=S,Se complexes by treatment of the π-arene thio-

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

or selenocarbonyl with high carbon monoxide pressure. The yields were 70 - 95% based on (π-arene)$Cr(CO)_2CX$ X=S,Se and 30 - 50% based on $Cr(CO)_6$.

5.1.2 Reactivity of thiocarbonyl pentacarbonyl complexes

Based on a comparison of organic carbonyl and thiocarbonyl compounds[30], the thiocarbonyl ligand is more polar and reactive than analogous carbonyl ligands. Evidence supporting this idea, is derived from the observed ease with which thiocarbonyls undergo nucleoplilic attack at the carbon[48], as in equation 5.

$$(CO)_5WCS + RNH_2 \longrightarrow (CO)_5 WCNR \qquad (5)$$

The chromium and tungsten thiocarbonyls were found to readily undergo substitution reactions as indicated in equation 6.

$$M(CO)_5 CS + L \longrightarrow \underline{trans} - M(CO)_4(CS)L \qquad (6)$$

L = pyridine, ortho-phenylenebisdimethylarsine[47]

Originally it was believed that the trans isomer was formed exclusively, but a study by B D Dombek and R J Angelici[27] suggests the presence of cis and trans isomers although the trans isomer was observed to be the predominant isomer (equation 6, L = PPh_3).

It was also found that the $M(CO)_5CS$ complexes undergo substitution reactions under milder conditions than those of the parent hexacarbonyl

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

complex. This observation and the fact that predominantly trans products were obtained during substitution reactions, suggests a labilization of the ligand trans to the thiocarbonyl ligand.

Similarly, the Ru-Cl distance trans to CSe in the complex $RuCl_2(CO)(CSe)(PPh_3)_2$ was found to be particularly long, demonstrating a strong trans influence for the selenocarbonyl ligand[50].

Furthermore $M(CO)_5CS$ complexes were found to be unreactive towards alkylating reagents and the nucleophilicity of the thiocarbonyl sulphur had to be increased by ligands such as DPE for alkylation to take place. The complexs $W(CO)_5CS$, trans $W(CO)_4(CS)(PPh_3)$ and $W(CO)_3(CS)DPE$ having $\nu(CS)$ frequencies of 1258, 1247 and 1215 cm^{-1} respectively did not react with the triethyloxonium ion whereas trans $[W(CO)_4(CS)I]^-$ ($\nu(CS)$ 1195cm^{-1}) and $W(CO)(CS)(DPE)_2$ (1161cm^{-1}) readily reacted with alkylating reagents[35,47].

5.2 Substitution reaction of $Cr(CO)_5CS$

The photochemical reaction of $Cr(CO)_5CS$ with 1,3-dithiane afforded trans $Cr(CO)_4(CS)(S(CH_2)_3SCH_2)$. Minute quantities of another complex formed as well, but was only observed on developed thin layer chromatography plates. The trans $Cr(CO)_4(CS)(\overline{S(CH_2)_3SCH_2})$ allocation is based on the single $\nu(CO)$ frequency at 1940cm^{-1}. The thiocarbonyl frequency recorded at 1233cm^{-1}, is 31cm^{-1} lower than in the starting material. This can be explained in terms of the increased electron density on the chromium donated by the sulphur-donor atom of the 1,3-dithiane ligand.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

An interesting mass spectrum of the complex was obtained. Two distinct distintegration pathways can be seen and are illustrated below.

Pathway 1

$$[Cr(CO)_4(CS)(\overline{S(CH_2)_3SCH_2})]^+ \xrightarrow{-4\ CO} [Cr(CS)(\overline{S(CH_2)_3SCH_2})]^+$$

$$\xrightarrow{-CS} [Cr(\overline{S(CH_2)_3SCH_2})]^+ \xrightarrow{-S(CH_2)_3SCH_2} [Cr]^+$$

Pathway 2

$$[Cr(CO)_4(CS)(\overline{S(CH_2)_3SCH_2})]^+ \xrightarrow{-CS} [Cr(CO)_4(\overline{S(CH_2)_3SCH_2})]^+$$

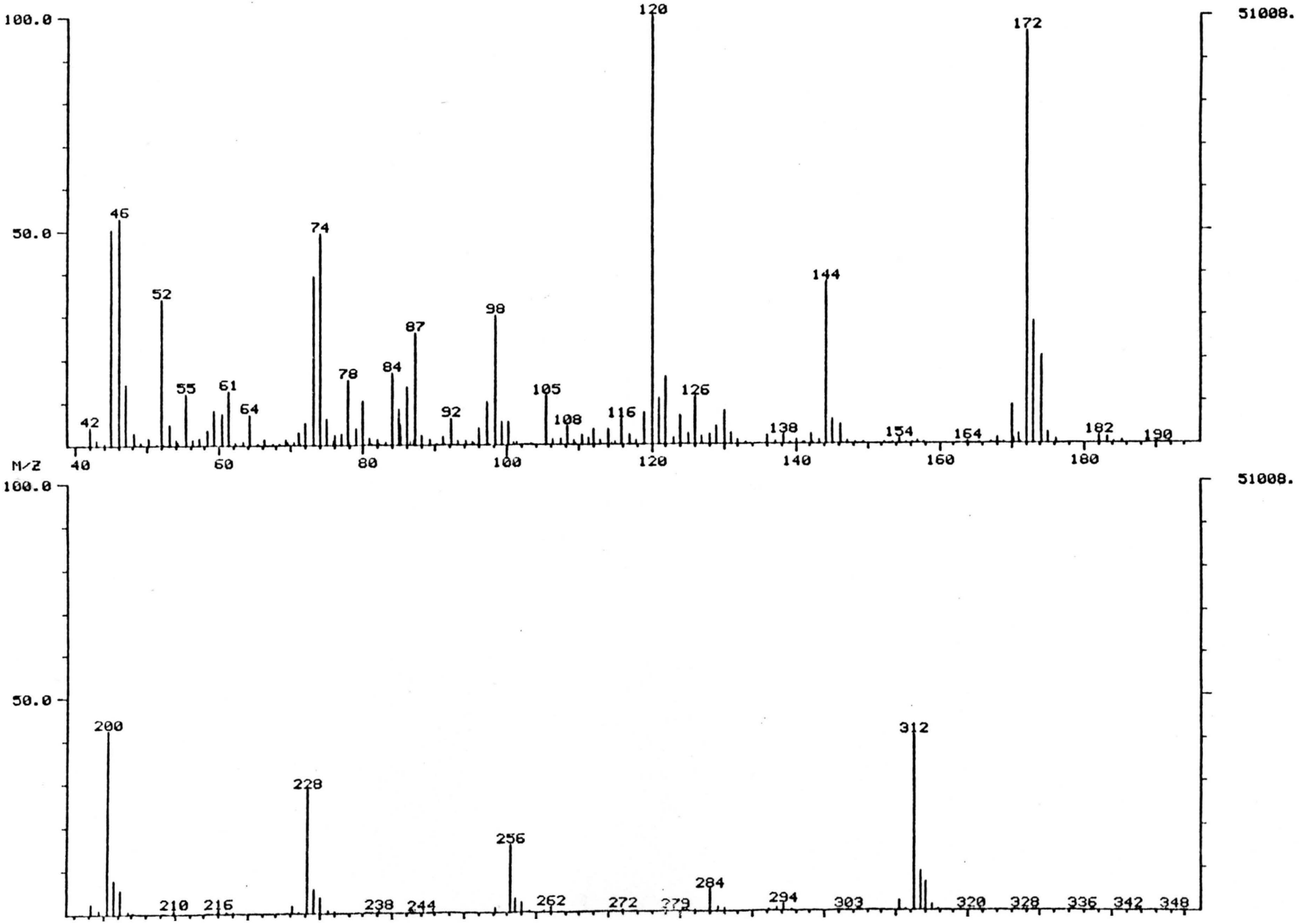
$$\xrightarrow{+CO} [Cr(CO)_5(\overline{S(CH_2)_3SCH_2})]^+ \xrightarrow{-5\ CO} [Cr(\overline{S(CH_2)_3SCH_2})]^+$$

$$\xrightarrow{-\overline{S(CH_2)_3SCH_2}} [Cr]^+$$

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

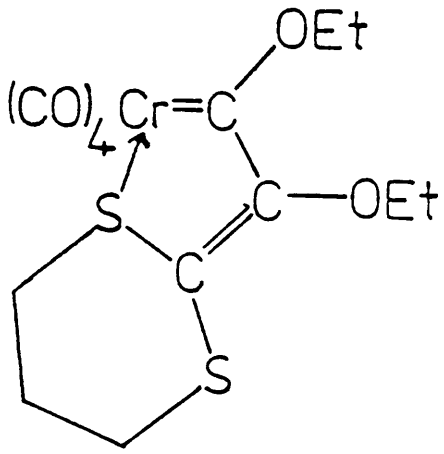
Mass spectrum of trans $Cr(CO)_4(CS)[S(CH_2)_3SCH_2]$ showing ion fragmentation



UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

5.3 Reaction of $Cr(CO)_5CS$ with $Li[\overline{S(CH_2)_3SCH}]$

The reaction of $Cr(CO)_6$ with the lithium (1,3-dithiane) salt gave a tetracarbonyl metallocyclic carbene-sulphur complex K indicated below.



K

Considering that a carbonyl insertion had to be involved in the formation of the complex, uncertainty surrounds the reaction mechanism. It was therefore decided to investigate the reaction of $Cr(CO)_5CS$ with Li $[\overline{S(CH_2)_3SCH}]$ in order to understand the involved mechanism by monitoring changes in thiocarbonyl frequencies. Four products were obtained and analyzed spectroscopically. The main product L is a yellow oil, the second product a blue complex M, the third product N is orange and lastly a brown product O was obtained. The spectroscopic properties of each of these complexes will be discussed.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

5.3.1 Infrared spectroscopy

From the carbonyl region in the Infrared it appears that L is a pentacarbonyl, M and N are trans tetracarbonyls and O a cis tetracarbonyl.

In the thiocarbonyl region complexes L and N showed no absorption while M and O showed a C - S bond order of approximately two. The possibility that a thioketene acted as donor ligand in M and O can be excluded owing to the absence of a ν(C=C=S) frequency at 1740cm^{-1} [51].

This implies that L and N contain modified thiocarbonyls, either thiocarbenes (:C(SEt)R) or thioethers (R_3C-SEt)[52] while M and O could contain thioketones. The Infrared absorptions are given in Table 13.

TABLE 13 IR frequencies of complexes L, M, N and O

Complex	ν(CO) (cm^{-1})	ν(CS) (cm^{-1})
L	1940(vs), 1979(w)	-
	2029(m)	
M	1938	1120
N	1934	-
O	1940, 1968, 1993	1119

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

5.3.2 Mass spectroscopy

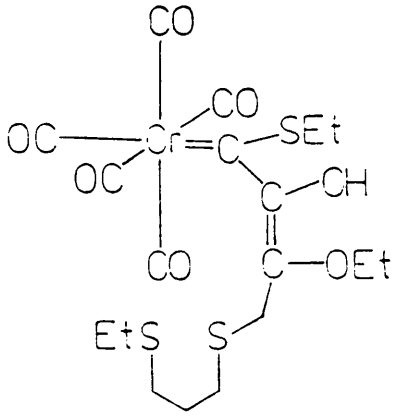
The molecular ion peak of the complexes in the mass spectrum were not observed but a fragment ion peak of 308 was observed in all four complexes. From this it was concluded that all four complexes consisted of similar fragments which are arranged in different order to give the molecular ion peak.

5.3.3 PMR spectroscopy

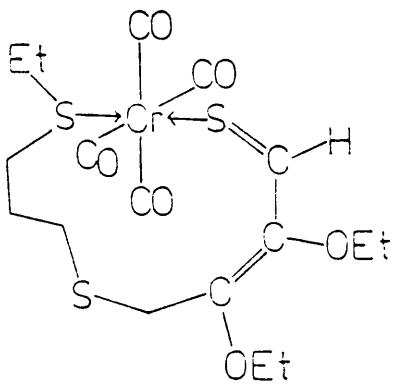
The proposed structures of L and M were largely based on the allocations made in the PMR spectra of the complexes. The first important conclusion derived from the spectra was the opening of the 1,3-dithiane ring. Such a ring opening has already been described[53].

Evidence for this conclusion is found in the comparison of the spectra of the closed ring.

The downfield peaks in L and N are comparable to protons found adjacent to a heteroatom bordering on the carbene carbon. However it is not certain whether the heteroatom is an oxygen or a sulphur atom. This chemical shift was not found in M. The proposed structures are illustrated below followed by Table 14 which shows the peak allocations.



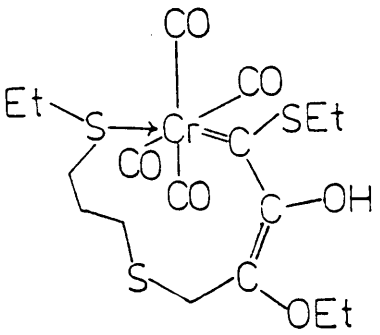
L



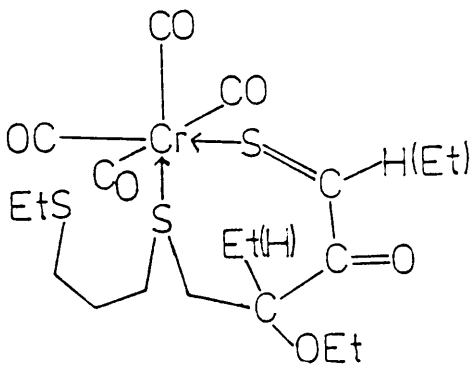
M

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA



N



O

TABLE 14 Chemical shifts of complexes L, M, N and O

Complex	Chemical shift
L	5,53-6,18 (m,2H,$SC\underline{H}_2$)
	4,11-4,58 (m,2H,$OC\underline{H}_2$)
	3,39-3,84 (m,2H,$OC\underline{H}_2$)
	2,78-3,03 (m,2H,CH_2-S-$C\underline{H}_2$)
	2,40 (s,2H,S-$C\underline{H}_2$-CH_2)
	1,98-2,34 (m,2H,S-CH_2-$C\underline{H}_2$)
	1,09-1,66(3 overlap. t,9H,X-$CH_2C\underline{H}_3$)
M	4,16 (s,1H,S=C($\underline{H}$)C)
	4,26(m,2H,C=C($OC\underline{H}_2CH_3$)-C)
	2,55-3,01 (m,6H,C-$C\underline{H}_2$-S,S-$C\underline{H}_2$-CH_2 and CH_2-$C\underline{H}_2$-S)
	2,25-2,58 (m,2H,CH_2-$C\underline{H}_2$-CH_2)
	1,13-1,56 (3 overlap. t,9H,X-$CH_2C\underline{H}_3$)
N and O	Similar peaks were obtained as for L and M

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

Additional observations for the substantiation of the proposed structures for M and O is the blue colour of the complex which is indicative of a sulphur coordinated thione as observed in the complex $(CO)_4 Cr[SC(SEt)C(Me)S(CH_2)_3S]$[54].

L and N are similar with respect to the organic ligand and L could possibly be converted to N and the cis isomer by photolysis.

The information supplied is insufficient to determine the reaction mechanism and further investigations are needed. In contrast to the $Cr(CO)_6$ case, the presence of the thiocarbonyl ligand seems to increase the reactivity of the trans carbonyl ligand and makes the carbonyl carbon more prone to nucleophilic attack.

5.4 Synthesis of products derived from $Cr(CO)_5CS$

5.4.1 Synthesis of trans tetracarbonyl (1,3 dithiane) chromium(0)

Owing to the high volatility of the $Cr(CO)_5CS$ complex, it was decided not to isolate this complex in crystal form. The autoclave reactions were thus carried out in a variety of different solvents (polar and non-polar) depending on the nature of the reactions to follow.

In this synthesis $Cr(\eta^6\text{-}C_6H_6)(CO)_2CS$ (2,30g, 10,00mmol) was dissolved in THF ($100cm^3$) and placed in the autoclave. Whilst stirring the solution a pressure of 130 bar carbon monoxide was applied and the

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

temperature of the solution was raised to 85°C. After 2,5 hours the solution was cooled to room temperature and the $Cr(CO)_5CS$ complex was obtained in high yield (>90%).

The $Cr(CO)_5CS$ solution was placed under nitrogen into the irradiation vessel with 1,3-dithiane (1,3g, 11,00mmol) and irradiated for six hours. The solvent was removed under reduced pressure and the product was purified by column chromatography (hexane:ether::2:1) to give a pure yellow oil (81%); $^{m}/_{e}$ 328(M^+).

5.4.2 Reaction of $Cr(CO)_5CS$ with $Li[\overline{S(CH_2)_3SCH}]$

As described above a solution of $Cr(CO)_5CS$ (1,18g, 5,00mmol) in ether ($75cm^3$) was obtained from the autoclave reaction.

1,3-Dithiane (0,60g, 5,00mmol) was dissolved in ether ($30cm^3$) and cooled to -25°C. To this solution BuLi ($4cm^3$ of a 1,8mol dm^{-3} solution) was added dropwise whilst stirring. The 1,3-dithiane salt was allowed to form over a period of 2 hours.

The prepared $Cr(CO)_5CS$ solution was slowly added to the 1,3-dithiane salt solution and the resulting mixture was stirred for another 2 hours at -25°C, thereafter for 1 hour at room termperature.

The solvent was removed under reduced pressure and the residue was dissolved in water ($70cm^3$). The salt solution was alkylated with $[Et_3O][BF_4]$ and the crude products L to O were obtained after extraction of the aqueous phase with ether (5 x $20cm^3$). The pure products L to O were obtained as oils after purification by column chromatography (hexane:dichloromethane::5:1).

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

CONCLUSION

Over the past 18 years a great deal of research has been carried out on the activation of CS and CS_2 by transition metal complexes. Nevertheless this field remains largely unexplored. In particular, little structural data on the 6 main types of thiocarbonyl complexes have been reported. In this work, a contribution to the end-to-end bridged thiocarbonyl was made.

The physical and chemical properties of thio- and selenocarbonyl complexes seem to point to the greater stability of these complexes compared to the analogous carbonyl ones, in agreement with theoretical predictions. This means that the present scarcity of metal-, thio- and selenocarbonyls is due to experimental procedure rather than the instability of the complexes.

The synthesis and reactivity of selenocarbonyl complexes will possibly be explored more extensively in the future, now that examples analogous to thiocarbonyl complexes have been reported.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

LITERATURE REFERENCES

1. W C Zeiss, Ann. Phys., 9 (1927) 932.
2. M P Schutzenberger, Annalen, 15 (1868) 100.
3. L Pauling, The Nature of the Chemical Bond, (1956) 385-392.
4. L Mond and F Quinke, J. Chem. Soc., 59 (1891) 604.
5. H Werner, Angew. Chem., 22 (1983) 927.
6. M C Baird and G Wilkinson, Chem. Comm., (1966) 514.
7. A J Chalk and J F Harrod, Organometal. Chem. Rev., 6 (1968) 119 and references therein.
8. I S Butler, Acc. Chem. Res., 10 (1977) 359.
9. B Nicholls and M C Whiting, J. Chem. Soc., (1959) 551.
10. G Jaouen and G Simmonneaux, Inorg. Synth., 19 (1978) 197.
11. I S Butler, N J Coville and D Cozak, J. Organometal Chem. 133 (1977) 59.
12. P Le Maux, G Simmonneaux, G Jaouen, L Ouahab and P Batial, J. Am. Chem. Soc., 100 (1978) 4312.
13. M Schindehutte, MSc Thesis, University of Pretoria, 1984.
14. G W Harris, M O Albers, J C A Boeyens and N J Coville, Organometallics, 2 (1983) 609.
15. N L Allinger, Organic Chemistry, Second Edition 1976, 343 - 348.
16. D G Carrol and S P McGlynn, Inorg. Chem., 7 (1968) 1285.
17. F A Cotton, A D Liehr and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1953) 175.
18. R.V. Emanuel and E W Randall, J. Chem. Soc. 17 (1969) 3002.
19. E O Fischer and S Schreiner, Chem. Ber., 92 (1959) 938.
20. A E Fenster and I S Butler, Can. J. Chem., 50 (1972) 598.
21. J O Glanville, J M Stewart and S O Grim, J. Organometal. Chem., 7 (1967) P 9.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

22. D Commereuc, I Douek and G. Wilkinson, J. Chem. Soc. A, (1970) 1771.

23. T Mizuta, T Suzaki and T Kwan, Nippon Kagaku Zasshi, 88 (1967) 573.

24. M Kubota and C R Carey, J. Organometal. Chem., 24 (1970) 491.

25. I S Butler and A E Fenster, J. Organometal. Chem., 66 (1974) 161.

26. A E Fenster and I S Butler, Inorg. Chem., 13 (1974) 914.

27. B D Dombek and R J Angelici, Inorg. Chem., 15 (1976) 1089.

28. L Busetto and R J Angelici, J. Am. Chem. Soc., 90 (1968) 3283.

29. W G Richards, Trans. Faraday Soc., 63 (1967) 257.

30. D L Lichtenberger and R F Fenske, Inorg. Chem., 15 (1976) 2015.

31. D Cozak and I S Butler, Spectrosc. Lett. 9(10)(1976) 673.

32. S S Woodard, R A Jacobson and R J Angelici, J. Organomet. Chem., 117 (1976) C75.

33. I S Butler, D Cozak and S R Stobart, Inorg. Chem., 16 (1977) 1779.

34. B D Dombek and R J Angelici, J. Am. Chem. Soc. 95 (1973) 7516.

35. B D Dombek and R J Angelici, J. Am. Chem. Soc. 97 (1975) 1261.

36. B D Dombek and R J Angelici, J. Am. Chem. Soc. 96 (1974) 7568.

37. J S Field and P J Wheatley, J. Chem. Soc., (1972) 2269.

38. J Y Saillard, G le Borgne and D Grandjean, J. Organometal. Chem., 94 (1975) 409.

39. P H Bird, A A Ismail and I S Butler, Inorg. Chem., 24 (1985) 2911.

40. R Arneri, A Efraty and M Huang, J. Am. Chem. Soc., 98 (1976) 639.

41. J W Dunker, J S Finer, J Clardy and R J Angelici, J. Organometal, Chem., 114 (1976) C49.

42. O Kolb and H Werner, Angew. Chem., 94 (1982) 207.

43. H Werner, K Leonhard, O Kolb, E Roettinger and H Vahrenkamp, Chem. Ber., 113 (1980) 1654.

44. B A Karcher and R A Jacobson, J. Organometal. Chem., 132 (1977) 387.

Digitised by the Department of Library Services in support of open access to information, University of Pretoria, 2022.