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THIOCARBONYL AND RELATED COMPLEXES OF THE TRANSITION METALS

PHILIP V. YANEFF

Department of Chemistry, Lash Miller Chemical Laboratories, University of Toronto, Toronto (Canada)

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CONTENTS

ABBREVIATIONS

diars = *o*-phenylenebisdimethylarsine
diphos = ethylenbis(diphenylphosphine)
PCy_3 = tricyclohexylphosphine
TCNE = tetracyanoethylene
THF = tetrahydrofuran
triphos = bis(2-diphenylphosphinoethyl)phenylphosphine

A. INTRODUCTION

Since an initial review on carbon disulphide complexes by Butler and Fenster [1], many new developments in the chemistry of carbon disulphide and thiocarbonyl complexes have appeared in the literature. It is now apparent that transition metal thiocarbonyl complexes may be prepared using either carbon disulphide or thiophosgene as the CS source. As over one hundred transition metal thiocarbonyl complexes have been reported, certain trends in their IR data and chemical reactivity have been observed and are correlated fully in this review.

After a survey of the various ways carbon disulphide may interact with a transition metal, the structure and bonding in these complexes will be examined using the data resulting from experimental techniques such as IR, NMR and X-ray crystallography. Finally, an area of interest which has recently received considerable attention is the reactivity of carbon disulphide and thiocarbonyl complexes towards nucleophilic and electrophilic reagents. The mode of attack and the nature of the products will be examined. The coverage of the literature is considered to be complete to November 1976.

B. CARBON DISULPHIDE COMPLEXES

I. σ-Bonded complexes

Relatively few examples of carbon disulphide complexes in which the ligand is bound to the metal solely through a sulphur atom have appeared in the literature. These σ-bonded CS_2 complexes coordinate at one site with no change in the oxidation state of the metal. The characteristic ν(S—C—S) vibration occurs in the 1500 cm^{-1} region, identical with that of liquid carbon disulphide and approximately 20 cm^{-1} lower than the gas phase frequency [2]. The few examples reported are, in some cases, not well characterized.

(i) Iron, ruthenium and osmium. The reaction of $Fe_2(CO)_9$ in carbon disulphide results in the isolation of $Fe(CO)_4(\pi\text{-}CS_2)$ and the formation of an orange solution proposed to contain $Fe(CO)_4(\sigma\text{-}CS_2)$, which could not be isolated [3]. The IR spectrum does not exhibit the ν(S—C—S) absorption characteristic of a σ-bonded CS_2 molecule but does show carbonyl absorptions corresponding closely to those found in $Fe(CO)_4L$ complexes.

Two similar products are obtained from the reaction of $Ru(CO)_2(PPh_3)_3$ with carbon disulphide [4]. The major product isolated is the π-complex, $Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ while the minor product, $Ru(CO)_2(PPh_3)_2(\sigma\text{-}CS_2)$ is obtained in 20% yield. The IR spectrum of this σ-bonded complex contains a medium intensity band at 1520 cm^{-1} but vacuum drying or recrystallization leads to its removal.

A complex which analyses as $RuCl_3(EPh_3)_2(CS_2)$(E= P,As) may be obtained from the reaction of $RuCl_3(EPh_3)_2MeOH$ with carbon disulphide under reflux conditions [5]. The only CS_2 absorption observed in the IR spectrum occurs at 1510 cm^{-1} which indicates a linearly bonded CS_2 group. The intensity of this band decreases upon recrystallization while drying the solid in vacuo has no effect on the solvated CS_2 group.

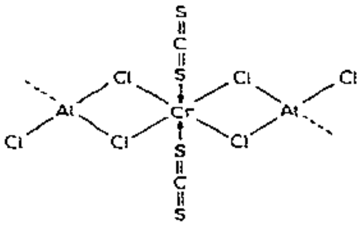
A σ-bonded CS_2 molecule has been observed as an intermediate in the insertion reaction of carbon disulphide into a transition metal—hydride bond [6]. In this reaction, $OsHCl(CO)(PCy_3)_2$ reacts in neat CS_2 to yield a complex which exhibited an IR absorption at 1510 cm^{-1}. The spectrum also contained bands at 917 and 790 cm^{-1} which were attributed to ν(CS) of the dithioformato complex, $OsCl(S_2CH)(CO)(PCy_3)_2$. Under more vigorous conditions, total conversion of the σ-bonded complex into the dithioformato complex was achieved.

(ii) Rhodium and iridium. $RhCl(PPh_3)_3$ readily reacts with CS_2 to give an unstable species which analyses as $RhCl(PPh_3)_2(CS_2)_2$ [7]. The IR spectrum of this complex exhibits strong absorptions at 1510 and 1028 cm^{-1} which are attributed to both σ- and π-bonded CS_2 ligands. The thiocarbonyl complex, *trans*-$RhCl(CS)(PPh_3)_2$ was also found to react with carbon disulphide yielding the cationic complex, $[Rh(CS)(PPh_3)_2(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$-$BPh_4$ [8].

Further examples of the σ-bonded species arise from the reaction of some iridium complexes with carbon disulphide [3,8]. The complex $IrCl(PPh_3)_3$ reacts with CS_2 to produce $[Ir(PPh_3)_3(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$. The salt, $[Ir(PPh_3)_3$-$(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$, slowly loses CS_2 at room temperature or pumping in a vacuum and results in the isolation of $[Ir(PPh_3)_3(\pi\text{-}CS_2)]^+$. A similar reaction was found to occur when *trans*-$IrCl(CS)(PPh_3)_2$ reacted with carbon disulphide. Initially, the complex $[Ir(CS)(PPh_3)_2(\sigma\text{-}CS_2)(\pi\text{-}CS_2)]^+$ is formed but the σ-bonded CS_2 is slowly lost to leave the π-complex, $[Ir(CS)(PPh_3)_2$-$(\pi\text{-}CS_2)]^+$. All these cationic iridium complexes were isolated as their tetraphenylborate salts.

(iii) Chromium. The only example of a σ-bonded CS_2 complex outside of the group VIII metals was reported by Brown and Hughes [9]. They

observed that the reaction of tricarbonyl benzene chromium with aluminum trichloride in nitromethane proceeds with quantitative loss of both the arene and carbonyl ligands of the π-complex. However, if carbon disulphide was used as solvent, they were able to isolate the crystalline product $Cr(AlCl_3)_2(CS_2)_2$(I). The IR spectrum of I gives a band at 1490 cm^{-1} which is the lowest value reported for a σ-bonded CS_2 molecule.

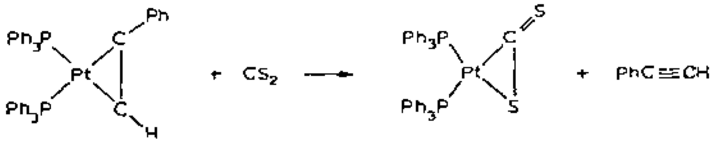


(I)

II. π-Bonded complexes

Two main synthetic techniques have been developed in the preparation of CS_2 complexes in which the ligand occupies two coordination sites on the metal. The most common involves oxidative addition of the metal. This preparative technique was first shown to be of synthetic value in the preparation of $M(PPh_3)_2(\pi\text{-}CS_7)(M{=}Pd,Pt)$ from $M(PPh_3)_4(M{=}Pd,Pt)$ and carbon disulphide [10,11]. This mode of coordination is readily characterized by bands appearing in the IR spectrum in the region 955—1235 and 632—653 cm^{-1}. These bands are assigned to the non-ring $\nu(C{=}S)$ vibration and the in-ring $\nu(C{-}S)$ vibrations, respectively.

The second synthetic procedure involves a ligand replacement reaction in which some formally unsaturated ligand is replaced by carbon disulphide. For example, the platinum complex, $Pt(PPh_3)_2(\pi\text{-}CS_2)$ may also be obtained by the displacement of the phenylacetylene group with carbon disulphide [12].

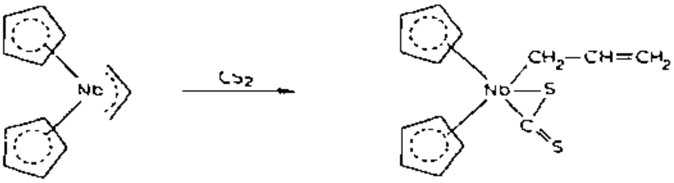


Although the oxidative addition of CS_2 to a transition metal has been the most common method of preparation, as in the complex species $(\eta^5\text{-}C_5H_5)_2V(\pi\text{-}CS_2)$ [3], $[RuCl(PPh_3)_3(\pi\text{-}CS_2)]Cl$ [13] and $IrI(CO)(PPh_3)_2(\pi\text{-}CS_2)$ [7], the ligand replacement reaction is a crucial step in the formation of the complex, $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\pi\text{-}CS_2)$ from $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and CS_2 [14].

At the time of publication of Butler and Fenster's review on carbon disulphide complexes [1], π-CS_2 complexes were limited to the group VIII platinum metals and manganese. Recently, the first π-CS_2 complexes of the metals niobium, osmium and cobalt have been reported in the literature.

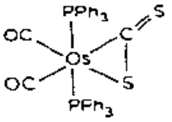
These will be discussed along with other new π-CS_2 complexes reported.

(i) Niobium. $(\eta^5$-$C_5H_5)_2Nb(\pi$-allyl) was found to react with carbon disulphide to form a red-violet solution from which red crystals of the complex II are isolated [15]. In this oxidative addition reaction of carbon disulphide, the π-allyl group rearranges to form a σ-allyl group.



(II)

(ii) Ruthenium and osmium. $Ru(CO)_2(PPh_3)_3$ reacts rapidly with carbon disulphide to form the octahedral complex $Ru(CO)_2(PPh_3)_2(\pi$-$CS_2)$ [16]. Its IR spectrum contains two carbonyl bands at 2010 and 1945 cm^{-1}, similar to bands at 2005 and 1945 cm^{-1} found in $Ru(O_2)(CO)_2(PPh_3)_2$ [17]. The two CO's are *cis* to each other and expected to be *trans* to the carbon disulphide. Preparation of the corresponding osmium complex, $Os(CO)_2(PPh_3)_2(\pi$-$CS_2)$ [16], required prior formation of $Os(CO)_2(PPh_3)_2(C_2H_4)$ (from $Os(CO)_2$-$(PPh_3)_3$ and C_2H_4) and reaction of ethylene adduct with stoichiometric amounts of carbon disulphide. The octahedral structure of complex III is illustrated.



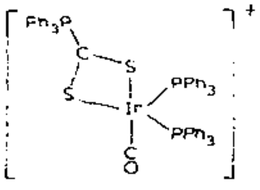
(III)

(iii) Cobalt and rhodium. Some new cyclopentadiene complexes of cobalt and rhodium have recently been reported [18,19]. The cobalt complex, $(\eta^5$-$C_5H_5)Co(PPh_3)_2$ was found to react rapidly with carbon disulphide to give the complex $(\eta^5$-$C_5H_5)Co(PPh_3)(\pi$-$CS_2)$ [18]. $(\eta^5$-$C_5H_5)Rh(PPh_3)_2$ only reacts with CS_2 slowly to produce the complex $(\eta^5$-$C_5H_5)Rh(PPh_3)(\pi$-$CS_2)$ [19]. This preparation was complicated by a side product, $(\eta^5$-$C_5H_5)$-$Rh(PPh_3)(CS_3)$, which could easily be removed by silica gel chromatography. This side product is considered to be similar to the product $IrCl(CS)(PPh_3)_2$-(CS_3) which has been reported for the reaction of $Ir(N_2)Cl(PPh_3)_2$ with CS_2 [20].

A green, paramagnetic complex consistent with the analytical formulation of $Co[P(OEt)_3]_3(\pi$-$CS_2)$ has just recently appeared in the literature [21]. It results from the reaction of $Co[P(OEt)_3]_4$ in carbon disulphide. The IR spectrum exhibits the characteristic $\gamma(CS)$ absorption at 1140 cm^{-1}.

(iv) Iridium. In 1968, Yagupsky and Wilkinson prepared a series of cationic π-CS_2 complexes of iridium and rhodium [8]. An X-ray structure of

$[Ir(CO)(PPh_3)_3(\pi\text{-}CS_2)]^+$ by Roper and co-workers [22] has shown that this is not a π-CS_2 complex but a 5 coordinate complex of iridium(I) containing the bidentate, sulphur-bound, triphenylphosphine—carbon disulphide zwitterion, as ligand. It seems probable that the other cationic iridium and rhodium complexes described in ref. 8 should now be reformulated similar to that of structure IV.

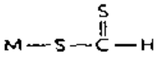


(IV)

III. CS_2 Insertion reactions

Carbon disulphide has the potential to insert into a variety of M—X bonds (M = transition metal; X=H, alkyl, amine, aryl, alkoxide, halide). Recently, significant developments in the insertion of CS_2 into a transition metal—hydride bond producing dithioformato complexes have been reported and it is these recent developments which will be discussed in this review. Also included are some earlier examples of iridium and platinum complexes, whose structural data are questionable now that numerous dithioformato complexes have been reported. For a coverage of the various insertions which may occur between a transition-metal complex and carbon disulphide see Butler and Fenster's review [1].

X-ray crystal data have revealed that the dithioformato ligand may be monodentate (V) or bidentate (VI) on the metal. Dithioformato complexes exhibit characteristic frequencies in their



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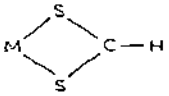


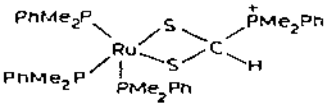
(VI)

IR spectra at 1215—1234, 908—930 and 775—784 cm^{-1}, which are attributed to the asymmetric stretching, symmetric stretching and bending modes, respectively, of the coordinated dithioformate. It would appear that proton NMR cannot differentiate between structures V and VI as well characterized examples of both coordination types have observed the dithioformato proton to absorb in the region δ 13.65—9.85 p.p.m. from internal TMS. Furthermore, there is no exchange of this proton with D_2O [23]. Examples of the monodentate coordination are very limited.

(i) Dithioformato complexes. Both $RuH_2(PPh_3)_4$ and $RuH_4(PPh_3)_3$ react with carbon disulphide to give the air stable product $Ru(S_2CH)_2(PPh_3)_2$ [24]. The IR spectrum contains three sets of bands at 1220, 1215; 915, 908; 782 and 775 cm^{-1} which were assigned to the asymmetric, symmetric and

bending modes of the coordinated dithioformates. The NMR spectrum contains a doublet due to the two dithioformato protons at δ 11.5 p.p.m. (J = 1.5 Hz). The proton splitting was reported to be field independent and must arise, therefore, from long range ^{31}P—H coupling. The presence of the doublet suggests that the two dithioformate groups are *cis* to one another, which was confirmed in a crystal structure [25,26].

The cationic dithioformato complex $[Ru(S_2CH)(PMe_2Ph)_4]PF_6$ has recently been synthesized by Singleton and co-workers from the reaction between CS_2 and $[RuH(PMe_2Ph)_5]PF_6$ [27]. It was observed to isomerize in methanol to the salt $[Ru\{S_2C(H)PMe_2Ph\}(PMe_2Ph)_3]PF_6$ (VII).

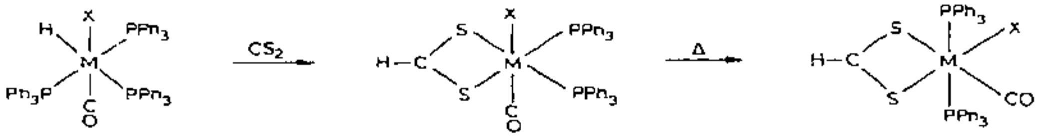


(VII)

The ^{1}H NMR spectrum of VII exhibits a unique hydrogen resonance at δ 6.25 p.p.m. which is much lower than expected for dithioformato group. The ^{13}C NMR spectrum shows the dithioformato carbon to be coupled to a ^{1}H nucleus and to one ^{31}P atom suggesting that the C—H bond of the S_2CH group had remained intact and that a phosphine ligand was attached to the dithioformato group. An X-ray structural determination is in accord with the experimental data.

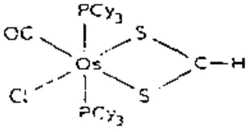
Recently, Robinson and Sahajpal reported a range of the insertion products resulting from the reaction of carbon disulphide with various transition metal—hydride complexes [28]. The hydrides $MHX(CO)(PPh_3)_3$ (M= Ru,Os; X= Cl,Br), $MH(OCOCF_3)(CO)(PPh_3)_3$(M= Ru,Os), $OsH_4(PPh_3)_3$, $IrHCl_2(PPh_3)_3$ and *mer*-$IrH_3(PPh_3)_3$ were found to react with CS_2 to form the dithioformato complexes, $MX(S_2CH)(CO)(PPh_3)_2$ (X= Cl,Br,$OCOCF_3$), $Os(S_2CH)_2(PPh_3)_2$, $IrCl_2(S_2CH)(PPh_3)_2$ and $IrH_2(S_2CH)(PPh_3)_2$, respectively. All complexes exhibit IR bands ca. 1215—1235 and 900—930 cm^{-1} attributed to $\nu(S_2CH)$ and NMR proton signals at δ 9.85 to 14.65 p.p.m.

The complexes $MX(S_2CH)(CO)(PPh_3)_2$(M= Ru,Os; X= Cl,Br) were found to exist in two isomeric forms which can easily be distinguished by their NMR spectra. If the reaction occurs under mild conditions, complex VIIIa is obtained which shows low-field proton NMR triplets at δ 11.87 p.p.m. [^4J(PH) ca. 8 Hz], while a more vigorous reaction produces complex VIIIb, whose NMR spectrum exhibits low-field triplets at δ 10.25 p.p.m. [^4J(PH) ca. 3 Hz].



(VIIIa) (VIIIb)

Moers et al. recently prepared some new carbonyl tricyclohexylphosphine complexes of ruthenium(II) and osmium(II) and studied their reaction with carbon disulphide [6,29,30]. The coordinatively unsaturated complexes, $MHX(CO)(PCy_3)_2$($M=Ru,Os$; $X=Cl,Br$) were observed to insert carbon disulphide into the metal—hydride bond forming the complexes $MX(S_2CH)(CO)(PCy_3)_2$. In the characterization of these complexes, they observed IR bands at 917 and 790 cm^{-1} which fall into the range accepted for the symmetric stretching and bending modes of the coordinated dithioformates. No NMR spectrum was obtained and as a result, the authors could not distinguish between structures IX or X, although IX is expected to be the more likely.



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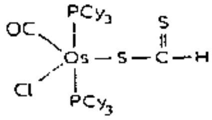


(X)

A recent investigation involved the insertion of CS_2 insertion into the platinum—hydride bond of *trans*-$PtH_2(PCy_3)_2$ [31]. The monodentate nature of the dithioformato ligand was confirmed by an X-ray structure of the product, *trans*-$PtH(S_2CH)(PCy_3)_2$. The IR spectrum exhibits the characteristic absorptions at 1240 and 1005 cm^{-1} of the dithioformato ligand while the proton NMR includes a resonance at δ 12.88 p.p.m. attributable to the dithioformato proton.

The kinetic results are in accord with a mechanism involving the addition of CS_2 to *trans*-$PtH_2(PCy_3)_2$ to give a five-coordinate labile intermediate, which rapidly collapses to the final product [31]. It is interesting to note that no reaction would occur between CS_2 and *trans*-$PtHCl(PCy_3)_2$ or *trans*-$PtH(S_2CH)(PCy_3)_2$ even under severe reaction conditions.

Monodentate dithioformato ligand is also proposed in a square planar platinum(II) system. Pallazzi et al. [32] characterized the products from the reaction of $PtHX(PPh_3)_2$ ($X=Cl,Br,I,CN$) with carbon disulphide. The IR spectrum of the product contains bands at 1050 and 930 cm^{-1} which are in the acceptable range for a dithioformato complex. The NMR spectrum shows a resonance at δ 2.05 p.p.m. which could be attributed to the proton attached to a carbon or a sulphur. As this value is not in the region acceptable for dithioformato complexes, it appears that further investigation in this system could prove useful. The formation of potassium dithioformate on treatment of this complex with potassium cyanide convinced the authors that the dithioformato ligand is monodentate in these complexes, with the proton attached to the carbon. Although they could not isolate a σ-bonded CS_2 intermediate as in the osmium case prior to insertion [6], kinetic data of the platinum system indicate that the CS_2 insertion occurs in two steps [32]. The proposed mechanism involves the formation of a five coordinate platinum complex containing a σ-bonded CS_2 molecule and then a

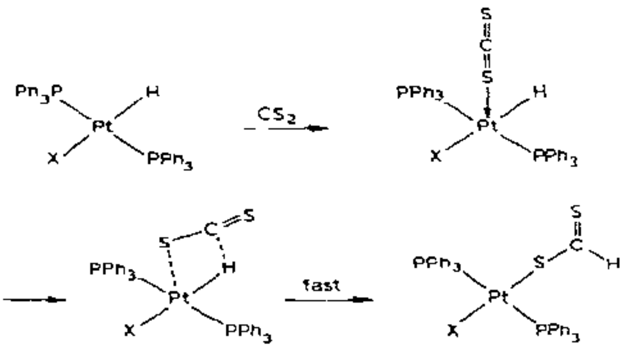


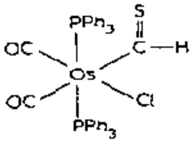
Fig. 1. Mechanism of CS$_2$ insertion into a Pt—H bond.

subsequent intramolecular migration of the hydride group as illustrated in Fig. 1.

Wilkinson and co-workers [33] reacted the iridium hydride complex IrH(CO)(PPh$_3$)$_3$ with CS$_2$ and monitored the reaction by NMR spectroscopy. The insertion product, proposed to be Ir(S$_2$CH)(CO)(PPh$_3$)$_2$, could not be definitively distinguished from Ir(CS$_2$H)(CO)(PPh$_3$)$_2$, due to lack of documentation on the chemical shift of the SH proton. The chemical shift observed around δ 5.0 p.p.m. may be indicative of the latter formulation.

IrH(CO)$_2$(PPh$_3$)$_2$ reacts with carbon disulphide to produce an iridium(III) species which contains two CS$_2$ molecules bonded per iridium atom [33]. Structures were proposed which fit the observed data and these were Ir(CO)(PPh$_3$)$_2$(π-CS$_2$)(CSSH) and Ir(CO)(PPh$_3$)$_2$(π-CS$_2$)(SSCH). No NMR signal for the proton was observed nor was any analysis reported for either compound. The dithioformato ligand might be expected to be monodentate in both these complexes.

Collins and Roper [34] recently reported the first example of a transition-metal thioformyl complex which results from the migratory-insertion of CS into the Os—H bond of OsHCl(CS)(PPh$_3$)$_3$ under CO. The IR spectrum of the product, Os(CHS)Cl(CO)$_2$(PPh$_3$)$_2$(XI) exhibits ν(CS) at 1010 cm^{-1} and ν(CO) at 2050 and 1970 cm^{-1}. In the proton NMR, the thioformyl proton appears at δ 16.97 p.p.m. [^3J(P—H) 2.2 Hz].

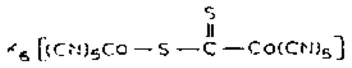


(XI)

IV. Bridging CS$_2$ complexes

Very few bridging CS$_2$ complexes have been reported. The first was K$_6$[(CN)$_5$CoCS$_2$Co(CN)$_5$] obtained from the reaction of K$_2$[Co(CN)$_5$] with

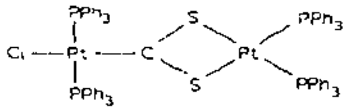
CS_2 [3,35]. There is some doubt in the manner by which the CS_2 molecule is bound to the cobalt atom although a recent study on the activation of CS_2 by metal carbonyl anions [36], would tend to support structure XII proposed by Wilkinson and co-workers [3].



$K_6[(CN)_5Co-S-\overset{\overset{S}{\|}}{C}-Co(CN)_5]$

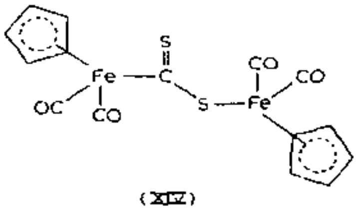
(XII)

A novel type of bridging CS_2 complex has been reported by Angelici and co-workers [37] who observed that the unstable thiocarbonyl complex, $[PtCl(CS)(PPh_3)_2]BF_4$, reacts with a solution of dichloromethane—hexane to give yellow crystals of the complex $[Cl(PPh_3)_2Pt(CS_2)Pt(PPh_3)_2]BF_4$. X-ray structural studies of complex XIII indicate square-planar geometry about each of the platinum atoms. It is interesting to note that if the second metal atom in both bridging CS_2 complexes is thought of as a hydrogen atom, these are the two ways a dithioformato ligand may bond to a transition metal.



(XIII)

An example of a bridging metallodithiocarboxylate group has been reported by Ellis et al. [38]. The complex, $(\eta^5\text{-}C_5H_5)(CO)_2FeCS_2Fe(CO)_2\text{-}(\eta^5\text{-}C_5H_5)$(XIV), results from the interaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with $(\eta^5\text{-}C_5H_5)Fe(CO)_2CS_2^-$.



(XIV)

In support of this formulation, the proton NMR spectrum of XIV in $CDCl_3$ exhibits only two sharp singlets at δ 5.17 and 5.03 p.p.m. which are due to the slightly different chemical environment of the cyclopentadienyl groups. The IR spectrum includes three ν(CS) bands at 1020, 1010 and 1000 cm^{-1}. The position and intensity of these bands are very similar to $(\eta^5\text{-}C_5Me_5)Fe(CO)_2CS_2Me$, which is known to have a monodentate MCS_2 group.

C. THIOCARBONYL COMPLEXES

I. Introduction

At the time of Butler and Fenster's review [1] about forty thiocarbonyl complexes had been well characterized and these were limited to the transition metals manganese, iron, ruthenium, rhodium and iridium. Since 1973 about eighty-five new thiocarbonyl complexes have appeared in the literature and these include the metals chromium, molybdenum, tungsten, osmium, nickel and platinum. These complexes will be discussed although ligand replacement reactions which result in the formation of new thiocarbonyl complexes will be reported in section E.

Terminal thiocarbonyl complexes are readily characterized from IR spectra by a very intense ν(CS) absorption in the range 1409—1161 cm^{-1} while ν(CS) for bridging thiocarbonyl complexes occurs in the range 1160—1106 cm^{-1}. This range almost certainly depends upon the oxidation state and the nature of the metal, although most metals are considered to be in a low oxidation state.

II. New thiocarbonyl complexes (Table 1)

(i) Chromium, molybdenum and tungsten. In a preliminary communication Dombek and Angelici [39] reported that the metal carbonyl anions $M_2(CO)_{10}^{2-}$ and $M(CO)_5^{2-}$ (M=Cr,Mo,W) were found to react with thiophosgene (Cl_2CS) to yield a mixture of $M(CO)_6$ and $M(CO)_5(CS)$ which could be separated by chromatographic techniques. The $Mo(CO)_5(CS)$ complex could not be isolated in pure form due to its apparent instability but the spectroscopic properties of the complex support its existence. The ν(CO) bands in the complexes were observed to occur at significantly higher frequencies than most other $M(CO)_5L$ complexes (e.g. $M(CO)_5(CNCH_3)$). This observation suggests that the thiocarbonyl group is effective at removing electron density from the metal.

In the full account Dombek and Angelici [40] give details for thiocarbonyl formation and a more convenient method of obtaining pure $W(CO)_5CS$. It is solely the $M_2(CO)_{10}^{2-}$ (M=Cr,W) dianions, produced from the reaction of $M(CO)_6$ with sodium amalgam in tetrahydrofuran, which react with excess thiophosgene to give, in very low yields, the thiocarbonyl complex $M(CO)_5$-(CS)(M=Cr,W). A more convenient method of obtaining $W(CO)_5(CS)$ involves the conversion of the $W(CO)_5(CS)/W(CO)_6$ mixture to $[WI(CO)_4$-$(CS)]NBu_4$ upon reaction with $I[NBu_4]$. This is possible as $W(CO)_6$ does not react under mild conditions and may be easily separated from the thiocarbonyl salt. The salt is then reacted with $AgBF_4$ under CO which reconverts it to $W(CO)_5(CS)$ in high yield. If ^{13}CO is used, then *trans*-$W(CO)_4$-$(^{13}CO)(CS)$ may be obtained in high yield [40[. Carbonyl substitution reactions such as the reaction of $M(CO)_5(CS)$ with ligands such as triphenylphosphine to yield the new thiocarbonyl complex, $M(CO)_4(CS)(PPh_3)$ will be discussed in section F.

TABLE 1

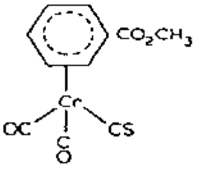
IR data of new thiocarbonyl complexes

Complex	ν(CS) (cm^{-1})	Medium	Ref.
$Cr(CO)_5(CS)$	1253	n-hexane	39
trans-$Cr(CO)_4(CS)(PPh_3)$	1230	CS_2	39
$Cr(CO)_3(CS)(diphos)$	1209	CS_2	40
$[CH_3CO_2\text{-}(\eta^6\text{-}C_6H_5)]Cr(CO)_2(CS)$	1225	CCl_4	41
$[CH_3CO_2\text{-}(\eta^6\text{-}C_6H_5)]Cr(CO)(CS)[P(OEt)_3]$	1201	CCl_4	41
$Mo(CO)_5(CS)$	1247	n-hexane	39
$W(CO)(CS)(diphos)_2$	1161	CH_2Cl_2	106
$[WH(CO)(CS)(diphos)_2]CF_3SO_3$	1207	CH_2Cl_2	106
trans-$W(CO)_4(CS)(PPh_3)$	1247	CS_2	39
trans-$W(CO)_4(CS)(NC_5H_5)$	1224	CS_2	39
$W(CO)_5(CS)$	1258	n-hexane	39
mer-$W(CO)_3(CS)(diphos)$	1215	CS_2	41
$WBr_2(CO)_2(CS)(PPh_3)_2$	1249	CS_2	105
$[WBr_3(CO)_3(CS)][2\text{-}CH_3\text{-}C_6H_4)_3PH]$	1260	KBr	105
$WI_2(CO)_2(CS)(diphos)$	1245	CS_2	105
$[WI(CO)(CS)(diphos)_2]I_3$	1232	CH_2Cl_2	105
$\{[W(CO)(diphos)_2(CS)]_2Ag\}BF_4$	1106	CH_2Cl_2	42
$W(CO)_3(CS)(diphos)$	1215	CS_2	40
$W(CO)_3(CS)(diars)$	1213	CS_2	40
$W(CO)(CS)(diphos)_2$	1161	CH_2Cl_2	40
[*trans*-$WI(CO)_4(CS)]NBu_4$	1195	CH_2Cl_2	40
[*trans*-$WBr(CO)_4(CS)]NBu_4$	1193	CH_2Cl_2	40
[*trans*-$WCl(CO)_4(CS)]NBu_4$	1193	CH_2Cl_2	40
mer-$W(CO)_3(CS)(bipy)$	1203	CS_2	40
$(\eta^5\text{-}C_5H_5)Mn(CS)(diphos)$	1206	CS_2	69
$\gamma\text{-}(\eta^5\text{-}C_5H_5)Mn(CS)(triphos)$	1203	CS_2	69
$\phi\text{-}(\eta^5\text{-}C_5H_5)Mn(CS)(triphos)$	1206	CS_2	69
$\gamma\text{-}(\eta^5\text{-}C_5H_5)(CS)Mn(triphos)Mn(CO)_2(\eta^5\text{-}C_5H_5)$	1204	CS_2	69
$\phi\text{-}(\eta^5\text{-}C_5H_5)(CS)Mn(triphos)Mn(CO)_2(\eta^5\text{-}C_5H_5)$	1208	CS_2	69
$\gamma\text{-}(\eta^5\text{-}C_5H_5)(CS)Mn(triphos)Cr(CO)_5$	1205	CS_2	69
$\phi\text{-}(\eta^5\text{-}C_5H_5)(CS)Mn(triphos)Cr(CO)_5$	1209	CS_2	69
$(\eta^5\text{-}C_5H_5)Mn(CS)(triphos{=}0)$	1203	CS_2	69
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)[P(OPh)_3]$	1254	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CS)(PMe_2Ph)_2$	1195	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CS)(PPh_3)_2$	1193	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CS)[P(OEt)_3]_2$	1214	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CS)[P(OMe)_3]_2$	1218	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CS)[P(OPh)_3]_2$	1219	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CS)[P(OCH_2CH_2Cl)_3]_2$	1223	CS_2	68
$[(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(NO)]SbF_6$	1339	KBr	45
$[CH_3\text{-}(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(NO)]^+$	1139	KBr	45
$[(\eta^5\text{-}C_5H_5)Mn(CS)(NO)(PPh_3)]^+$	1310	KBr	45
$[(\eta^5\text{-}C_5H_5)Mn(CS)(NO)(AsPh_3)]^+$	1310	KBr	45
$[(\eta^5\text{-}C_5H_5)Mn(CS)(NO)(SbPh_3)]^+$	1308	KBr	45
$[(\eta^5\text{-}C_5H_5)Mn(CS)(NO)]_2$	1150, 1118	KBr	47
$[CH_3\text{-}(\eta^5\text{-}C_5H_4)Mn(CS)(NO)]_2$	1123	KBr	47
$(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$	1266	CS_2	14
$[CH_3\text{-}(\eta^5\text{-}C_5H_4)]Mn(CO)_2(CS)$	1271	Nujol	
	1262	CS_2	14

TABLE 1 (cont'd)

Complex	ν(CS) (cm^{-1})	Medium	Ref.
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)[P(C_6H_{11})_3]$	1222	CS_2	68
	1230	n-hexane	68
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(PMe_2Ph)$	1228	CS_2	68
	1234	hexane	
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(PPh_3)$	1231	CS_2	68
	1236	hexane	
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(AsPh_3)$	1231	CS_2	68
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(SbPh_3)$	1230	CS_2	68
	1237	hexane	68
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)[P(OEt)_3]$	1236	CS_2	68
	1243	hexane	
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)[P(OMe)_3]$	1239	CS_2	68
	1245	hexane	
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)[P(OCH_2CH_2Cl)_3]$	1240	CS_2	68
	1247	hexane	
$[(\eta^5\text{-}C_5H_5)Mn(CO)(CS)]_2(diphos)$	1226	CS_2	14
	1230	Nujol	
$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)_2$	1305, 1235	CS_2	14
	1308, 1240	Nujol	
$(\eta^5\text{-}C_5H_5)Mn(CS)_2(C_8H_{14})$	1289, 1217	CS_2	14
$(\eta^5\text{-}C_5H_5)Mn(CS)_3$	1338, 1240	CS_2	14
trans-$[\eta^5\text{-}C_5H_5)Fe(CO)(CS)]_2$	1131	CS_2	48
cis-$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)]_2$	1124	CS_2	48
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CSCH_3)(CO)_2(CS)]^+$	1178	CH_2Cl_2	48
$[(\eta^5\text{-}C_5H_5)Fe(CS)(CNC_6H_5)]PF_6$	1310	CH_2Cl_2	79
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)[P(C_5H_4F)_3)]PF_6$	1325	Nujol	79
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)(PCy_3)]PF_6$	1315	Nujol	79
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)(P(C_6H_4OCH_3)_3)]PF_6$	1310	Nujol	79
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)(PPh_3)]PF_6$	1320	Nujol	79
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)(SbPh_3)]PF_6$	1321	Nujol	79
$[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)(AsPh_3)]PF_6$	1325	Nujol	79
$RuCl_2(CO)(CS)(PPh_3)_2$	1302	Nujol	16
$RuBr_2(CO)(CS)(PPh_3)_2$	1298	Nujol	4
$RuI_2(CO)(CS)(PPh_3)_2$	1290	Nujol	4
$RuI(OH)(CO)(CS)(PPh_3)_2$	1295	Nujol	4
$[RuCl_2(CS)(PPh_3)_2]_2$	1290	Nujol	49
$(PPh_3)_2ClRuCl_3Ru(CS)(PPh_3)_2$	1284	Nujol	49
$(PPh_3)(CS)ClRuCl_3Ru(CS)(PPh_3)_2$	1300	Nujol	49
$(PPh_3)Cl_2RuCl_3Ru(CS)(PPh_3)_2$	1303	Nujol	49
$[RuCl_3(CS)(PPh_3)_2]BPh_4 \cdot 2(CH_3)_2CO$	1272	Nujol	49
$OsHCl(CS)(PPh_3)_3$	1280	Nujol	34
$OsHCl(CO)(CS)(PPh_3)_2$	1295	Nujol	34
$OsCl_2(CO)(CS)(PPh_3)_2$	1315	Nujol	16
$[IrCl_2(CO)(CS)(PPh_3)_2]PF_6$	1409	Nujol	52
$IrCl_3(CS)(PPh_3)_2$	1368	Nujol	52
$Ni(CS)_4$	1305	—	53
$[PtCl(CS)(PPh_3)_2]^+$	1400	—	37

The reaction of $[CH_3CO_2\text{-}(\eta^6\text{-}C_6H_5)]Cr(CO)_2(\eta^2\text{-}C_8H_{14})$ with carbon disulphide in the presence of triphenylphosphine gives complex XV in 60% yield [41]. The formation of the thiocarbonyl complex probably proceeds via prior formation of a π-CS_2 complex which is subsequently attacked by the triphenylphosphine in a manner analogous to that of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ [14].



(XV)

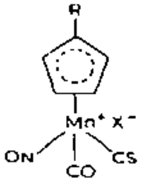
The reaction of $W(CO)(CS)(diphos)_2$ with $W(CO)_5(acetone)$ in dichloromethane yields the complex $(diphos)_2(CO)WCSW(CO)_5$ [42]. This is the first complex reported to contain a linear bridging thiocarbonyl ligand. The $\nu(CS)$ stretching frequency of the linear thiocarbonyl ligand was indirectly observed to be under the diphos ligand absorption at 1095 cm^{-1}. Similar adducts are formed with silver and mercury salts. In the silver case, silver tetrafluoroborate reacts with two moles of $W(CO)(CS)(diphos)_2$ to give the dimer, $[(diphos)_2(CO)WCSAgSCW(CO)(diphos)_2]BF_4$ which has $\nu(CS)$ at 1106 cm^{-1}.

(ii) Manganese. The first thiocarbonyl complex of manganese $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ has been prepared in low yield by the reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_8H_{14})$ with carbon disulphide [43]. When the reaction is repeated in the presence of triphenylphosphine, the reaction occurs rapidly in quantitative yield [14]. Substituents on the cyclopentadiene ring do not affect the reaction as $[CH_3\text{-}(\eta^5\text{-}C_5H_4)]Mn(CO)_2(\eta^2\text{-}C_8H_{14})$ reacts with carbon disulphide yielding the thiocarbonyl complex, $[CH_3\text{-}(\eta^5\text{-}C_5H_4)]Mn(CO)_2(CS)$.

Kinetic data and IR evidence suggest that thiocarbonyl formation proceeds by an S_N1 mechanism which involves slow loss of C_8H_{14} in the rate determining step forming the coordinatively unsaturated species, $(\eta^5\text{-}C_5H_5)Mn(CO)_2$. This species then undergoes a rapid reaction with carbon disulphide, followed by sulphur abstraction by triphenylphosphine [14].

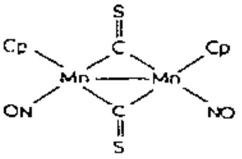
Thiocarbonyl complexes such as $(\eta^5\text{-}C_5H_5)Mn(CO)(CS)_2$ and $(\eta^5\text{-}C_5H_5)Mn(CS)_3$, which are the only examples known to contain more than one thiocarbonyl group per metal atom (except $Ni(CS)_4$ which is matrix isolated), may be prepared by various photochemical and ligand replacement reactions [44]. These will be discussed in section F.

Some new transition-metal thiocarbonyl nitrosyl complexes have been reported by Efraty et al. [45], who synthesized the $[R\text{-}(\eta^5\text{-}C_5H_4)Mn(CO)(CS)(NO)]^+(R{=}H,CH_3)$ cation (XVI) from the reaction of $[R\text{-}(\eta^5\text{-}C_5H_4)]Mn(CO)_2(CS)$ with either $NOSbF_6$ or NO_2PF_6. As well as thiocarbonyl absorptions in the 1339—1308 cm^{-1} region, these complexes exhibit ν(NO) absorptions in the region 1793—1847 cm^{-1}. These values are in the region accepted for linear *sp* hybridized species [46].

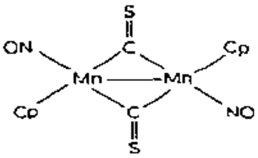


(XVI)

The dimeric complex $[(\eta^5\text{-}C_5H_5)Mn(CS)(NO)]_2$, is obtained when $(\eta^5\text{-}C_5H_5)Mn(CS)(NO)I$ is reacted with zinc dust in diglyme solution [47]. The low thiocarbonyl frequencies of 1150 and 1118 cm^{-1} suggest it is a bridging thiocarbonyl ligand. The ^1H NMR spectrum consists of two singlets due to the cyclopentadiene group which suggests a mixture of the *cis* (XVII) and *trans* (XVIII) isomers.



(XVII)



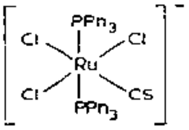
(XVIII)

(iii) Iron, ruthenium and osmium. In a recent communication Angelici and co-workers [48] reported the preparation and structure of $[(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(CS)]_2$, the thiocarbonyl analogue of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. It is synthesized by reacting $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]CF_3SO_3$ with sodium hydride in tetrahydrofuran. A mixture of *cis* and *trans* isomers is produced but these may be separated by chromatography. The IR data for the *trans* isomer show ν(CS) at 1131 cm^{-1} and a single ν(CO) at 1979 cm^{-1}, while the *cis* isomer shows ν(CS) at 1124 cm^{-1} and ν(CO) at 2011 and 1982 cm^{-1}. These data are consistent with bridging CS groups and terminal CO groups, and are confirmed by an X-ray structure [48]. The above complex $[(\eta^5\text{-}C_5H_5)\text{-}Mn(CS)(NO)]_2$ may be considered to be analogous to this complex of iron.

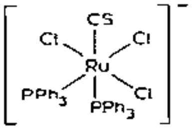
Ruiz-Ramirez et al. showed that the reaction of $[RuCl_3(EPh_3)_2MeOH]$-(E=P,As) with carbon disulphide gives a σ-bonded CS_2 complex [5]. When the bromo-analogue, $[RuBr_3(EPh_3)_2MeOH]$ reacts with carbon disulphide a thiocarbonyl complex which analyses as $RuBr_3(CS)(EPh_3)_2$(E=P,As) is isolated. Shorter reaction times give a mixture of the thiocarbonyl complex and the σ-bonded complex $RuBr_3(EPh_3)_2(\sigma\text{-}CS_2)$.

When the thiocarbonyl complex $[RuCl_2(CS)(PPh_3)_2]_2$, prepared earlier by Wilkinson and co-workers [13] reacts with Ph_4AsCl/HCl in acetone for several days, the new thiocarbonyl complex $Ph_4As[RuCl_3(CS)(PPh_3)_2]$ ·

$2Me_2CO$ is obtained [49]. This complex has a ν(CS) absorption at 1272 cm^{-1} in the IR and a strong absorption at 320 cm^{-1} which is characteristic of a *trans* $RuCl_2$ arrangement consistent with either structure XIXa or XIXb.

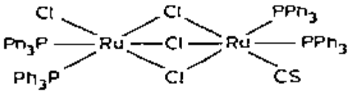


(XIXa)



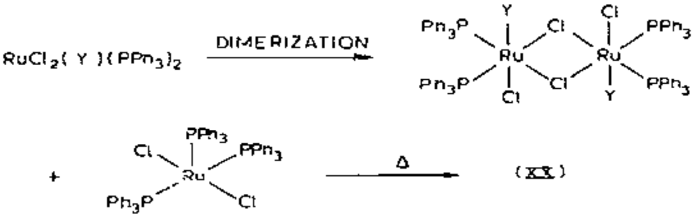
(XIXb)

An attempt to prepare the complex ion $[RuX(PPh_3)_3(\pi\text{-}CS_2)]^+$(X= Cl,Br) as reported by Wilkinson and co-workers [13] resulted in the formation of the dimeric species $[(Ph_3P)_2ClRuCl_3Ru(CS)(PPh_3)_2]$ [49]. The structure XX is consistent with the analytical data and ^{31}P NMR spectrum of this complex.



(XX)

It was originally believed that the tri-μ-chloro complex (XX) was formed from $[(Ph_3P)_2Cl(CS)RuCl_2RuCl(CS)(PPh_3)_2]$ by an intramolecular transfer of chloride ion which was accompanied by displacement of a thiocarbonyl group. Attempts to carry out this conversion have been unsuccessful so an alternate mechanism has been suggested [50]. Good evidence for the feasibility of this mechanism has been obtained from the synthesis of the corresponding carbonyl complexes.



(Y = CO,CS)

The dimeric complex $[RuCl_2(CS)(PPh_3)_2]_2$ [13] reacts with acetone to yield yellow crystals which analyse as $[(Ph_3P)(CS)ClRuCl_3Ru(CS)(PPh_3)_2]\cdot Me_2CO$ [49]. The structure of this complex is proposed to be analogous to XX. In support of this structure, the IR spectrum exhibits a thiocarbonyl absorption at 1300 cm^{-1} and bands at 326, 288 and 259 cm^{-1} which may indicate both terminal and bridging chloride ligands. The ^{31}P NMR spectrum of the complex consists of strong peaks at 48.1 and 37.7 p.p.m. of relative intensity 1 : 2. This spectrum is considered to be analogous to the ^{31}P NMR spectrum of the complex $[(Ph_3P)_2ClRuCl_3Ru(CO)(PPh_3)_2] \cdot Me_2CO$ [49].

Roper and co-workers [16] synthesized some thiocarbonyl compounds of ruthenium and osmium. Both $Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ and $Os(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ can be converted to the thiocarbonyl derivatives $RuCl_2(CO)(CS)(PPh_3)_2$ and $OsCl_2(CO)(CS)(PPh_3)_2$. Because of the similarity between these thiocarbonyl complexes and the selenocarbonyl complex $RuCl_2(CO)(CSe)(PPh_3)_2$ of known structure [51], both thiocarbonyl complexes are believed to have a *trans* arrangement of phosphines and a *cis* arrangement of the CO and CS ligands. The very high ν(CO) value of 2050 cm^{-1} in these thiocarbonyl complexes is attributable to the marked π-acceptor capacity of the CS ligand.

Subsequently Roper and co-workers [108] reported the first example of an osmium (0) thiocarbonyl complex. They observed that $[Os(CO)_2(PPh_3)_2(CS_2Me)]I$ reacts with $NaBH_4$ to give $Os(CO)_2(CS)(PPh_3)_2$ and MeSH. Collins and Roper [34] also described the complex $OsHCl(CS)(PPh_3)_3$ and its reaction with carbon monoxide to yield $OsHCl(CS)(CO)(PPh_3)_2$.

(iv) Rhodium and iridium. Thiophosgene (Cl_2CS) has been used as the CS source in a new route to some thiocarbonyl complexes of iridium (III) and rhodium (III) [52]. Curtis and Kubota [52] reported the reaction of thiophosgene with $IrCl(N_2)(PPh_3)_2$, $[Ir(CO)(CH_3CN)(PPh_3)_2]PF_6$ and $RhCl(PPh_3)_3$ to yield the six-coordinate products $IrCl_3(CS)(PPh_3)_2$, $[IrCl_2(CO)(CS)(PPh_3)_2]PF_6$ and $RhCl_3(CS)(PPh_3)_2$, respectively. Although thiophosgene was found to react with $[Rh(CO)_2Cl]_2$, $[RhCl(CO)_2(PPh_3)_2]_2$ and $IrCl(CO)(PPh_3)_2$, no definite products were reported.

(v) Nickel and platinum. The matrix isolation technique is responsible for the synthesis of the first thiocarbonyl complex of nickel. The cocondensing of nickel atoms and a mixture of CS and argon results in the formation of $Ni(CS)_4$ [53]. This is the only example of a complex which contains only the thiocarbonyl ligand in the coordination sphere of the metal. This complex was detected from a mass spectrum, which contained peaks corresponding to the parent ion of $Ni(CS)_4$, and from the IR spectrum which exhibited ν(CS) at 1305 cm^{-1}.

Evidence for the thiocarbonyl complex $[PtCl(CS)(PPh_3)_2]BF_4$ has been reported by Angelici and co-workers [37] from the reaction of $PtCl[C(S)OMe](PPh_3)_2$ in dichloromethane with boron trifluoride. The IR spectrum of this complex shows a very strong absorption at 1400 cm^{-1} which is attributed to ν(CS). Hydrolysis of the CS ligand readily occurs; the 1400 cm^{-1} absorption of the CS ligand disappears with the appearance of a new absorption at 2115 cm^{-1} from ν(CO) of the hydrolysis product, $[PtCl(CO)(PPh_3)_2]^+$.

$[PtCl(CS)(PPh_3)_2]^+$ has also been prepared from the reaction of thiophosgene with $Pt(PPh_3)_3$ or $Pt(PPh_3)_2(C_2H_4)$ [52]. The IR spectrum consists of a strong absorption at 1400 cm^{-1} attributed to ν(CS) of the cationic thiocarbonyl and a weaker absorption at 2105 cm^{-1}, which shows some decomposition to the carbonyl complex has occurred.

D. SELENOCARBONYL COMPLEXES

For many years, it has been known that both CO and CS complexes may be readily synthesized and attempts to isolate the analogous CSe species have been unsuccessful, even at very low temperatures [54]. Although recent investigations have resulted in the formation of carbon diselenide complexes of nickel and rhodium [55], ruthenium [51], iridium [56] and platinum [55,56], only $Ru(CO)_2(PPh_3)_2(\pi\text{-}CSe_2)$ has been successfully converted into a selenocarbonyl complex.

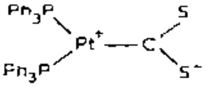
Butler et al. [57] reported that both $(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)$ and $[CH_3CO_2\text{-}(\eta^6\text{-}C_6H_5)Cr(CO)_2(THF)]$ react with CSe_2 in the presence of excess triphenylphosphine to give the selenocarbonyl complexes, $(\eta^5\text{-}C_5H_5)\text{-}Mn(CO)_2(CSe)$ and $[CH_3CO_2\text{-}(\eta^6\text{-}C_6H_5)Cr(CO)_2(CSe)]$. These complexes were characterized from the extremely intense ν(CSe) absorption in the IR at 1105 and 1071 cm^{-1}, respectively.

In a manner similar to the preparation of $RuX_2(CO)(CS)(PPh_3)_2$ (X=Cl,Br,I) [16], Roper and co-workers [51] synthesized the corresponding selenocarbonyl derivative, *cis*-$RuX_2(CO)(CSe)(PPh_3)_2$. An X-ray structural determination of the dichloro complex confirms the similarity between CS and CSe as potential ligands in metal complexes.

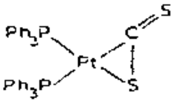
E. STRUCTURE AND BONDING

1. π-CS_2 complexes (Table 2)

When Baird and Wilkinson isolated the novel complex $Pt(PPh_3)_2(\pi\text{-}CS_2)$ [10], they proposed two possible structures for this compound; XXIa being similar to that of $Et_3P^+CS_2^-$, while XXIb is similar to that proposed for $Pt(PPh_3)_2(\pi\text{-}C_2H_2)$. Structure XXIb was favoured and this was subsequently confirmed in an X-ray structure determination [11].

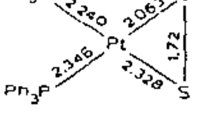


(XXIa)



(XXIb)

More recently, this structure was reinvestigated by Mason and Rae [58] and their relevent data are presented.



$<Ph_3P-Pt-PPh_3$	107.1°
$<Ph_3P-Pt-S$	107.9°
$<S-C-S$	136.2°

It appears that upon coordination to a transition metal, the linear CS_2 molecule becomes bent with an S—C—S bond angle of 136.2° and a mean

TABLE 2

Carbon—sulphur absorptions for new π-CS_2 complexes

Complex	ν(C=S) (cm^{-1})	Ref.
$(\eta^5$-$C_5H_5)_2(\sigma$-allyl$)Nb(\pi$-$CS_2)$	1135	15
$Ru(CO)_2(PPh_3)_2(\pi$-$CS_2)$ [a]	1118	16
$Os(CO)_2(PPh_3)_2(\pi$-$CS_2)$ [a]	1118	16
$(\eta^5$-$C_5H_5)Co(PPh_3)(\pi$-$CS_2)$	1115, 1170	18
$Co[P(OEt)_3]_3(\pi$-$CS_2)$	1140	31
$(\eta^5$-$C_5H_5)Rh(PPh_3)(\pi$-$CS_2)$	1180	19

[a] Medium : Nujol.

C—S bond length of 1.626 Å. In the free molecule, this bond length is 1.554 Å, so it seems that the lower bond order upon coordination could result from either ligand-to-metal charge transfer or electron transfer from the metal to antibonding orbitals of the ligand or both.

The coordination of CS_2 to the metal centre affects the metal—phosphine bonds in two ways. Firstly, the large P—Pt—P bond angle of 107.1° results from the necessity to reduce the non-bonded repulsions between phenyls which is not observed with the corresponding angle in carbonatobis(triphenylphosphine)platinum of 98.5° [59]. In an alternate explanation, it is proposed [58] that the large bond angle in the CS_2 complex may reflect the fact that only the CS_2 ligand has appreciable Lewis acid properties and that *d*-orbital involvement in the metal—phosphorus bonds in $Pt(PPh_3)_2(\pi$-$CS_2)$ is consequently less than in the corresponding carbonato complex. The second point involves the *trans*-bond weakening effect of the CS_2 ligand. The suggested explanation includes the idea that the overlap of metal *d*-orbitals with the carbon will be greater than that with sulphur so that the Pt—P bond *trans* to the carbon atom will have a lower π-character than that *trans* to the sulphur.

Finally, Mortimer et al. [60] showed from solution calorimetry that the strength of the Pt—CS_2 bond in $Pt(PPh_3)_2(\pi$-$CS_2)$ is slightly stronger than the corresponding Pt—C_2H_4 bond in $Pt(PPh_3)_2(\pi$-$C_2H_4)$.

II. Dithioformato complexes (Table 3)

Since the initial preparation of the dithioformato complex $Ir(S_2CH)(CO)(PPh_3)_2$ by Wilkinson and co-workers [33], the insertion reaction of CS_2 into a metal—hydride bond has become of great interest. In this com-

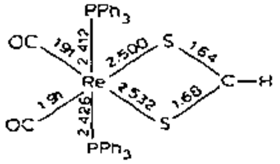


TABLE 3

Carbon—sulphur absorptions (cm^{-1}) for new dithioformato complexes

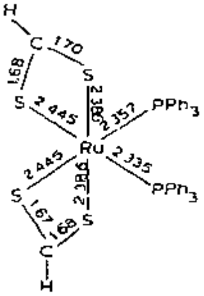
Complex [a]	$\nu_{asym}(S_2CH)$	$\nu_{sym}(S_2CH)$	Ref.
$Ru(S_2CH)_2L_2$ [b]	1220, 1215 [c]	915, 908	24
$RuCl(S_2CH)(CO)L_2$	1230	925	28
$RuCl(S_2CH)(CO)(PCy_3)_2$ [c]	—	917	29
$RuBr(S_2CH)(CO)L_2$	1235	925	28
$RuBr(S_2CH)(CO)(PCy_3)_2$ [d]	—	923	30
$Ru(S_2CH)(OCOCF_3)(CO)L_2$	1230	925	28
$Os(S_2CH)_2L_2$	1220, 1215	910, 902	28
$OsCl(S_2CH)(CO)L_2$	1235	920	28
$OsCl(S_2CH)(CO)(PCy_3)_2$ [c]	—	912	29
$IrH_2(S_2CH)L_2$	1235	930	28
$IrCl_2(S_2CH)L_2$	1230	915	28
trans-$PtH(S_2CH)(PCy_3)_2$	1240	1005	31

[a] $L = PPh_3$. [b] $\delta(S_2CH)$ 784, 775 cm^{-1}. [c] Medium: Nujol. [d] Medium: KBr.

plex, the authors could not distinguish between a $-CS_2H$ or $-S_2CH$ mode of bonding. The latter form was suggested to be correct when a crystal structure of the dithioformato complex $Re(S_2CH)(CO)_2(PPh_3)_2$ was obtained [61].

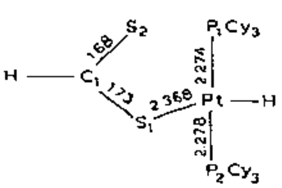
The overall structure of this compound has octahedral coordination around the rhenium atom. The observed equivalence of the two S—C and two Re—S bonds in the complex indicates that the electron density is the same on both sulphur atoms and supports the electronic distribution of complete delocalization similar to that of carboxylate anions, i.e. $(H{-}C\overset{S}{\underset{S}{\langle}})$.

The crystal structure of the complex *cis*-$Ru(S_2CH)_2(PPh_3)_2$ is the first example of a transition-metal complex containing two dithioformato ligands bound to the central atom [25,26]. The ruthenium environment is distorted with the dithioformato ligands *cis* to one another. Although a *trans* configuration might have been expected to minimize interaction between the two bulky triphenylphosphine groups, the observed *cis* configuration shows the importance of π-donation from the metal.



The C—S distances are all close to 1.68 Å which implies complete delocalization in the HCS_2 ligand as found in the previous rhenium complex. This is further supported by the NMR spectrum which shows the carbon protons to be very strongly deshielded at δ 11.5 p.p.m. The Ru—S bond distance *trans* to the triphenylphosphine ligand is 2.45 Å, whereas *trans* to the sulphur it is 2.39 Å. This implies a higher *trans* influence of the triphenylphosphine ligand.

The first X-ray structure of a monodentate dithioformato ligand has been reported by Albinati et al. [31] for the complex *trans*-$PtH(S_2CH)(PCy_3)_2$. The structure and relevent data are shown.



$\angle Pt-S_1-C_1$	111.2°
$\angle P_1-Pt-P_2$	161.1°
$\angle P_1-Pt-S_1$	99.9°
$\angle P_2-Pt-S_1$	99.4°
$\angle S_1-C_1-S_2$	129.0°

The two C—S bond distances reported were observed to be essentially equal within the standard deviations. This implies a certain degree of electron delocalization in the S—C—S group. In comparison with the bidentate dithioformato complexes $Ru(S_2CH)_2(PPh_3)_2$ or $Re(S_2CH)(CO)_2(PPh_3)_2$, it appears that the C—S bond distance is unaffected by the mode of coordination of the dithioformato ligand.

III. Thiocarbonyl complexes

The ligand CS might be expected to have bonding properties similar to those of CO. It would bond therefore through the carbon to the metal, be stabilized by back-donation from the metal and be more likely to be found in anionic complexes, or in those having the metal in a low oxidation state. This, in general, has been found to be the case. As in carbonyl complexes, the most readily accessible and sensitive technique to determine their presence is IR spectroscopy. A variety of other physical techniques has been applied to thiocarbonyl complexes but these have concentrated on comparing analogous carbonyl and thiocarbonyl systems, rather than within a series of thiocarbonyl complexes.

(i) Theoretical studies. An early molecular orbital study by Richards [62] forms the basis for most comparison studies. In comparing the energy levels of the diatomics CO and CS, he showed the highest occupied levels in carbon monosulfide (7σ) to contain a high proportion of carbon $2p$ character, and to be of higher energy than the corresponding orbital in CO (5σ). This would imply that CS could be a better σ-donor than CO. In addition, the corresponding empty orbitals on CS, suitable for accepting π-electron density on the metal, are at lower energy than those in CO, so it has been considered to be a better π-acceptor. Physical measurements have supported this con-

clusion that CS bonds more strongly to an electron-rich metal, than does CO.

A very recent investigation of the electronic structure of transition-metal thiocarbonyl complexes via photoelectron spectroscopy and theoretical calculations has been reported by Lichtenberger and Fenske [63]. In this report, they obtained the He I photoelectron spectra of $M(CO)_5(CS)$-($M = Cr, W$) and $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$. Their study confirms the early predictions of Richards [62] that the CS group is a slightly better σ-donor than CO. This improved donor ability results from the additional charge on the carbon atom, both from the less electronegative sulfur atom and the improved π-acceptor ability of CS, which destabilizes the σ-donor orbital.

Also indicated by the data is the superior π-acceptor ability of the CS group. These appreciable differences in the structure of the CO and CS ligands have little consequence on the remaining carbonyl portion of the molecule. This is a result of the fact that, although the thiocarbonyl group reduces the electron density at the metal available for back-donation to the CO groups, the metal orbitals have also been destabilized. This results in a slightly weaker M—C(O) bond which is in agreement with the observation that the *trans* carbonyls of the $M(CO)_5(CS)$ complexes are labilized toward thermal substitution with ligands, L.

(ii) IR and Raman studies. For carbonyls, the pattern of the stretching vibrations in their IR spectra gives information on the number and stereochemistry of such ligands in a complex. This has had limited applicability in thiocarbonyl chemistry since most known complexes contain only one such group. However, where detailed analysis of the spectra of examples with more than one linkage has been carried out, the expected patterns have been obtained [14,44]. For carbonyls, the frequency of the stretching vibration indicates the degree of interaction of the ligand with the metal, by comparison with $\nu(CO)$ at 2143 cm^{-1} in the free gas. The corresponding vibration for CS, obtained by trapping the molecule in a CS_2 matrix occurs at 1274 cm^{-1} [64]. At present, the frequency range for this mode in thiocarbonyl complexes is 1106—1409 cm^{-1}.

Whereas the lowered frequencies can be explained in terms of π-back-bonding with the metal, the substantially higher frequencies clearly demonstrate that for CS complexes, in contrast to CO complexes, considerable mixing with other vibrational modes must occur.

The recent normal coordinate calculations of Butler et al. [65] clarify this situation. Their studies indicate that the CO and CS stretching modes are not mixed, but the CS stretching modes are appreciably mixed with $\nu[M—C(S)]$. Moreover, their study of the $M(CO)_5(CS)(M = Cr, W)$ force constants [65] are in support of the following chemical observations; the increased labilization of the CO group *trans* to CS and the increased stability of the M—C(S) bond over the M—C(O) bond with regard to substitution.

Square-planar complexes of Ir(I) and Rh(I) show an increase in $\nu(CS)$ upon oxidative addition of about 50 cm^{-1}. For example, $\nu(CS)$ occurs at 1328 cm^{-1} in *trans*-$IrCl(CS)(PPh_3)_2$ and at 1370 cm^{-1} in $IrCl(CS)(PPh_3)_2$-

(TCNE) [66]. Similarly, in *trans*-$RhCl(CS)(PPh_3)_2$, ν(CS) occurs at 1299 cm^{-1} but rises to 1355 cm^{-1} in $RhCl(CS)(PPh_3)_2$(TCNE). The effect of positive charge on the carbonyl and thiocarbonyl frequencies may be seen in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ [67] and the isoelectronic $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-(CS) [14]. In the former, ν(CO) appears at 2093 and 2064 cm^{-1} and γ(CS) at 1348 cm^{-1}. In the latter example, these occur at 2010, 1959 and 1271 cm^{-1} respectively.

Replacing the carbonyl in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ by triphenylphosphine to give $(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(PPh_3)$ drops ν(CS) from 1266 to 1231 cm^{-1} [14]. Changing triphenylphosphine in this complex to the more basic dimethylphenylphosphine causes an expected slight drop to 1228 cm^{-1} [68] but if the same change is made in $(\eta^5\text{-}C_5H_5)Mn(CS)(PPh_3)_2$, the frequency shows a slight rise from 1193 to 1195 cm^{-1}. Frequency shifts of the thiocarbonyl stretching vibration are as expected from analogous carbonyl systems if fairly major changes take place within the complex. Smaller changes can lead to anomalous shifts.

Little work has been done in characterizing the δ(MCS) modes. In a series of $(\eta^5\text{-}C_5H_5)Mn(CS)$(polyphosphine) complexes [69], these were found in the range 530—550 cm^{-1}, some 60 cm^{-1} lower than δ(MCO) in the corresponding carbonyl complexes. In an IR and Raman spectral study on $[CH_3CO_2\text{-}(\eta^6\text{-}C_6H_5)]Cr(CO)_2(CS)$ [70], the δ(MCS) bending modes were reported at 595 and 521 cm^{-1}.

Integrated IR intensities of the stretching vibrations for CO and CS have been measured in the complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ [71] and found to be significantly higher for the CS ligand. Neglecting the fact that the thiocarbonyl absorption is not pure 'CS', is not expected to alter the result. Previous related studies in carbonyl systems [72] have suggested that the values obtained are highly dependent upon the extent of π-bonding between the metal and CO. If the argument can be extended to CS, this shows the ligand to have a much stronger π-accepter ability than CO.

Only two types of bridging thiocarbonyls have been reported. The first type (see structures XVII, XVIII) is carbon bridging and has been reported for the complexes $[R\text{-}(\eta^5\text{-}C_5H_4)Mn(CS)(NO)]_2(R{=}CH_3,H)$ [42] and $[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)]_2$ [47]. The thiocarbonyl stretching frequencies for these complexes are found in the range 1150—1118 cm^{-1}, the lowest values reported to date. It is of interest to note that the mass spectrum of the manganese compounds show loss of NO before that of CS, suggesting that the latter forms stronger metal—ligand bonds.

The second type of bridging thiocarbonyl is of the type MCSM. Oxygen bonded adducts of carbonyls are uncommon and are only found in those systems where there is extensive back-bonding onto the ligand [73]. The terminal thiocarbonyl with the lowest ν(CS) reported to date is *cis*-W(CO)-(CS)$(diphos)_2$ (1161 cm^{-1}). This complex reacts with $(Me_2CO)W(CO)_5$ to give $(diphos)_2(CO)WCSW(CO)_5$ [42]. As with the oxygen-adducts of carbonyls, the carbonyl stretching frequency of the $W(CO)(diphos)_2$

fragment rises, and the thiocarbonyl absorption at 1161 cm^{-1} disappears. It is suspected to be under the strong diphos absorption at 1095 cm^{-1}.

Thiocarbonyl absorptions have been observed in the region 1264—1261 cm^{-1} in the Raman spectrum of $M(CO)_5(CS)(M{=}Cr,W)$ [65]. The broadness and weakness of these absorptions contrasts their IR counterparts which are usually extremely narrow and intense. This lack of strong Raman activity is surprising in view of the high polarizability expected for CS bonds. The results of Lichtenberger and Fenske [63] explain this observation quite well. They indicate that as a result of the empty π^*-levels of the CS ligand being coupled to the filled π-levels of the CS through the metal π-levels, there is a reduction in the polarizability change along the CS bonds during the stretching motion, and since the intensity of a Raman band is proportional to the square of the polarizability change, the intensities of the ν(CS) modes will be weak as observed.

(iii) NMR studies. For carbonyl complexes, use of ^{13}C NMR has been made to estimate the electron density at the carbon atom of the ligand. Although the method has been criticized in its general applicability [74], and on its inverse relationship to related studies in IR force constants [75], Bodner and Todd [76] argued that for a closely related series of compounds, the carbonyl carbon resonance is deshielded with increasing electron density at the metal centre. For the series of complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$, the order of increasing electron density at the metal with ligand L is $CS < CO < P(OPh)_3 < P(OMe)_3 < PBu_3 < PPh_3 < C_8H_{14} < C_5H_{10}NH$ [77]. For the corresponding series $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]^+$, the order $CS \sim CO < PPh_3 < NH_3$ was obtained. This order shows that CS has the highest π-acceptor/σ-donor ratio towards a metal centre.

The ^{13}C resonances of the thiocarbonyl carbon are amongst the lowest reported. In $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$, it is found at 335 p.p.m. downfield from TMS, shifted almost 110 p.p.m. from the CO resonance [78]. Similarly in a series of cationic iron thiocarbonyl complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)L]\text{-}PF_6(L{=}CO,PPh_3,PCy_3)$, Busetto and Palazzi [79] reported the ^{13}C resonances to be in the region 320—316 p.p.m. These values fall into the range generally found for transition metal carbene complexes [80,81]. These results would also support the polar resonance structure $M{-}\overset{+}{C}{=}\overline{S}$ being important. The linkage is different from other transition metal stabilized carbenes in that the CS ligand is clearly a good π-acceptor [16]. Support for this is found in other systems. For example, in $RuCl_2(CO)(CS)(PPh_3)_2$ [16], the carbonyl stretch is the highest reported for divalent ruthenium.

Square planar Ir(I) and Rh(I) complexes containing CS show less tendency to undergo oxidative-addition than analogous CO—complexes. Although HCl adds to *trans*-$RhCl(CO)(PPh_3)_2$ it does not do so to *trans*-$RhCl(CS)(PPh_3)_2$ [82]. In the similar iridium complexes, hydrogen gas adds to *trans*-$IrCl(CO)(PPh_3)_2$ but not to *trans*-$IrCl(CS)(PPh_3)_2$ [8]. Reductive elimination of hydrogen from $[IrH_2(CO)(CS)L_2]^+$ (L = phosphine) takes place much more rapidly than from $[IrH_2(CO)_2L_2]^+$ [83]. All these reactions suggest that the

CS ligand has lowered the electron density at the metal.

(iv) Mössbauer spectra. For the cationic iron complexes [(η^5-C_5H_5)-Fe$(CO)_2$L]PF_6 (L=CO,CS,PPh_3), Busetto and co-workers [84] reported the ^{57}Fe Mössbauer spectra. From the isomer shifts of these ligands, the authors were able to conclude that the electron density on the iron nucleus decreases in the following order: CS > CO > PPh_3.

(v) Mass spectral data. In their attempt to gain further insight on the bonding of transition-metal thiocarbonyls, Efraty et al. [85] reported the mass spectral data of [R-(η^5-C_5H_4)Mn$(CO)_2$(CS)](R=H,CH_3; X=O,S). Although both types of complexes were observed to undergo similar fragmentations, it was noted that the carbonyls were both lost in preference to the thiocarbonyl group. A comparison of the bond energies revealed that D(Mn$^+$—CS) was 25—40% greater than D(Mn$^+$—CO) in the corresponding carbonyl complex. A result of questionable validity arises from their suggestion that coordinated thiocarbonyl has a lower π-acidity than the carbonyl ligand. In view of numerous examples to the contrary, these mass spectral results are misleading, particularly since this conclusion was based on appearance potentials of the various fragment ions without a detailed knowledge of their structure.

(vi) X-ray structural determinations. X-ray structural determinations for five complexes containing terminal thiocarbonyl ligands are now available (Table 4). They are for the complexes *trans*-RhCl(CS)$(PPh_3)_2$ [86], [Ir$(CO)_2$-(CS)$(PPh_3)_2$]PF_6 · Me_2CO [87], [(CS)$(PPh_3)_2$RuCl_3RuCl$(PPh_3)_2$] [88], [CH_3CO_2-(η^6-C_6H_5)Cr$(CO)_2$(CS)] [89] and *trans*-W$(CO)_4$(CS)(CNC_6H_{11}) [90]. The first two structures have been discussed previously [1]. In both cases, the M—C(S) bond length was found to be substantially shorter than those measured for M—C(O), showing a considerable degree of metal—ligand multiple bonding. The ruthenium complex was, unfortunately, sufficiently disordered such that no accurate bond distances relating to the CS ligand could be obtained. Both chromium and tungsten complexes confirm the

TABLE 4

Crystallographic and IR data for thiocarbonyl complexes

Complex [a]	M—C(O) (A)	M—C(S) (A)	C—S (A)	ν(CS) (cm^{-1})
[MeCO_2-(η^6-C_6H_5)]Cr$(CO)_2$(CS)	1.85 1.85	1.80	1.57	1205
trans-W$(CO)_4$(CNC_6H_{11})(CS)	2.06	1.94	1.55	1240
RhCl(CS)$(PPh_3)_2$	1.86 [b]	1.80	1.54	1299
[Ir$(CO)_2$(CS)$(PPh_3)_2$]PF_6 · $(Me)_2CO$	1.92 1.95	1.87	1.51	1391

[a] [(CS) $(PPh_3)_2$RuCl_3RuCl $(PPh_3)_2$] was sufficiently disordered such that no accurate bond distances relating to the CS ligand could be obtained. [b] From RhCl(CO)$(PPh_3)_2$.

observation from previous structures, that the M—C(S) bond is shorter than the M—C(O) bond. They also show that as back-bonding in the thiocarbonyl ligand becomes more important, measured by the lowering of ν(CS), the carbon—sulphur bond length increases.

The first crystal structure containing a selenocarbonyl ligand has been reported [51]. In $RuCl_2(CO)(CSe)(PPh_3)_2$, the CO and CSe ligands are *cis* to each other and *trans* to the two chlorines. The Ru—Cl bond lengths, 2.427 Å *trans* to CO and in particular 2.480 Å *trans* to CSe, are very long compared to Ru—Cl bond lengths in other Ru(II) complexes (2.29—2.39 Å) [91], suggesting a strong *trans*-influence by the selenocarbonyl. The metal—carbon distance of M—C(Se) of 1.83 Å is appreciably shorter than the 1.89 Å for M—C(O). The difference is very close to that found in the M—C(O)/M—C(S) system (Table 4).

F. REACTIVITY OF π-CS_2 AND CS COMPLEXES

1. π-CS_2 complexes

Transition metal π-CS_2 complexes react with either electrophilic or nucleophilic reagents producing two distinctively different types of complexes. Thus attack by alkyl halides gives thio-alkylated species while reaction with triphenylphosphine leads to sulphur abstraction from the CS_2 ligand resulting in the formation of a thiocarbonyl.

On complexation with the metal, the carbon disulphide can be expected to become more electron-rich, particularly at the sulphur atoms. This leads to the possibility of alkylation at both sulphur atoms, but so far monoalkylation is most common.

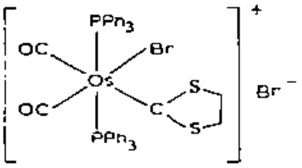
$(\eta^5\text{-}C_5H_5)_2(\sigma\text{-allyl})Nb(\pi\text{-}CS_2)$ (page 187) reacts with various alkyl iodides producing the monoalkylated complexes $(\eta^5\text{-}C_5H_5)_2(\sigma\text{-allyl})NbI(CS_2R)$, (R=Me,Et,n-Pr,n-Bu) [15]. The IR spectra exhibit ν(CS) modes ca. 1120 s, ca. 770 m and ca. 670 w.

Monoalkylated species are also obtained from the reaction of $Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ with methyl iodide [4,16]. The initial product is the cationic complex $[Ru(CO)_2(PPh_3)_2(CS_2Me)]^+$, in which the dithioester ligand is bidentate. The IR spectrum contains a medium absorption at 1110 cm^{-1}, assignable to ν(CS). A carbonyl is easily lost from the complex, being replaced by added anions to give $[RuX(CO)(PPh_3)_2(CS_2Me)]$(X=Cl,Br,I). Ligands similar to the dithioester have been prepared by attack of nucleophiles on carbonyls [92].

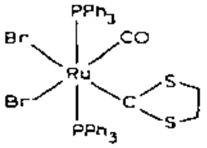
Action of acids HX(X=Cl,Br,I) on $RuX(CO)(PPh_3)_2(CS_2Me)$ gives the corresponding thiocarbonyl complex, $RuX_2(CO)(CS)(PPh_3)_2$ [16]. $Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ also reacts with the same acids to give equal amounts of $RuX_2(CO)_2(PPh_3)_2$ and $RuX_2(CO)(CS)(PPh_3)_2$.

$Os(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ has been reported to react with stoichiometric amounts of methyl iodide to produce the cationic complex, $[Os(CO)_2(PPh_3)_2(CS_2Me)]^+$ [16]. $Os(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ also reacts with excess methyl iodide yielding a mixture of $[Os(CO)_2(PPh_3)_2(CS_2Me)]^+$ and $[OsI(CO)_2(PPh_3)_2\{C(SMe)_2\}]^+$. In the cationic dithiocarbene complex, the sulphur ligand is now monodentate.

Dihaloalkanes have the potential to react with π-CS_2 complexes to form dithioheterocyclic ligands. $Os(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ has been reported to react with 1,2-dibromoethane resulting in the formation of the cationic complex XXII [93]. 1,2-dibromoethane has also been found to react with $Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$, but the neutral product, $RuBr_2(CO)(PPh_3)_2(\overline{CSCH_2CH_2S})$ (XXIII) was obtained [4].

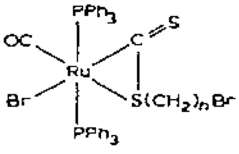


(XXII)



(XXIII)

$Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ was also found to react with other dihaloalkanes such that the product obtained depends upon the length of the alkane chain and upon the reaction conditions used [4]. For example, when $Ru(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$ reacts with methylene dibromide, 1,3-dibromopropane or 1,4-dibromobutane, the monoalkylated neutral species $RuBr(CO)(PPh_3)_2[CS_2(CH_2)_nBr]$ (n = 1,3,4) is obtained. These three complexes, XXIV, contain single $\nu(CO)$ absorption in the region 1926—1930 cm^{-1} and a medium intensity band in the 1075 cm^{-1} region for $\nu(CS)$.



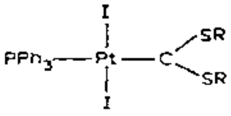
n = 1,3,4

(XXIV)

The complexes, $RuBr(CO)(PPh_3)_2[CS_2(CH_2)_nBr]$ (n = 3,4) are able to undergo further reaction in toluene decomposing to the thiocarbonyl complex, $RuBr_2(CO)(CS)(PPh_3)_2$ [4]. The IR spectrum exhibits $\nu(CS)$ at 1298 cm^{-1} and a very high $\nu(CO)$ at 2025 cm^{-1}. This high $\nu(CO)$ frequency is due to the marked π-acceptor capacity of the CS ligand.

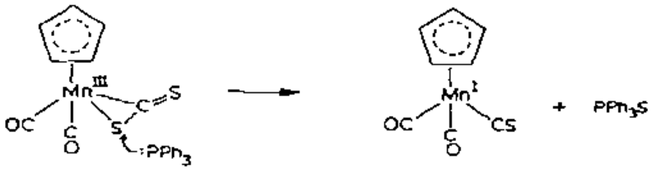
A reinvestigation [94] of some earlier work of Baird and Wilkinson [7], has shown that when $Pt(PPh_3)_2(\pi\text{-}CS_2)$ reacts with either neat methyl or ethyl iodide at room temperature, the products isolated are cationic monodentate dithiocarbene complexes of general formula $[PtI(PPh_3)_2\{C(SR)_2\}]^+$ (R=Me,Et). Strong IR bands are observed at 998 cm^{-1} together with weak bands in the ranges 950—940 cm^{-1} and 850—840 cm^{-1}, which are attributed to the monodentate carbene containing two equivalent CS bonds.

When solutions of $Pt(PPh_3)_2(\pi\text{-}CS_2)$ in methyl or ethyl iodide are allowed to react under reflux for longer periods of time, the neutral carbene complex, XXV, is obtained.

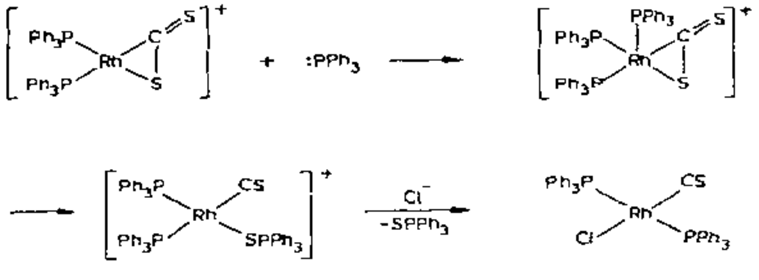


(XXV)

A well-established method for the preparation of thiocarbonyl complexes is through the reaction of triphenylphosphine on coordinated carbon disulphide [14,41,95]. Normally only alkylphosphines react with carbon disulphide itself. It has been shown that $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_8H_{14})$ reacts with CS_2 in the presence of triphenylphosphine to give $(\eta^5\text{-}C_5H_5)Mn(CO)_2\text{-}(CS)$ [14]. The complex is obtained in much poorer yield in the absence of triphenylphosphine. The proposed mechanism [14] is by attack of free phosphine at the bound sulphur



An alternative mechanism which explains the formation of *trans*-RhCl(CS)-$(PPh_3)_2$ is similar to that proposed in the catalytic oxidation of phosphine to phosphine oxide, at a transition metal through discrete steps of oxidative addition by dioxygen, migratory insertion of an oxygen atom leading to reduction with subsequent elimination of phosphine oxide [96]. A corresponding scheme for thiocarbonyl formation would be



II. CS complexes

(i) Nucleophilic attack at the thiocarbonyl ligand. The thiocarbonyl carbon has been observed to exhibit a greater reactivity pattern than the carbonyl carbon towards nucleophilic attack. This has been attributed to the reaction being frontier controlled [107]. In this approach, the highest molecular orbital of the nucleophile interacts with the lowest unoccupied molecular orbital of the thiocarbonyl—carbonyl complex.

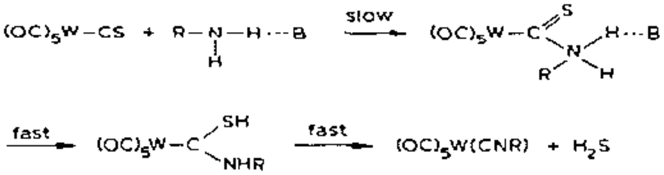
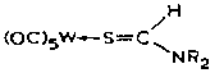


Fig. 2. Proposed mechanism for the formation of $W(CO)_5(CNR)$.

Dombek and Angelici [39] reported the formation of the isocyanide complexes $M(CO)_5(CNR)(M{=}Cr,Mo,W;\ R{=}Me,Cy,Ph,n\text{-}Bu,t\text{-}Bu)$ from the nucleophilic attack of primary amines on the appropriate thiocarbonyl complex. These complexes were characterized from the $\nu(CN)$ vibration of the isocyanide ligand occurring in the 2177—2173 cm^{-1} region. Kinetic studies reveal the reaction is overall third order; first order in $W(CO)_5(CS)$ and second order in amine [97]. The mechanism in Fig. 2 is consistent with these results.

The substituted complexes *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)_2$ were observed to react much more slowly than $W(CO)_5(CS)$ with primary amines [39,97]. This effect was attributed to the electron-releasing effect on the phosphine relative to CO and is reflected in the lower $\nu(CS)$ frequency (1241 cm^{-1}) in *cis*- and *trans*-$W(CO)_4(CS)(PPh_3)$ as compared to $W(CO)_5(CS)$ (1258 cm^{-1}). The authors also noted that *trans*-$W(CO)_4(CS)(PPh_3)$ undergoes reaction less rapidly than the *cis* isomer which suggested that a greater amount of electron density is transmitted to the CS group when it is *trans* to the phosphine ligand.

$W(CO)_5(CS)$ also reacts with secondary amines [97], but in contrast to an earlier report [39], give thioformamide complexes (XXVI).



$(R_2 = (CH_3)_2, (CH_2)_5)$

(XXVI)

Other nucleophiles such as azide ion or glycine methyl ester, $H_2NCH_2CO_2CH_3$, were also found to react with $W(CO)_5(CS)$ to give the products $[W(CO)_5(NCS)]^-$ and $W(CO)_5(CNCH_2CO_2CH_3)$, respectively. If *trans*-$W(CO)_4(^{13}CO)(CS)$ is reacted with azide ion or primary amines, *trans*-$W(CO)_4(^{13}CO)(NCS)$ and *trans*-$W(CO)_4(^{13}CO)(CNR)$ are produced and the stereochemistry at the metal centre is unchanged [97].

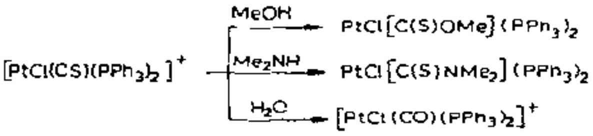


Fig. 3. Nucleophilic reactions of $[PtCl(CS)(PPh_3)_2]^+$.

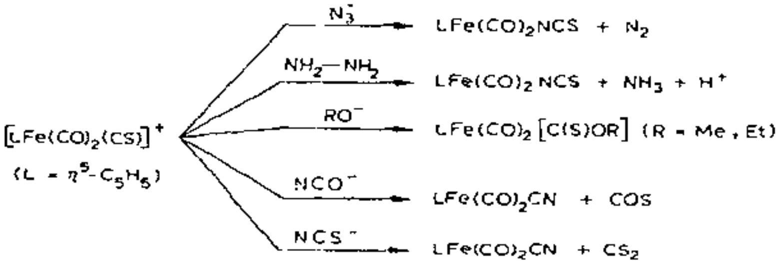


Fig. 4. Nucleophilic reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+$.

Although milder nucleophiles such as alcohols or water do not react with $W(CO)_5(CS)$, they will react with thiocarbonyl complexes which are more electrophilic. Consequently, the cationic thiocarbonyl complex, $[PtCl(CS)(PPh_3)_2]^+$ is susceptible to nucleophilic attack by amines, alcohols and water [40] as illustrated in Fig. 3.

The cationic thiocarbonyl complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]^+$ exhibits a very high $\nu(CS)$ absorption at 1348 cm^{-1} and consequently is also very reactive towards various nucleophiles [67]. It appears that three different reaction products are obtainable and these products depend upon the nature of the attacking nucleophile [98]. These reactions are summarized in Fig. 4.

Busetto and Palazzi [79] examined the reactions between primary amines and the cationic thiocarbonyl complex, $[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)L]PF_6$, ($L{=}PPh_3, PCy_3, P(p\text{-}FC_6H_4)_3$; $R{=}CH_3, C_6H_{11}, C_6H_5$). The isocyanide complexes which result $[(\eta^5\text{-}C_5H_5)Fe(CO)(CNR)L]PF_6$ tend to show the general applicability of these amine reactions. Further investigation on the reaction between methylamine and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ has shown that $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CNR)]PF_6$ is formed, which contradicts their earlier report that $[(\eta^5\text{-}C_5H_5)Fe(CO)_2C(S)NHCH_3]PF_6$ is formed [98].

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ was also reported to react with an excess of phenyl isocyanide to give $[(\eta^5\text{-}C_5H_5)Fe(CNC_6H_5)_2(CS)]PF_6$ [79]. In this complex, both carbonyls have been replaced by the isocyanide ligand. The IR spectra of these complexes include absorptions in the region 2195—2140 cm^{-1} attributable to $\nu(CN)$ and 1996—1950 cm^{-1} attributable to $\nu(CO)$. If the reaction is carried out with stoichiometric amounts of phenyl isocyanide, the IR spectrum shows additional absorptions at 2130, 2030 and 1330 cm^{-1} attributable to $\nu(CN)$, $\nu(CO)$ and $\nu(CS)$, respectively of $[(\eta^5\text{-}C_5H_5)Fe(CO)(CS)(CNC_6H_5)]PF_6$.

These results indicate that despite the greater π-acceptor capacity of CS relative to CO, the CS group is always the reactive site in the reaction of nucleophiles independent of the nucleophile used and the charge on the central metal. This illustrates the basic point that the electrophilic character of the thiocarbonyl carbon is markedly greater than that of the carbonyl carbon.

1. $M(CO)_5(CS) + PPh_3 \rightarrow$ *cis*- and *trans*-$M(CO)_4(CS)(PPh_3) + CO$
   $(M = Cr, W)$
2. $W(CO)_5(CS) + L \rightarrow$ *trans*-$W(CO)_4(CS)L + CO$
   $(L = py, diars)$
3. $M(CO)_5(CS) + L \rightarrow$ *mer*-$M(CO)_3(CS)L + 2CO$
   $(M = Cr, W; L = diphos)$
4. $W(CO)_3(CS)(L) + L \rightarrow$ *cis*-$W(CO)(CS)(L)_2 + 2CO$
   $(L = diphos)$
5. $W(CO)_5(CS) + Bu_4NX \rightarrow Bu_4N[$*trans*-$WX(CO)_4(CS)] + CO$
   $(X = Cl, Br, I)$

Fig. 5. Ligand reactions of $M(CO)_5(CS)(M{=}Cr,W)$.

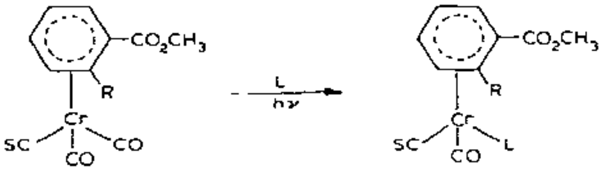
(ii) Carbonyl replacement reactions. Crystal structure determminations of thiocarbonyl complexes have indicated that the M—C(S) bond is significantly shorter than the M—C(O) bond in the related carbonyl complex, which implies a greater metal—ligand bond strength in the former complex. Also using the theoretical calculations of Richards [62] and the photoelectron measurements of Lichtenberger and Fenske [63] which suggest that the CS ligand is a better σ-donor and a better π-acceptor than the CO ligand, it is understandable that the attack of Lewis bases on metal carbonyl—thiocarbonyl complexes results in preferential displacement of the carbonyl ligand.

Poliakoff [99] demonstrated that UV photolysis of $M(CO)_5(CS)(M{=}Cr,W)$ in Ar or CH_4 matrices at 20 K produces a mixture of two isomeric forms of $M(CO)_4(CS)$ and molecular CO. This confirms the greater strength of the M—C(S) bond over that of M—C(O), as there is no loss of CS under these conditions. The IR spectra of ^{13}CO-enriched compounds show that both isomers have square-pyramidal structures; one has C_{4v} symmetry with the CS group in the axial position, and the other C_s symmetry with a basal CS group. Further work [100] has shown that this photolysis of $W(CO)_5(CS)$ occurs in two stages: loss of CO, followed by an excited-state arrangement of the photoproduct, $W(CO)_4(CS)$. If *trans*-$W(CO)_4(^{13}CO)(CS)$ is used in Ar or CH_4 matrices, then the major product is *cis*-$W(CO)_3(^{13}CO)(CS)$, with the CS group in the axial position. Subsequent irradiation with visible light regenerates $W(CO)_4(^{13}CO)(CS)$ but principally as the *cis* isomer.

Thermal substitution reactions have resulted from the reaction of $M(CO)_5$-$(CS)(M{=}Cr,W)$ with group VA donor ligands, L, to yield $M(CO)_4(CS)L$ complexes [39,40]. It was originally believed that the *trans* isomer was formed exclusively, but subsequent study suggests the presence of *cis* and *trans* isomers, although the *trans* isomer is observed to predominate [40]. The complete range of these reactions are illustrated in Fig. 5.

In this last reaction, ^{13}C NMR studies have indicated complete preference for the loss of the *trans* carbonyl in this substitution process as illustrated in the reaction

$$trans\text{-}W(CO)_4(^{13}CO)(CS) + X^- \rightarrow [trans\text{-}W(CO)_4(CS)]^- + {}^{13}CO$$

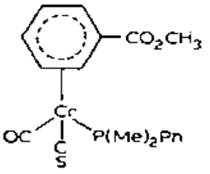


R = H, CH_3
L = PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, $P(Me)_2Ph$

Fig. 6. Photochemical ligand displacement reactions of [1-CH_3CO_2, 2-R-(η^6-C_6H_4)]-$Cr(CO)_2(CS)$.

Certain chromium thiocarbonyl complexes have been observed to undergo ligand replacement of a CO ligand under photochemical conditions [41,101—103]. Thus the complex, [1-CH_3CO_2, 2-R(η^6-C_6H_4)]$Cr(CO)_2CS$-R=H,CH_3) was found to react with the ligand L, producing the new thiocarbonyl complexes, [1-CH_3CO_2, 2-R(η^6-C_6H_4)]Cr(CO)(CS)L. These reactions are given in Fig. 6.

When R=H, these chromium(0) complexes owe their optical activity to the chiral chromium centre. The magnetic non-equivalence of the two methyl groups on the phosphine ligand illustrates the optical activity of the metal centre (XXVII). The ^{1}H NMR of these methyl groups in $CDCl_3$ consists of two doublets at δ 1.85 and δ 1.97 p.p.m. The doublet arises from ^{31}P coupling (J = 8.5 Hz).



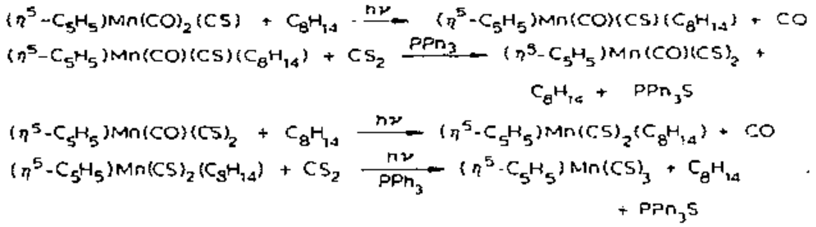
(XXVII)

The first ligand substitution reaction on thiocarbonyl complexes of manganese was the photochemical reaction of (η^5-C_5H_5)$Mn(CO)_2(CS)$ with C_8H_{14} to produce the thiocarbonyl complex (η^5-C_5H_5)Mn(CO)(CS)(C_8H_{14}) [44]. Some reactions of this complex which lead to the isolation of di- and tri-thiocarbonyl derivatives are illustrated in Fig. 7.

Kinetic studies [104] indicate that the thermal reaction of (η^5-C_5H_5)-Mn(CO)(CS)(C_8H_{14}) with triphenylphosphine to yield (η^5-C_5H_5)Mn(CO)(CS)-(PPh_3) is in accord with an S_N1 dissociative mechanism. The data indicate that the rate determining step is the rupture of the manganese—olefin bond and then subsequent fast reaction with tripheylphosphine to yield the product.

$$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(C_8H_{14}) \xrightarrow[-C_8H_{14}]{\text{slow}} [(\eta^5\text{-}C_5H_5)Mn(CO)(CS)]$$

$$\xrightarrow[\text{fast}]{PPh_3} (\eta^5\text{-}C_5H_5)Mn(CO)(CS)(PPh_3)$$



$$(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS) + C_8H_{14} \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Mn(CO)(CS)(C_8H_{14}) + CO$$

$$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(C_8H_{14}) + CS_2 \xrightarrow{PPh_3} (\eta^5\text{-}C_5H_5)Mn(CO)(CS)_2 + C_8H_{14} + PPh_3S$$

$$(\eta^5\text{-}C_5H_5)Mn(CO)(CS)_2 + C_8H_{14} \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)Mn(CS)_2(C_8H_{14}) + CO$$

$$(\eta^5\text{-}C_5H_5)Mn(CS)_2(C_8H_{14}) + CS_2 \xrightarrow[PPh_3]{h\nu} (\eta^5\text{-}C_5H_5)Mn(CS)_3 + C_8H_{14} + PPh_3S$$

Fig. 7. Photochemical reactions of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$.

In a study of the substitution reactions of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ with group VA ligands, Coville and Butler [68] were able to prepare two different types of thiocarbonyl complexes. The reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ in THF leads to the unstable complex $(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(THF)$ which could be reacted with the ligand L to produce the thiocarbonyl complex $(\eta^5\text{-}C_5H_5)$-$Mn(CO)(CS)L$, where L= PPh_3, $AsPh_3$, $SbPh_3$, PMe_2Ph, $P(C_6H_{11})_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ and $P(OCH_2CH_2Cl)_3$. If the complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2$-$(CS)$ is reacted with excess ligand under photochemical conditions in benzene, both CO ligands are replaced and the complex $(\eta^5\text{-}C_5H_5)Mn(CS)L_2$, is obtained (L=$PPh_3$, PMe_2Ph, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$ and $P(OCH_2CH_2Cl)_3$). The lower value of the ν(CS) vibrational mode in the $(\eta^5\text{-}C_5H_5)Mn(CS)L_2$ complexes as compared to $(\eta^5\text{-}C_5H_5)Mn(CO)(CS)L$ indicates that the C—S bond has become weaker with the strengthening of the Mn—C(S) bond.

Another indication of the stronger metal—carbon bonding of thiocarbonyl ligands as compared to carbonyl ligands is illustrated in the reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ with some polydentate organophosphine ligands [69]. Both diphos and triphos react with $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ to yield two isomers of the complex $(\eta^5\text{-}C_5H_5)Mn(CS)L$. The isomeric triphos complexes are believed to be diastereomers resulting from the bidentate coordination of two of the adjacent phosphorus atoms on the triphos ligand. These are illustrated in Fig. 8. The diastereomer with the larger R_f value is designated the γ-isomer, while the other is referred to as the ϕ-isomer.

The triphos derivative $(\eta^5\text{-}C_5H_5)Mn(CS)$(triphos), was found to react with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ producing two products which analyzed as $(\eta^5\text{-}C_5H_5)$-$(CS)Mn$(triphos)$Mn(CO)_2(\eta^5\text{-}C_5H_5)$ [69]. $(\eta^5\text{-}C_5H_5)Mn(CS)$(triphos) also reacts with $Cr(CO)_5(THF)$ forming the dimeric complex $(\eta^5\text{-}C_5H_5)(CS)$-$Mn$(triphos)$Cr(CO)_5$.

$[(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(NO)]SbF_6$ is reported to undergo facile carbonyl substitution reactions with various Lewis bases to afford products of the type $[(\eta^5\text{-}C_5H_5)Mn(CS)(NO)L]SbF_6$ where L= PPh_3, $AsPh_3$, $SbPh_3$ [45].

Recently, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ has been reported to react with various group VA ligands affording complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)$-$(CS)L]PF_6$(L= $P(FC_6H_4)_3$, PCy_3, PPh_3, $AsPh_3$, $SbPh_3$) [79]. The IR spectra of the new derivatives include one ν(CO) absorption (2037—2020 cm^{-1}) and

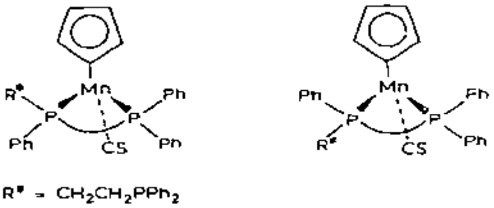


Fig. 8. Two diastereomers of (η^5-C_5H_5)Mn(CS)(triphos).

one ν(CS) absorption (1325—1315 cm^{-1}). The ν(CS) stretching modes decrease as the basicity of the ligand L increases indicating that the ν(CS) follows the same trend with change of L as generally observed for the carbonyl complexes.

(iii) Electrophilic attack at the thiocarbonyl ligand. The greater electrophilic character of the CS ligand, as compared to that of the CO ligand has been readily shown by the preferential attack of nucleophiles on the thiocarbonyl carbon. In view of the larger negative charge on the sulphur atom and its lower electronegativity as compared to oxygen, Lewis acids would be expected to form sulphur-bound adducts of suitable metal thiocarbonyls under circumstances where the carbonyl ligand does not.

Dombek and Angelici [40] observed that W(CO)(CS)$(diphos)_2$, which is prepared by reacting $W(CO)_3$(CS)(diphos) with molten diphos, reacts with a wide variety of Lewis acids. Thus when W(CO)(CS)$(diphos)_2$ is reacted with $W(CO)_5$(acetone), it gives a complex which analyses as $(diphos)_2$(CO)W(CS)-$W(CO)_5$. This novel binuclear complex reacts with triphenylphosphine in CH_2Cl_2 to yield W(CO)(CS)$(diphos)_2$ and $W(CO)_5(PPh_3)$.

W(CO)(CS)$(diphos)_2$ also reacts with HgX_2(X=Cl,I) to give the complex, $(diphos)_2$(CO)WCSHgX_2 [40,105]. In this complex, ν(CS) appears to be overlapped with a ligand absorption band near 1095 cm^{-1}, which is lower than the original CS band by approximately 65 cm^{-1}. An ionic, diamagnetic complex is formed when W(CO)(CS)$(diphos)_2$ reacts with $AgBF_4$ in CH_2Cl_2 or acetone.

$$2W(CO)(CS)(diphos)_2 + AgBF_4 \rightarrow [(diphos)_2(CO)_2WCSAgSC(CO)(diphos)]_2BF_4$$

Compared to W(CO)(CS)$(diphos)_2$, ν(CO) in this bridging complex is increased from 1838 to 1869 cm^{-1}, while ν(CS) decreased from 1161 to 1106 cm^{-1}.

It is apparent from these studies that in a complex where the electron density on the metal is sufficiently high and the ν(CS) frequency is sufficiently low, the sulphur atom of a thiocarbonyl ligand may act as a donor towards other metals. It is also clear that the S of the CS group in W(CO)(CS)$(diphos)_2$ is a better donor than the O of the CO.

Electron-rich thiocarbonyl complexes react rapidly with organic electrophiles to give *S*-alkylated derivatives as illustrated [105,106].

$$W(CO)(CS)(diphos)_2 + RSO_3F \xrightarrow{EtO^+BF_4^-} [(diphos)_2(CO)W(CSR)]SO_3F$$

R = Me, Et

As there are no new absorptions in the region 1160—1400 cm^{-1}, the thiocarbonyl band has apparently shifted to lower frequency and appears overlapped with a diphos ligand absorption. These derivatives are the first known examples of the *S*-alkylthiocarbonylium ligand, CS—R$^+$.

The recently reported bridging thiocarbonyl complex, *cis*-[(η^5-C_5H_5)-Fe(CO)(CS)]$_2$ [48], was found to react readily with CH_3OSO_2F, yielding the cationic complex, [(η^5-C_5H_5)$_2$$Fe_2(CO)_2$(CS)($CSCH_3$)]$^+$, which contains a methylated bridging thiocarbonyl group. The ν(CS) of the thiocarbonyl ligand increases to 1178 cm^{-1} which is 54 cm^{-1} greater than in the original *cis* dimer.

W(CO)(CS)(diphos)$_2$ is protonated by CF_3SO_3H, but in contrast to its reaction with Et_3OBF_4 and $MeSO_3F$, the addition occurs at the metal [105,106]. In this complex [WH(CO)(CS)(diphos)$_2$]CF_3SO_3, both the carbonyl ν(CO) and the thiocarbonyl ν(CS) frequencies have increased from the parent complex and the thiocarbonyl absorption appears at 1207 cm^{-1}. The NMR signal of the proton in [WH(CO)(CS)(diphos)$_2$]$^+$ appears 2.12 p.p.m. downfield from the NMR signal of the proton in [WH(CO)$_2$(diphos)$_2$]$^+$. This difference in chemical shifts is an indication of the substantial decrease in the electron density at the metal centre caused by replacing CO with CS.

The anionic thiocarbonyl complex, *trans*-[WI(CO)$_4$(CS)]$^-$ was found to react with alkylating agents [105,106] and some of its reactions with organic electrophiles are illustrated in Fig. 9.

In the acyl compounds, the ν(CO) absorption occurs at 1737 cm^{-1} and the ν(CS) absorption could not be located. Other thiocarbonyl complexes such as W(CO)$_5$(CS), W(CO)$_4$(CS)(PPh_3) and W(CO)$_3$(CS)(diphos), which have ν(CS) frequencies of 1258, 1247 and 1215 cm^{-1}, respectively, did not react with the triethyloxonium ion. The evident conclusion which may then be drawn is that only thiocarbonyl complexes having ν(CS) below approximately 1200 cm^{-1} will be reactive towards electrophiles.

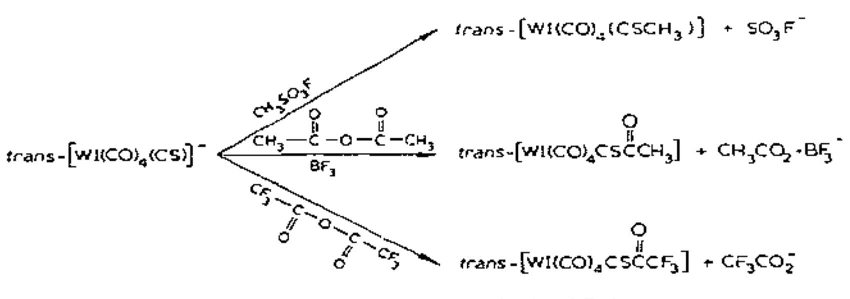


Fig. 9. Alkylation reactions of *trans*-[WI(CO)$_4$(CS)]$^-$.

(iv) Oxidative-addition reactions. The tungsten(0) complex, $W(CO)_5(CS)$ has been reported by Dombek and Angelici [105] to oxidatively add Br_2 in the presence of PPh_3 and result in the formation of $WBr_2(CO)_2(CS)(PPh_3)_2$. The IR spectrum of the product includes two ν(CO) absorptions at 2014 and 1959 cm^{-1} and one ν(CS) absorption at 1249 cm^{-1}. Similarly, W(CO)(CS)(diphos)$_2$ adds I_2 in the presence of CO to yield the complex $WI_2(CO)_2(CS)$(diphos) [105].

G. CONCLUSION

It is evident from the vast number of publications which have appeared over the last four years that the chemistry of thiocarbonyl and related complexes is an extremely active field. Since the bulk of recent transition-metal thiocarbonyl chemistry focuses on their reactivity patterns, perhaps over the next few years these patterns will be firmly established. Of all the areas examined in this review, possibly the synthesis and reactivity of selenocarbonyl complexes will be explored more fully now that a few examples analogous to thiocarbonyl complexes have been reported.

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