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Review

ACTIVATION OF CARBON DISULPHIDE BY TRANSITION METAL COMPLEXES

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I. Introduction

In 1931, Duncan et al. [1] reported that carbon disulphide reacts with copper mercaptides (Cu—SR) to give trithiocarbonates (Cu—SSCSR). However, this initial discovery was not followed up and the subject of activation of carbon disulphide by transition metal complexes lay dormant for over three decades. It came to light again in 1966 when Baird and Wilkinson [2] synthesized the first thiocarbonyl complexes, *trans*-$RhX(CS)(PPh_3)_2$ (X = Cl, Br), from the reactions of $RhX(PPh_3)_3$ with CS_2. Since then, a number of metal thiocarbonyls have been prepared by reactions in which CS_2 acts as the source of the CS ligand in the formation of M—CS bonds. These reactions, however, represent only one aspect of the activation of CS_2 by transition metal complexes. In fact, papers published over the past seven years indicate that CS_2 itself can coordinate to transition metals to form four distinctly different types of complexes.

A review of the activation of carbon disulphide by transition metal complexes has not yet appeared in the literature despite the growing interest in this field. In the present review an attempt has been made to summarize the known reactions of CS_2 with transition metal complexes. Since most of the new complexes formed have been identified chiefly by infrared spectroscopy, it was felt worthwhile to tabulate the pertinent infrared data immediately following the review. The literature coverage is considered to be complete to March 1973.

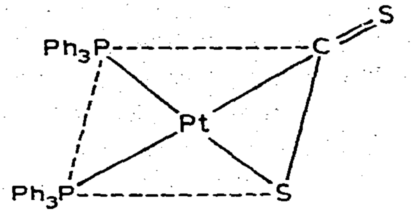
II. Carbon disulphide complexes

A. π-CS_2 complexes

The first examples of transition metal complexes to exhibit so-called "π-CS_2 coordination" were the carbon disulphide complexes of platinum and palladium. These complexes, together with a related complex of nickel, will be discussed first; following this, the π-CS_2 complexes of vanadium, iron, ruthenium, rhodium and iridium will be described. The π-CS_2 complexes of manganese believed to be intermediates in the formation of π-cyclopentadienylmanganese thiocarbonyl complexes will be considered later (see p. 182).

1. Platinum, palladium and nickel

During their investigation of potential methods for the synthesis of transition metal thiocarbonyl complexes, Baird and Wilkinson [3] discovered that $Pt(PPh_3)_3$ reacts with CS_2 to form the stable adduct, $Pt(PPh_3)_2(CS_2)$. They proposed the square-planar structure I for this complex. Moreover, they noted the similarity of this structure to that of the π-arylacetylene complexes, $Pt(PPh_3)_2$(acetylene) [4]. In fact, they were able to obtain $Pt(PPh_3)_2(CS_2)$ by displacement of the phenylacetylene group in $Pt(PPh_3)_2(PhC_2H)$ by CS_2. The platinum carbon disulphide complex and its palladium analogue can also be prepared by treatment of $M(PPh_3)_4$ (M = Pd, Pt) with CS_2 [5, 6].

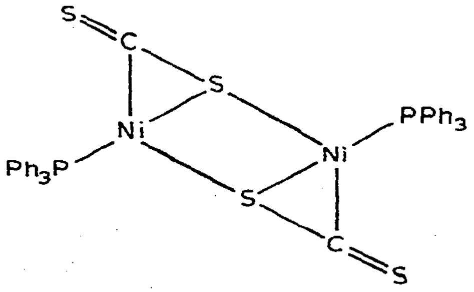


(I)

The π-CS_2 coordination suggested for $Pt(PPh_3)_2(CS_2)$ has been confirmed by three-dimensional X-ray diffraction of the complex [5, 7] and of its palladium analogue [6]. The geometry of the CS_2 ligand is modified drastically upon coordination. Uncoordinated CS_2 is linear with a C—S bond length of 1.554 Å. The coordinated molecule is bent with S—C—S bond angles of 136.2° and 140° for the platinum and palladium complexes, respectively; the mean C—S bond lengths are 1.626 Å for $Pt(PPh_3)_2(CS_2)$ and 1.64 Å for its palladium analogue. The geometry around the central metal atom in the two complexes is essentially similar. The metal atom and the four atoms coordinated to it are almost coplanar in both cases.

Triphenylstibine displaces the CS_2 group from $Pt(PPh_3)_2(\pi\text{-}CS_2)$ and its palladium analogue to yield the tetracoordinated species, $Pt(PPh_3)_2(SbPh_3)_2$ and $Pd(PPh_3)_2$-$(SbPh_3)_2$ [6]. However, with Diphos * the two triphenylphosphine groups in $Pd(PPh_3)_2$-$(\pi\text{-}CS_2)$ are substituted, resulting in the formation of a new π-CS_2 complex, Pd(Diphos)-$(\pi\text{-}CS_2)$.

Baird and Wilkinson [8] failed to obtain the nickel analogue of the platinum and palladium π-CS_2 complexes. Reaction of $Ni(CO)_2(PPh_3)_2$ with CS_2 affords a complex of stoichiometry, $Ni(PPh_3)(CS_2)$, which has a much simpler X-ray powder pattern than those for the palladium and platinum π-CS_2 complexes. The nickel complex is dimeric in solution but could be polymeric when solid. The structure proposed for the dimer involves sulphur bridging between the two nickel atoms (II).



(II)

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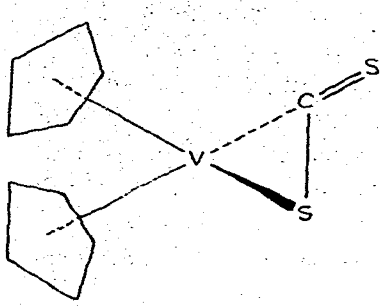
* Diphos = 1, 2-bis(diphenylphosphino) ethane.

2. Vanadium

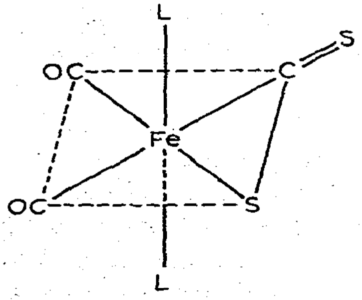
Baird et al. [9] have reported that CS_2 reacts with the purple complex, Cp_2V (Cp = π-C_5H_5), to give a green solution. This solution is extremely air-sensitive but a π-CS_2 complex could be identified by spectroscopic means. In addition to bands due to the Cp moiety, there is a strong absorption in the IR spectrum at 1141 cm^{-1}. A similar band is also present in the spectra of the platinum and palladium π-CS_2 complexes. Consequently, the 1141 cm^{-1} band was assigned as a C=S stretching frequency. The tetrahedral structure III is supported by the ESR spectrum of the green solution which indicates the presence of vanadium(IV).



(III)

3. Iron and ruthenium

The iron(II) complex, $Fe(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$, has been prepared by the reaction of $Fe_2(CO)_9$ and CS_2 in the presence of PPh_3 [9]. A more stable complex is obtained when $P(p\text{-}FC_6H_4)_3$ is used instead of PPh_3; a less stable one is produced when the reaction is carried out in the presence of $P[p\text{-}(MeO)C_6H_4]_3$. The tris(p-fluorophenyl)phosphine complex undergoes phosphine exchange with excess of PPh_3 to give the triphenylphosphine complex. A hexacoordinated structure (IV) was proposed for the complexes.

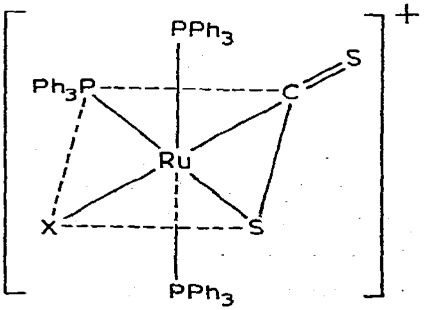


(IV)

Busetto et al. [10] have postulated that the intermediate, $[CpFe(CO)_2CS_2]^-$, is formed during the synthesis of the iron thiocarbonyl cation, $[CpFe(CO)_2CS]^+$ (see p. 175).

However, no decision was made as to the nature of the CS_2 coordination in the complex.

The reaction of PPh_3 with $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ in refluxing CS_2 solution yields the ionic species, $[RuCl(PPh_3)_3(\pi\text{-}CS_2)]Cl$; the bromo analogue has also been prepared [11]. Structure V is suggested for these cationic species.



(V)

X = Cl or Br

4. *Rhodium and iridium* *

The reactions of CS_2 with a variety of rhodium and iridium complexes have been investigated. Details of some of these reactions are given in Fig. 1*a*.

When $RhCl(PPh_3)_3$ is treated with CS_2 a rather unstable complex analysing approximately as $RhCl(PPh_3)_2(CS_2)_2$ is produced [8]. The IR spectrum of this complex exhibits two strong bands at 1510 and 1020 cm^{-1}. The latter band is roughly in the same region as the $\nu(C{=}S)$ frequency for $Pt(PPh_3)_2(\pi\text{-}CS_2)$ and $Pd(PPh_3)_2(\pi\text{-}CS_2)$. Consequently, this frequency has been assigned to a π-bonded CS_2 ligand. The presence of the 1510 cm^{-1} band has been attributed to a CS_2 molecule coordinated to the rhodium atom through one of its sulphur atoms (structure VI).

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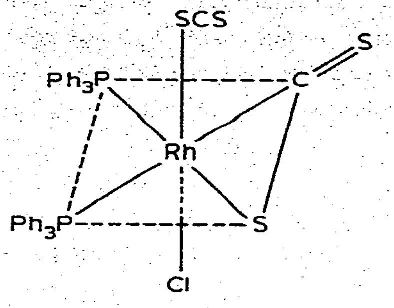
[*] In 1963, Marko et al. [12] reported the preparation of the first cobalt carbonyl disulphide complex, allegedly $Co_4(CO)_{10}CS_2$. The complex is formed in low yield from the reaction of $Co_2(CO)_8$ with CS_2. In a subsequent publication [13], the same authors indicated that an isomer of the above CS_2 complex could be obtained by varying the $Co_2(CO)_8/CS_2$ ratio. However, X-ray diffraction studies have indicated that the true compositions of the "isomers" are in fact $Co_3(CO)_8CS_2[SCo_3(CO)_7]$ [14] and $[SCo_3(CO)_7](SC)(S)[CCo_3(CO)_9]$ [15], respectively. Details of these studies have not yet been published.

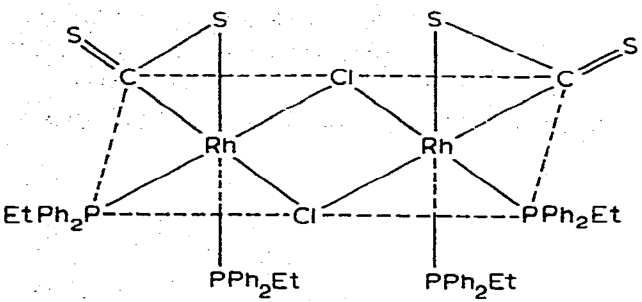


(VI)

Yagupsky and Wilkinson [16] have prepared several cationic π-CS_2 complexes isolable as their tetraphenylborate salts. For instance, reaction of $RhCl(PPh_3)_3$ with CS_2 in the presence of MeOH and excess PPh_3 affords $[Rh(PPh_3)_3(CS_2)(\pi\text{-}CS_2)]^+$. This cation is believed to contain an S-bonded CS_2 group similar to that shown above for $RhCl(PPh_3)_2$-$(CS_2)(\pi\text{-}CS_2)$. This CS_2 group is readily lost from the complex to yield the stable cation, $[Rh(PPh_3)_3(\pi\text{-}CS_2)]^+$.

Addition of CS_2 to *trans*-$RhCl(CO)(PPh_3)_2$ in MeOH in the presence of excess PPh_3 produces a blue solution. Treatment of this blue solution with sodium tetraphenylborate results in precipitation of $[Rh(CO)(PPh_3)_3(\pi\text{-}CS_2)]BPh_4$. The thiocarbonyl analogue, *trans*-$RhCl(CS)(PPh_3)_2$ (see p. 177), also reacts with CS_2 in the presence of MeOH and excess PPh_3 to give $[Rh(CS)(PPh_3)_2(CS_2)(\pi\text{-}CS_2)]^+$ and $[Rh(CS)(PPh_3)_2(\pi\text{-}CS_2)]^+$.

A complex, analysing as $RhCl(CS)_2(PPh_2Et)_2$, can be obtained from the reaction of the rhodium(III) hydride, $RhCl_2H(PPh_2Et)_3$, with CS_2 [17]. Infrared data for this complex are compatible with the structure VII.



(VII)

Addition of $SnCl_2$ in ethanol to a CS_2 solution of $RhCl(PPh_3)_3$ and PPh_3 affords the complex, $Rh(PPh_3)_2(\pi\text{-}CS_2)(SnCl_3)$ [16]. The chemistry of the analogous iridium complexes is very similar to that of the rhodium complexes discussed above [16]. Cationic species are also produced in the presence of MeOH, PPh_3 and CS_2 (Fig. 1(b)).

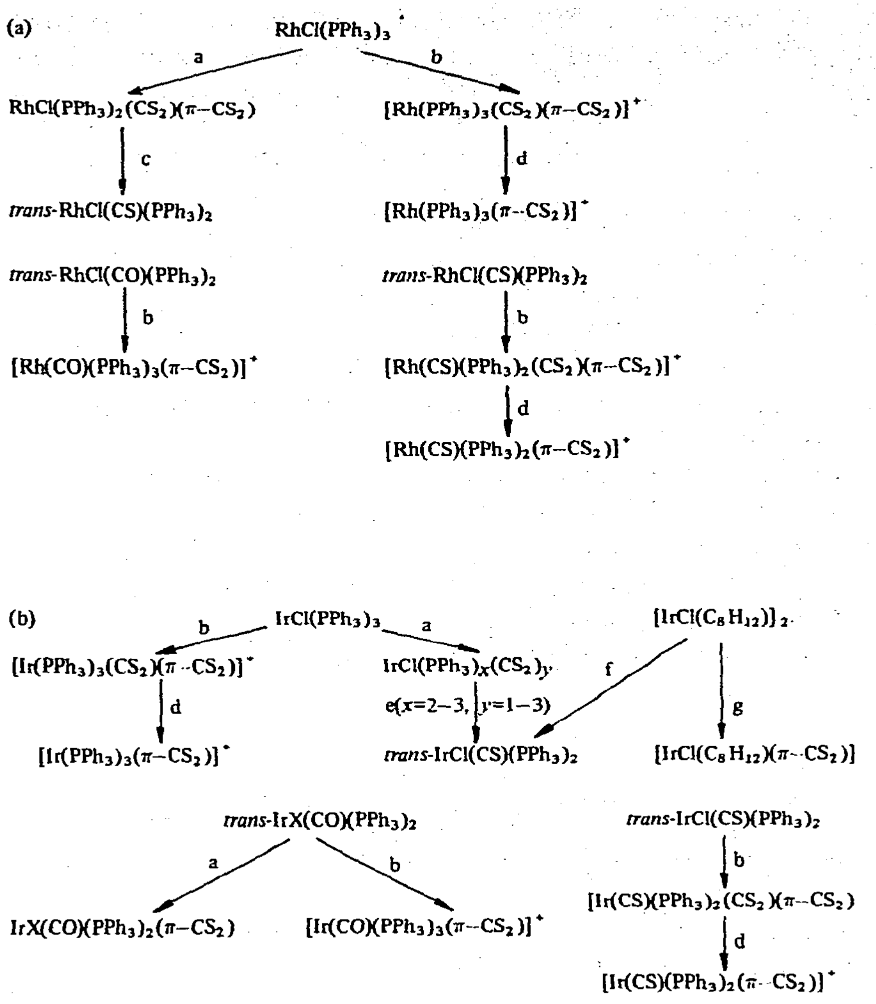
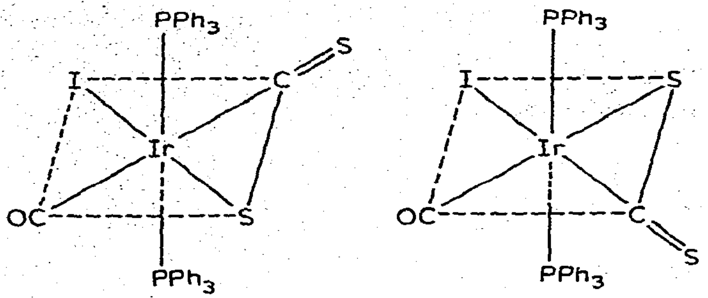


Fig. 1. Typical reactions of rhodium and iridium complexes with CS_2 [8, 9, 16]. a, in CS_2; b, in CS_2 and in the presence of PPh_3 and MeOH; c, in $CHCl_3$ followed by addition of MeOH; d, in vacuo; e, upon heating in $CHCl_3$; f, in CS_2 and in the presence of PPh_3 and $CHCl_3$; g, in CS_2 and CH_2Cl_2.

The reaction of *trans*-$IrCl(CO)(PPh_3)_2$ with CS_2 produces a mixture of unreacted starting material and the new complex, $IrCl(CO)(PPh_3)_2(\pi\text{-}CS_2)$ [8]. All attempts to separate the two complexes failed. However, when the iodo analogue, *trans*-$IrI(CO)(PPh_3)_2$, is used instead, the pure complex, $IrI(CO)(PPh_3)_2(\pi\text{-}CS_2)$, can be isolated. Its infrared spectrum in CS_2 solution exhibits two bands in the π-CS_2 region at 1188 m and 1165 s cm^{-1}. Consequently, it was proposed that the complex is in fact a mixture of two isomers (VIII) which differ in the orientation of the π-bonded CS_2 group.



(VIII)

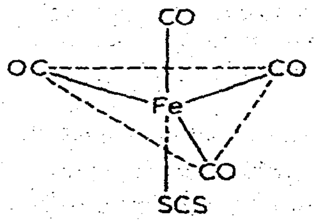
Deeming and Shaw [18] have isolated the analogous dimethylphenylphosphine complex, $IrCl(CO)(PPhMe_2)_2(\pi\text{-}CS_2)$. The NMR spectrum of the complex consists of two 1/2/1 triplets. However, because two triplets would be expected for each of the two possible π-CS_2 isomers, it was suggested that only one isomer is presented in solution. This may also be true for the solid state as there is only one Ir—Cl stretch observed (at 252 cm^{-1}).

A dimeric chlorine-bridged structure containing two π-CS_2 groups has been proposed for the complex of stoichiometry $IrCl(C_8H_{12})(CS_2)$, which is the product of the reaction between the 1, 5-cyclooctadiene complex, $[IrCl(C_8H_{12})]_2$, and CS_2 [9].

B. S-Bonded complexes

There are only a few complexes in which a CS_2 molecule is believed to be bonded to a transition metal solely through a sulphur atom. Some of these for rhodium and iridium have already been described in the previous section since they also contain π-bonded CS_2 groups.

Purely on the basis of IR data in the CO stretching region, a complex with structure IX allegedly results from the reaction of $Fe_2(CO)_9$ with CS_2 [9].



(IX)

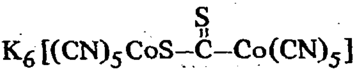
A complex of stoichiometry, $Pt(Me)I(PPh_3)_2CS_2$, has been isolated from the reaction of $Pt(Me)I(PPh_3)_2$ with CS_2 [17]. The strong band in the spectrum at 1520 cm^{-1} was taken to be indicative of an S-bonded CS_2 molecule. The ease of CS_2 dissociation from the complex supports this suggestion.

C. Complexes with bridging CS_2 groups

The complex, $K_6[(CN)_5CoCS_2Co(CN)_5]$ has been obtained independently by Mizuta et al. [19] and by Baird et al. [9] from the reaction of $K_2[Co(CN)_5]$ with CS_2. The two research groups differ in their ideas on the proposed mode of CS_2 bridging in the complex. The Japanese chemists prefer a structure (X) in which there are two Co–S bridges, while the British group consider that the CS_2 molecule is C-bonded to one Co atom and S-bonded to the other (XI).

$K_6[(CN)_5Co{-}S{=}C{=}S{-}Co(CN)_5]$

(X)



$K_6[(CN)_5CoS{-}\overset{\overset{S}{\|}}{C}{-}Co(CN)_5]$

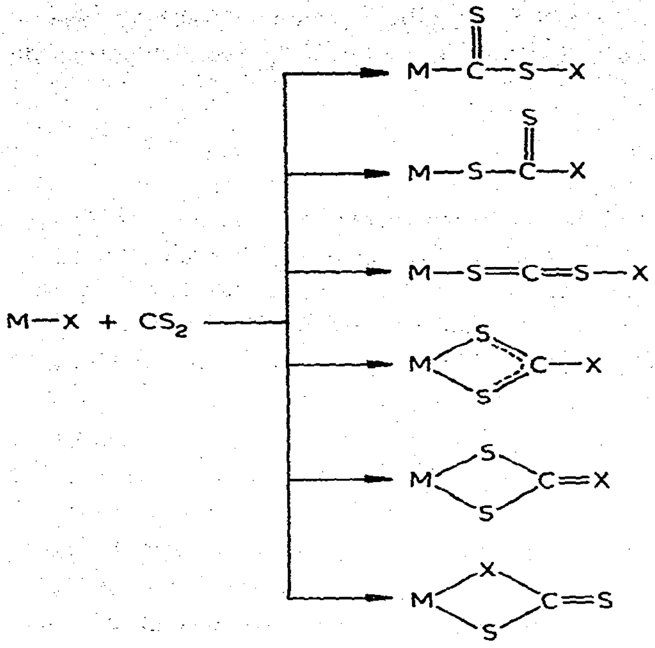
(XI)

Direct reaction of $IrCl(PPh_3)_3$ with CS_2 leads to green solutions from which complexes of stoichiometry, $IrCl(PPh_3)_x(CS_2)_y$ ($x = 2$–$3, y = 1$–3), can be obtained [16]. The actual composition of the complexes depends critically on the experimental conditions employed. Owing to their instability, the exact nature of these compounds has not been determined. However, from IR data alone, it was suggested that $IrCl(PPh_3)_3(CS_2)$ and $IrCl(PPh_3)_2(CS_2)_3$ might be dimeric with bridging CS_2 groups and that in the latter an S-bonded CS_2 group might also be present.

A special case of CS_2 bridging results from the reaction of the anions, $(1,2\text{-}B_9C_2H_{11})_2M^-$ (M = Fe, Co) with CS_2 in the presence of $AlCl_3$ and HCl. Zwitterionic species are formed which have an $-SCH^+-S$ bridge between the two π-bonded dicarbollide ligands of the complex [20].

D. CS_2 insertion complexes

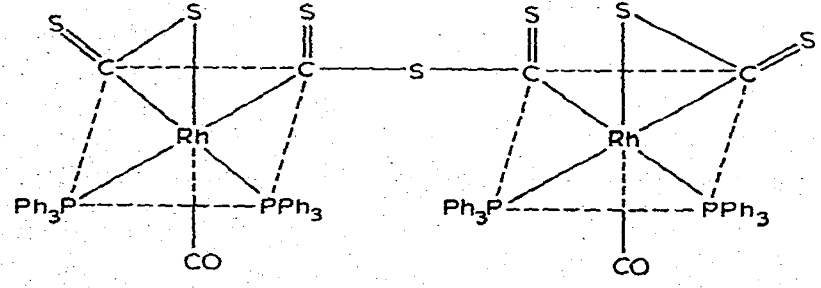
Although insertion reactions between main group metal complexes and CS_2 have been known for some time [21], very little work had been reported until recently on similar reactions with transition metal complexes. Potentially, the insertion of a CS_2 molecule into an M–X bond (M = transition metal, X = H, alkyl, aryl, amine, alkoxide, etc.) could lead to a variety of known or new dithio compounds:



The known CS_2 insertion reactions of transition metal complexes will be discussed according to the nature of the metal–ligand bond into which the CS_2 molecule inserts.

1. Metal–hydrogen bonds

Recently, Commereuc et al. [17] have reported that CS_2 inserts into metal–hydrogen bonds of d^8 rhodium, iridium, and platinum complexes. For example, reaction of $RhH(CO)(PPh_3)_3$ with CS_2 leads to the formation of a compound of stoichiometry, $[Rh(CO)(PPh_3)_2(C_2S_3)]_2S$. The low solubility of this compound in organic solvents precluded a molecular weight determination. In its IR spectrum there is no Rh–H absorption but there is a strong band at 993 cm^{-1} which was assigned to a π-CS_2 group. The absence of the metal hydride group in the complex was also confirmed by proton NMR spectroscopy. Structure XII was suggested for the complex; it can be arrived at by coupling together two molecules of the insertion product, $Rh(CO)(PPh_3)_2(\pi$-$CS_2)(CSSH)$, with elimination of H_2S.



(XII)

The CS_2 insertion reactions of iridium hydrides such as $IrH(CO)(PPh_3)_3$ have been monitored by NMR spectroscopy [17]. In this case, the following reaction scheme was proposed:

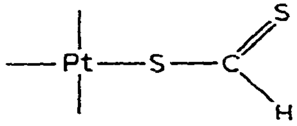
$$\begin{array}{l} IrH(CO)(PPh_3)_3 + CS_2 \rightarrow PPh_3 + IrH(CO)(PPh_3)_2(\pi\text{-}CS_2) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow H^- \text{ transfer} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad Ir(CO)(PPh_3)_2(CSSH) \end{array}$$

The lack of documentation on the chemical shift of the SH proton precluded a distinction between a –CSSH or –SSCH type of bonding in the insertion product.

The reaction of $IrH(CO)_2(PPh_3)_2$ with CS_2 yields a solid which analyses as $Ir(CO)(PPh_3)_2(CS_2)_2$ [17]. Infrared data point to an increase of the oxidation state of the iridium atom and to the presence of a π-CS_2 group. Although the two formulations compatible with an Ir^{III} complex containing two CS_2 molecules are $Ir(CO)(PPh_3)_2(\pi\text{-}CS_2)(CSSH)$ and $Ir(CO)(PPh_3)_2(\pi\text{-}CS_2)(SSCH)$, no NMR signal attributable to –CSSH or –SSCH protons was observed.

Interaction of CS_2 with the π-cyclopentadienyl hydride complexes, Cp_2WH_2 and Cp_2ReH, has also been studied but no definite products were obtained [17].

Pallazzi et al. [22] have obtained the insertion products, $PtX(PPh_3)_2(SSCH)$ (X = Cl, Br, I, CN), from the reactions of *trans*-$PtXH(PPh_3)_2$ with CS_2. The chloro complex, $PtCl(PPh_3)_2(SSCH)$, has two new bands in its IR spectrum at 1050 and 930 cm^{-1} but no Pt–H absorption. Structure XIII is preferred for the –SSCH group.



(XIII)

This choice was made on the basis that the complex does not exhibit acidic properties. Moreover, treatment of the complex with KCN yields potassium dithioformate, KS_2CH.

Kinetic data [22] seem to indicate that there are two steps in the formation of $PtCl(PPh_3)_2(SSCH)$: (1) S-coordination of CS_2 to produce a labile species and (2) intramolecular hydrogen migration in a four-centre transition state to form the insertion product.

Another complex prepared by CS_2 insertion into a metal–hydrogen bond for which X-ray data are available is $Re(CO)_2(PPh_3)_2(SSCH)$ [23]. This complex, which is prepared [24] by refluxing a CS_2 solution of $ReH(CO)_2(PPh_3)_2$, contains a chelated dithioformato group. Although the presence of a hydrogen atom associated with the CS_2 group could not be detected by X-ray diffraction, spectroscopic data indicate that the original hydride ligand has been transferred to the carbon atom of the CS_2 entity. Moreover, although it was not mentioned in the above work, the bonding parameters for the four-membered chelate ring in $Re(CO)_2(PPh_3)_2(SSCH)$ are essentially similar to those observed for $Re(CO)_4(SSCPh)$ which is also obtained by a CS_2 insertion process (see below). The results for $Re(CO)_2(PPh_3)_2(SSCH)$ led Albano et al. [23] to suggest that the related iridium complex, $Ir(CO)(PPh_3)_2(CSSH)$, described earlier must also contain a chelated dithioformato group.

Einstein et al. [25] have shown that CS_2 will insert at room temperature into the M–H bonds of *fac*-$Mn(CO)_3(Diphos)H$ and *fac*-$Mn(CO)_3(Ph_2PCH_2PPh_2)H$ (M = Mn, Re) to form $M(CO)_3(Diphos)(SSCH)$ and $M(CO)_3(Ph_2PCH_2PPh_2)(SSCH)$, respectively. The molecular arrangement of the M(SSCH) moiety was confirmed by single crystal X-ray diffraction of the manganese bis(diphenylphosphino)methane complex. The four complexes are of particular interest because they are among the first for which laser Raman data have been obtained. The $\nu(CS)$ modes are of relatively high intensity and fall in the region 999–649 cm^{-1}.

2. *Metal–carbon bonds*

Complexes of the type, $M(CO)_4(SSCR)$ (M = Mn, Re; R = Ph, CF_3), have been prepared by treatment of the appropriate free dithioacid with $M(CO)_5R$ [26, 27]. An alternative synthetic route to $Re(CO)_4(SSCPh)$ and a variety of new dithiocarboxylato complexes of manganese and rhenium has been reported by Lindner et al. [28–30]. The reactions involve direct CS_2 insertion into metal–carbon bonds.

$$M(CO)_5R + CS_2 \xrightarrow[80\text{–}150^\circ]{3\text{–}5\ \text{days}} M(CO)_4(SSCR) + CO$$

$$(M = Mn,\ R = Me,\ Ph,\ p\text{-}MeC_6H_4;$$
$$M = Re,\ R = Me,\ Ph,\ p\text{-}MeC_6H_4,\ p\text{-}ClC_6H_4,\ PhCH_2,\ Ph_3C)$$

An X-ray diffraction study of $Re(CO)_4(SSCPh)$ indicates that the dithio group acts as bidentate ligand and the coordination around the central metal is pseudo-octahedral [31]. The vibrational spectra of the manganese and rhenium complexes are in agreement with the observed pseudo-C_{2v} molecular symmetry [28, 30].

Lindner et al. [30] have noted that the trend towards CS_2 insertion into the $M(CO)_5R$ complexes is the same as that observed for the "CO insertion" reactions of the pentacarbonylmanganese(I) complexes, $Mn(CO)_5R$, viz., the reaction is more facile with an aromatic than with an aliphatic derivative. The rhenium dithiocarboxylates are more stable than their manganese analogues. The dithiobenzoato derivative, $Re(CO)_4(SSCPh)$, undergoes CO substitution by PPh_3 to give the tricarbonyl derivative, *fac*-$Re(CO)_3PPh_3(SSCPh)$.

During the course of their work on the CS_2 insertion reactions of a variety of transition metal complexes, Commereuc et al. [17] prepared a complex of stoichiometry, $RhI_2(Me)(CS_2)(PPh_3)_2 \cdot C_6H_6$, from the reaction of $RhI_2(Me)(PPh_3)_2 \cdot C_6H_6$ with CS_2. It was suggested that the complex contains a dithiomethyl ester group –CSSMe. However, in view of the CS_2 insertion reactions described earlier, it seems much more likely that the $MeCS_2$ in this complex is S-bonded and chelated to the rhodium atom. Moreover, such a structure is in accord with the tendency of Rh^{III} to become hexacoordinated.

A complex of stoichiometry, $Rh(Ph)(PPh_3)_3(CS_2)_2$, has been isolated from the reaction of $Rh(Ph)(PPh_3)_3$ with CS_2 [17]; a structure containing both a π-CS_2 and a dithiophenyl ester group was proposed. However, the dithiobenzoato complexes, $M(CO)_4$-(SSCPh) (M = Mn, Re), exhibit an IR band at 1267 cm^{-1} which is very close to that assigned to a dithiophenyl ester group at 1261 cm^{-1}. Consequently, it seems much more likely that the PhCSS group in the rhodium complex is S- rather than C-bonded.

3. *Metal–nitrogen bonds*

Vetter et al. [32, 33] have prepared *N,N*-dialkyldithiocarbamates of phosphorus and arsenic by the insertion of CS_2 into P–N and As–N bonds. This method has been extended to the early transition metals by Bradley et al. [34, 71]. In particular, complexes of Ti^{IV}, V^{IV}, and Zr^{IV} give the hitherto unknown tetrakis (*N,N*-dialkyldithiocarbamato) complexes:

$$M(NR_2)_4 + 4CS_2 \longrightarrow M(SSCNR_2)_4$$
$$(M = Ti, Zr, R = Me, Et, n\text{-}Pr; M = V, R = Me, Et)$$

In the case of pentakis (*N,N*-dimethylamido) derivatives of niobium and tantalum, different products are obtained.

$$Nb(NMe_2)_5 + 5CS_2 \longrightarrow Nb(SSCNMe_2)_4 + 1/2(Me_2NCS_2)_2$$
$$Ta(NMe_2)_5 + 5CS_2 \longrightarrow Ta(SSCNMe_2)_5$$

McCormick and Kaplan [35] have synthesized a series of dithiocarbamates of Ni^{II} by the direct insertion of CS_2 into Ni–N bonds of a variety of amine complexes, e.g. $[Ni(En)_3]Cl_2$ and $[Ni(Amp)_3]Cl_2$ *.

Carbon disulphide also gives insertion products with $[tetraaziridinenickel]^{2+}$ and $[tetrakis(2\text{-}methylaziridine)nickel]^{2+}$ [36]. Infrared data suggest that the resulting complexes contain N, S- rather than the expected S, S-bonded ligands.

4. *Metal–oxygen and metal–sulphur bonds*

Insertion of CS_2 into metal–oxygen and metal–sulphur bonds in alkoxides and mercaptides leads to the formation of metal xanthates and metal trithiocarbonates, respectively

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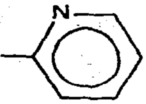
* En = ethylenediamine ; Amp = H_2NCH_2– 

e.g. with $Ni(OMe)_2$, nickel methylxanthate $[Ni(SSCOMe)_2]$ is formed [37].

As early as 1931, it was known that copper mercaptides react with CS_2 to give Cu^I alkyltrithiocarbonates [1]. More recently, it has been shown that the trithiocarbonates of molybdenum and tungsten, $CpM(CO)_2(SSCSR)$ (M = Mo, W; R = Me, Ph), can be obtained in a similar way from $CpM(CO)_3SR$ or $[CpM(CO)_2SR]_2$ [38]. Also, spectroscopic evidence indicates that the corresponding nickel complexes, $[CpNiSR]_2$ (R = Me, Et), undergo CS_2 insertion to give the unstable species, CpNi(SSCSR) [39].

While investigating the reactions of $Pt(PPh_3)_2O_2$ with various unsaturated molecules, Hayward et al. [40] discovered that this complex and its palladium analogue react with CS_2 to give the known dithiocarbonates, $Pt(PPh_3)_2(SSCO)$ and $Pd(PPh_3)_2(SSCO)$, respectively.

5. *Metal–halogen bonds*

There is only one example of CS_2 inserting into a metal–halogen bond viz., the formation of $[Pt(PPh_3)_2(SSCF)]HF_2$ from the reaction of $[PtF(PPh_3)_3]HF_2$ with CS_2 [41]. The crystal structure of this complex displays pseudo-square-planar coordination around the metal with the FCSS group bonded through the two sulphur atoms.

III. Thiocarbonyls

The first examples of transition metal thiocarbonyl complexes, *trans*-$RhX(CS)(PPh_3)_2$ and $RhX_3(CS)(PPh_3)_2$ (X = Cl, Br), were synthesized by Baird and Wilkinson [2] in 1966. Since then, relatively few thiocarbonyl complexes have been prepared and even these have been restricted to certain Group VIII metals and manganese. Furthermore, in sharp contrast to metal carbonyls, only three metal thiocarbonyls containing more than one CS group attached to a central metal have so far been identified.

The discovery of the first transition metal thiocarbonyls prompted Richards [42] to undertake a molecular orbital calculation for the CS molecule. The ground state electronic configurations for the CO and CS molecules are: CO, $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(5\sigma)^2\,(1\pi)^4$; CS, $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2\,(6\sigma)^2\,(7\sigma)^2\,(2\pi)^4$. The calculation indicated that while the 7σ and 2π orbitals are almost degenerate the 7σ orbital is localized largely on the carbon atom and the 2π is a bonding orbital distributed on both the carbon and the sulphur atoms. The two electrons in the 7σ orbital constitute a lone pair which can be used to bond the CS group to a metal in a thiocarbonyl complex. This situation is similar to that for CO in metal carbonyls in which the 5σ lone pair is used. Moreover, the pair of electrons in the 7σ orbital of CS should be more readily available since the energy of this orbital is -0.4705 a.u. as compared to -0.5704 a.u. for the 5σ CO orbital. Furthermore, there appears to be a greater possibility of backbonding in thiocarbonyls than in carbonyls. The energy of the empty 3π antibonding orbital on CS is $+0.0848$ a.u. which is significantly lower than the energy $+0.1507$ a.u. of the equivalent 2π antibonding orbital on CO.

The above conclusions were based on calculation of the wave function for CS and CO at their equilibrium internuclear distances. Richards repeated his calculations for three internuclear CS distances to see if there was any significant change when the bond was stretched during complex formation. He found that while the energy of the 7σ orbital decreases slightly with increasing interatomic distance, the energy of the 3π orbital decreases somewhat more rapidly. In other words, the availability of the 7σ electrons for σ-bonding is affected only slightly by the increase in interatomic distances expected during complex formation, whereas the empty 3π antibonding orbital becomes more readily available for backbonding.

Richards felt that his analysis revealed that thiocarbonyls should be significantly more stable than their carbonyl counterparts because CS is favoured over CO both in terms of σ and π bonding. This conclusion appears to be contradicted by the present paucity of thiocarbonyls. However, some fragmentary experimental data for the known thiocarbonyl complexes do suggest that CS is a better π-acceptor than CO and so should be more strongly bound to a transition metal than is CO.

A. Group VIII metals

1. Iron

The cationic iron thiocarbonyl complex $[CpFe(CO)_2CS]^+$ has been synthesized [10] from $[CpFe(CO)_2]^-$ and CS_2.

$$[CpFe(CO)_2]^- + CS_2 \longrightarrow [CpFe(CO)_2CS_2]^- \xrightarrow{MeI}$$

$$CpFe(CO)_2(CSSMe) \xrightarrow{HCl} [CpFe(CO)_2CS]^+Cl^- + MeSH$$

Attempts to isolate the two proposed intermediates in this reaction were unsuccessful. However, the IR spectrum of the reaction mixture after addition of MeI was consistent with the presence of a dithioester.

It should be mentioned that $[CpFe(CO)_2CS]^+$ was first prepared [43] by the following reaction sequence:

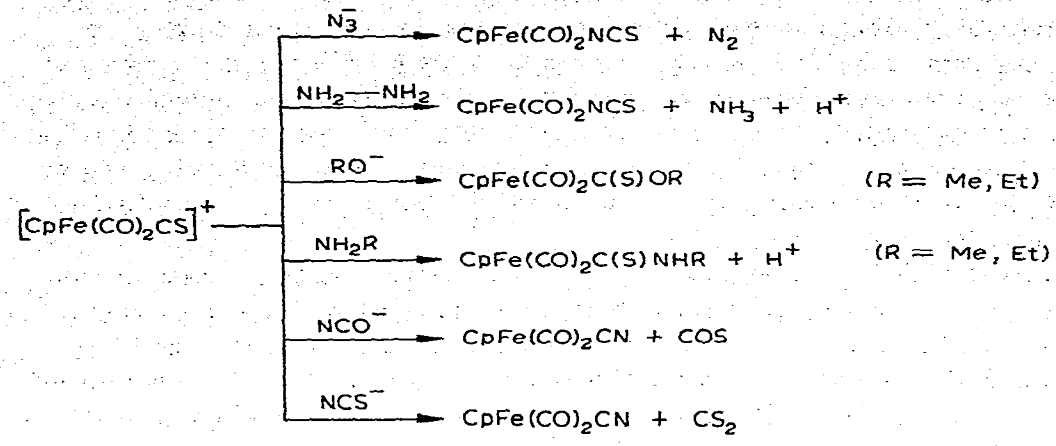
$$[CpFe(CO)_2]^- + ClC(S)OR \longrightarrow \underset{(R = Me, Et)}{CpFe(CO)_2C(S)OR} \xrightarrow{HCl}$$

$$[CpFe(CO)_2CS]^+Cl^- + ROH$$

This represents the only example of the formation of an M–CS bond where CS_2 does not act as the CS donor.

Busetto et al. [44] have investigated the reactions of $[CpFe(CO)_2CS]^+$ with various nucleophilic agents. Three different types of reactions were observed depending upon the nature of the nucleophile.

In all the reactions described above, the nucleophilic attack occurs at the CS group.



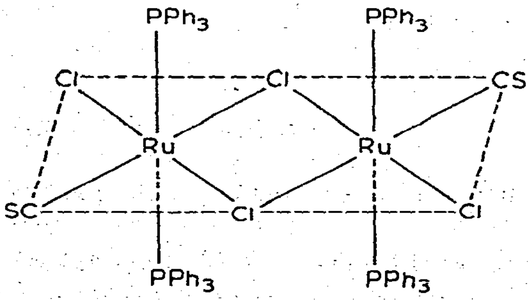
Consequently, it was suggested that the electrophilic character of the thiocarbonyl carbon atom in $[CpFe(CO)_2CS]^+$ is significantly higher than that of the carbonyl carbon atoms.

The ^{57}Fe Mössbauer spectra of a variety of cationic complexes of the type $[CpFe(CO)_2L]^+$ (L = monodentate ligand including CO and CS) have been investigated [45]. On the basis of isomer shifts, it was concluded that CS is a better π-acceptor than is CO.

2. *Ruthenium*

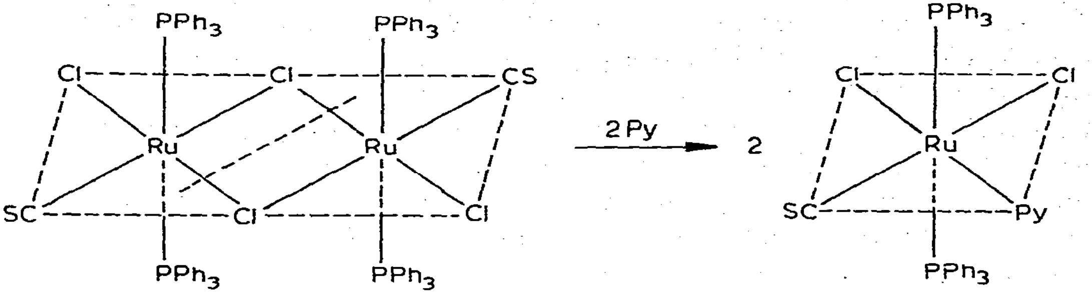
As mentioned earlier (see p. 165), the reaction of $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ with CS_2 and excess PPh_3 leads exclusively to the formation of the π-CS_2 complex, $[RuCl(PPh_3)_3(\pi\text{-}CS_2)]Cl$. However, in the absence of PPh_3, the π-CS_2 complex precipitates out of solution and concentration of the filtrate affords the dimer $[RuCl_2(CS)(PPh_3)_2]_2$.

On the basis of IR evidence, structure XIV (or a similar one with *cis*-CS groups) was proposed for the complex; for steric reasons the PPh_3 groups were considered to be *trans* to each other. The bromo analogue is also known.



(XIV)

The reactions of the chloro complex with CO, Py, Bipy and *o*-Phen have been investigated [11]*. As expected, the complex undergoes cleavage reactions typical of a halogen-bridged species, e.g.:



The anionic ruthenium thiocarbonyl, $[RuCl_3(CS)(PPh_3)_2]^-$, prepared from $[RuCl_2(CS)(PPh_3)_2]_2$ and Cl^-, has been reported recently [46]. This complex is as yet the only example of a thiocarbonylmetallate.

3. Cobalt

The evidence for a thiocarbonyl complex of cobalt is by no means conclusive. Among the numerous sulphur-containing products of the reaction of $Co_2(CO)_8$ with CS_2 is a complex of stoichiometry, $Co_3(CO)_6CS_2$ (yield 1.5%) [13]. Its infrared spectrum exhibits one band at 1011 cm^{-1} and it was suggested that this could indicate a triply-bridged CS group. The proposed structure consists of a triangle of three $Co(CO)_2$ units bonded to an apical trivalent sulphur atom with CS group bridging on the other side of the cluster.

4. Rhodium

It was mentioned earlier (p. 165) that $RhCl(PPh_3)_3$ reacts with CS_2 to form the rather unstable complex, $RhCl(PPh_3)_2(CS_2)(\pi\text{-}CS_2)$. Dissolution of this complex in $CHCl_3$, followed by addition of MeOH and subsequent removal of the solvent yields the thiocarbonyl, *trans*-$RhCl(CS)(PPh_3)_2$, in 50% yield [9]. Among the side-products of the reaction are PPh_3S and PPh_3O. That PPh_3 is the sulphur-acceptor was demonstrated by repeating the reaction in the presence of excess PPh_3. Addition of a 1/1 mixture of MeOH and CS_2 to $RhCl(PPh_3)_3$ and PPh_3 leads to the formation of an emerald-green solution. The cationic species, $[Rh(PPh_3)_3(\pi\text{-}CS_2)]^+$, can be precipitated from this solution as its tetraphenylborate salt. However, if CS_2 is removed from the solution before precipitation of the π-CS_2 complex, orange crystals of *trans*-$RhCl(CS)(PPh_3)_2$ are formed in almost quantitative yield. The residual solution contains all the abstracted sulphur in the form of PPh_3S.

The molecular structure of *trans*-$RhCl(CS)(PPh_3)_2$ has been determined by de Boer et al. [47]. Although there is a slight distortion, the structure contains the expected

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* Py = pyridine, Bipy = bipyridine, *o*-Phen = *o*-phenanthroline.

square-planar coordination around the rhodium atom together with a nearly-linear thiocarbonyl ligand (∠ Rh—C—S, 177.2°). The Rh—C distance (1.787 Å) in the complex is appreciably shorter than that in the carbonyl analogue, *trans*-$RhCl(CO)(PPh_3)_2$ (1.86 Å), suggesting a greater Rh—C double bond character for the former.

The Rh^I thiocarbonyl undergoes oxidative addition with Cl_2 to give the Rh^{III} derivative, $RhCl_3(CS)(PPh_3)_2$ [2, 9]. (The analogous bromo compounds have also been prepared.) In contrast to its carbonyl analogue, *trans*-$RhCl(CS)(PPh_3)_2$ does not add HCl. It was suggested that this could indicate a lowering of the non-bonding electron density on the metal resulting from the better π-acceptor character of CS. Moreover, it has proved experimentally impossible to replace the thiocarbonyl ligand in the complex by CO (1 atm, 25°) and the complex decomposes following attack by MeI and $HgCl_2$. These results were also explained in terms of the π-acidity of CS.

Treatment of *trans*-$RhCl(CS)(PPh_3)_2$ with LiSCN gives the S-bonded thiocyanato complex, *trans*-$Rh(CS)(SCN)(PPh_3)_2$ [9]. The thiocarbonyl complex also reacts easily with tetracyanoethylene (TCNE) to give $RhCl(CS)(PPh_3)_2(TCNE)$ [48]. Infrared data seem to support a hexacoordinated structure with TCNE bonded to the rhodium atom via metal—carbon σ-bonds.

The reaction of *trans*-$RhCl(CS)(PPh_3)_2$ with CS_2 to give complexes containing CS and π-CS_2 ligands has been discussed already (see p. 166).

5. *Iridium*

The chemistry of the iridium thiocarbonyl, *trans*-$IrCl(CS)(PPh_3)_2$, has been studied somewhat more extensively than that of its rhodium analogue. The complex was first prepared in low yield by Yagupsky and Wilkinson [16] from $IrCl(PPh_3)_3$ or $[IrCl(C_8H_{12})]_2$ and CS_2. In the case of $IrCl(PPh_3)_3$, an unidentified product exhibiting a strong infrared absorption at 1360 cm^{-1}, was also formed.

Kubota and Carey [49] have reported a high yield synthesis of *trans*-$IrCl(CS)(PPh_3)_2$ using *trans*-$IrCl(PPh_3)_2(N_2)$ as the starting material. The reaction scheme (Fig. 2) clearly demonstrates that the nature of the products formed in the reactions of transition metal complexes with CS_2 is highly dependent on the experimental conditions employed. The presence of PPh_3 and MeOH is essential to the formation of *trans*-$IrCl(CS)(PPh_3)_2$.

The structures proposed for the intermediates, $IrCl(PPh_3)_2C_2S_5$ and $IrCl(CS)(PPh_3)_2CS_3$, were based on the similarity of their infrared absorption patterns in the 1050—800 cm^{-1} region to that of Ni^{II} complexes containing the perthiocarbonato ligand, CS_4^-. The complex, $IrCl(CS)(PPh_3)_2CS_3$ (ν(CS) 1360 cm^{-1}) was thought to be the unidentified complex observed by Yagupsky and Wilkinson [16] in their synthesis of *trans*-$IrCl(CS)(PPh_3)_2$. Thermal decomposition of either $IrCl(PPh_3)_2C_2S_5$ or $IrCl(CS)(PPh_3)_2CS_3$ yields a complex which was formulated tentatively as $IrCl(CS)(PPh_2)_2CS_3$. The formation of PPh_3S as a by-product of the reactions involving PPh_3 indicates that the latter acts as the sulphur acceptor in the synthesis of thiocarbonyls in Fig. 2.

The low yields and experimental difficulties in their synthetic methods prompted Yagupsky and Wilkinson [16] to restrict their investigation of the chemistry of *trans*-

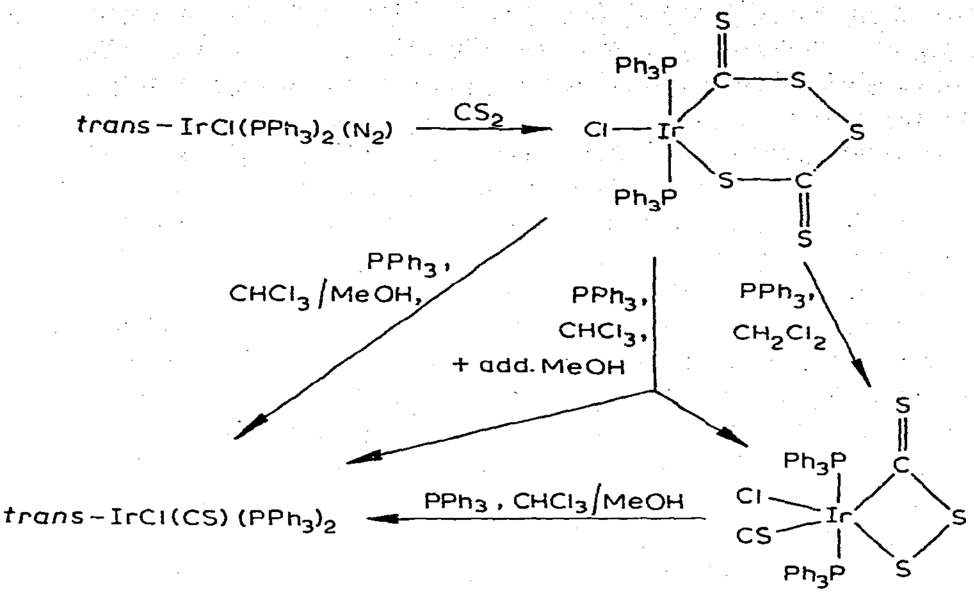

Fig. 2.

$IrCl(CS)(PPh_3)_2$ mainly to a spectroscopic survey. In contrast to its carbonyl analogue, *trans*-$IrCl(CS)(PPh_3)_2$ does not oxidatively add molecular hydrogen. However, treatment of *trans*-$IrCl(CS)(PPh_3)_2$ with CO and SO_2 gives the adducts, $IrCl(CO)(CS)(PPh_3)_2$ and $IrCl(CS)(SO_2)(PPh_3)_2$, respectively. The structure of the latter is believed to be similar to that of its carbonyl analogue, $IrCl(CO)(SO_2)(PPh_3)_2$, viz., a tetragonal pyramid with the SO_2 group in the apical position bound to the metal through the sulphur atom.

The hydride, $IrH(CS)(PPh_3)_3$, formed from the reaction of *trans*-$IrCl(CS)(PPh_3)_2$ with $NaBH_4$ in the presence of excess PPh_3, was actually isolated. Its NMR spectrum indicated a trigonal-bipyramidal structure with equivalent equatorial PPh_3 groups.

Recently, Fitzgerald et al. [50] demonstrated the Lewis basicity of *trans*-$IrCl(CS)(PPh_3)_2$ by successfully forming adducts with boron trichloride, boron tribromide, tetracyanoethylene and fumaronitrile. No reaction took place with boron trifluoride, ethylene or acrylonitrile. The boron trihalide adducts could not be assigned a definitive stoichiometry while the two other adducts were of 1/1 stoichiometry. The BCl_3 adduct readily undergoes hydrolysis to form the hydrogen chloride oxidative addition product, $IrHCl_2(CS)(PPh_3)_2$. The thiocarbonyl stretching frequency, $\nu(CS)$, of the parent complex increases by about 25 cm^{-1} upon adduct formation. These shifts were interpreted as indicating the diminished transition metal basicity of the thiocarbonyl complex compared to its carbonyl analogue.

The cationic thiocarbonyls of iridium, $[Ir(CO)_2(CS)L_2]^+$ ($L = PPh_3, PCy_3$) *, were

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* Cy = cyclohexyl, C_6H_{11}.

prepared recently by Mays and Stefanini [51] by bubbling CO through a $CHCl_3$ solution of the appropriate tetracoordinated complex, *trans*-$IrCl(CS)L_2$; the tricyclohexylphosphine derivative, *trans*-$IrCl(CS)(PCy_3)_2$, was synthesized from *trans*-$IrCl(CS)(PPh_3)_2$ in a phosphine exchange reaction.

The crystal structure of $[Ir(CO)_2(CS)(PPh_3)_2][PF_6] \cdot Me_2CO$ shows that the cation has a trigonal bipyramidal geometry with the phosphines in mutually *trans* positions [72]. The Ir—C(S) group is linear (178.2°) and the Ir—C(S) distance (1.867Å) is significantly shorter than the Ir—C(O) distances (mean 1.938Å) providing further support for the better σ-donor and π-acceptor properties of CS compared to CO.

The chemistry of the thiocarbonyl cations was investigated and compared to that of the related tricarbonyls in order to determine the extent of reactivity change brought about by the replacement of a CO group by CS [51]. Whereas the the tricarbonyl cations undergo facile reversible addition of H_2 to give hexacoordinate dihydrides, the thiocarbonyl complex, $[Ir(CO)_2(CS)(PPh_3)_2]^+$, fails to add H_2 under the same conditions. This observation prompted the preparation of $[Ir(CO)_2(CS)(PCy_3)_2]^+$ in the first place, since a kinetic investigation of the complexes, $[IrH_2(CO)_2L_2]^+$, had shown that the more basic the phosphine the less readily was hydrogen displaced from the dihydride. The complex, $[IrH_2(CO)_2(PCy_3)_2]^+$, was the most stable (kinetically) with respect to hydrogen loss. The thiocarbonyl tricyclohexylphosphine derivative, $[Ir(CO)_2(CS)(PCy_3)_2]^+$, does in fact add H_2 to give the dihydride $[IrH_2(CO)(CS)(PCy_3)_2]^+$. Spectroscopic data for this complex and the dideuteride analogue indicate that hydride and carbonyl ligands are in mutually *trans* positions.

Carbon monoxide replaces hydrogen in $[IrH_2(CO)(CS)(PCy_3)_2]^+$ more readily than in any of the $[IrH_2(CO)_2L_2]^+$ cations and in particular, loss of H_2 from the CO analogue, $[IrH_2(CO)_2(PCy_3)_2]^+$, is very slow by comparison. It was suggested that this could be attributed to the better π-acceptor properties of CS compared to CO, thereby lowering the electron density at the metal and so destabilizing the Ir^{III} state compared with Ir^{I}. This stability of thiocarbonyls towards H_2 addition has been noted already for *trans*-$IrCl(CS)(PPh_3)_2$ (see p. 169).

Neither $[Ir(CO)_2(CS)(PPh_3)_2]^+$ nor $[Ir(CO)_2(CS)(PCy_3)_2]^+$ forms adducts with dimethylacetylene dicarboxylate, although the carbonyl cations $[Ir(CO)_3L_2]^+$ do so at room temperature. The complexes, *trans*-$IrCl(CS)L_2$, can be regenerated easily by Cl^- attack on the cations, $[Ir(CO)_2(CS)L_2]^+$. This reaction is similar to that of $[Ir(CO)_3L_2]^+$ to give *trans*-$IrCl(CO)L_2$.

Reaction of $[CpFe(CO)_2CS]^+$ with MeO^- in anhydrous MeOH leads to the formation of the thioester, $CpFe(CO)_2C(S)OMe$ (see p. 175). However, in the case $[Ir(CO)_2(CS)(PPh_3)_2]^+$, nucleophilic attack takes place at the carbon atom of a coordinated carbonyl rather than at that of the thiocarbonyl group. This results in the formation of the ester $Ir(CO)(CS)(PPh_3)_2C(O)OMe$. Protonation of this ester regenerates the complex, $[Ir(CO)_2(CS)(PPh_3)_2]^+$. The reaction of $[Ir(CO)_2(CS)(PPh_3)_2]^+$ with $PMePh_2$ affords the monocarbonyl cation, $[Ir(CO)(CS)(PMePh_2)_3]^+$.

Mays and Stefanini [51] also investigated the formation of other cationic species from *trans*-$IrCl(CS)L_2$. In these reactions, the square-planar thiocarbonyl complexes behave in an analogous way to *trans*-$IrCl(CO)L_2$. For example, with $NOBF_4$, the pentacoordinated cations, $[IrCl(CS)(NO)L_2]^+$, are produced. The structure of these cations is probably similar to that of $[IrCl(CO)(NO)(PPh_3)_2]^+$ which has been shown by X-ray diffraction to be square-pyramidal with a bent Ir—N—O linkage. With Diphos, *trans*-$IrCl(CS)(PPh_3)_2$ gives $[Ir(CS)(Diphos)_2]^+$ which is analogous to $[Ir(CO)(Diphos)_2]^+$.

B. Manganese

The monothiocarbonyl complex, $CpMn(CO)_2CS$, was first prepared in low yield (< 10%) by reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 at about 40° for approximately 1 week [52]. The reaction is complicated by the formation of minute quantities of $CpMn(CO)_3$ and various unidentified carbonyl and/or carbon disulphide-containing complexes. When the same reaction is repeated in the presence of excess PPh_3, the thiocarbonyl complex is produced in essentially quantitative yield after 24 h [53]. The only other products are PPh_3S and *cis*-cyclooctene (C_8H_{14}). Infrared evidence and kinetic data [54] for the reaction suggest that it proceeds by an S_N1 dissociative mechanism involving the slow loss of C_8H_{14} in the rate-determining step to form the coordinatively unsaturated species $CpMn(CO)_2$ which then undergoes rapid reaction with CS_2, followed by sulphur abstraction by PPh_3. The complete proposed mechanism is shown in Fig. 3.

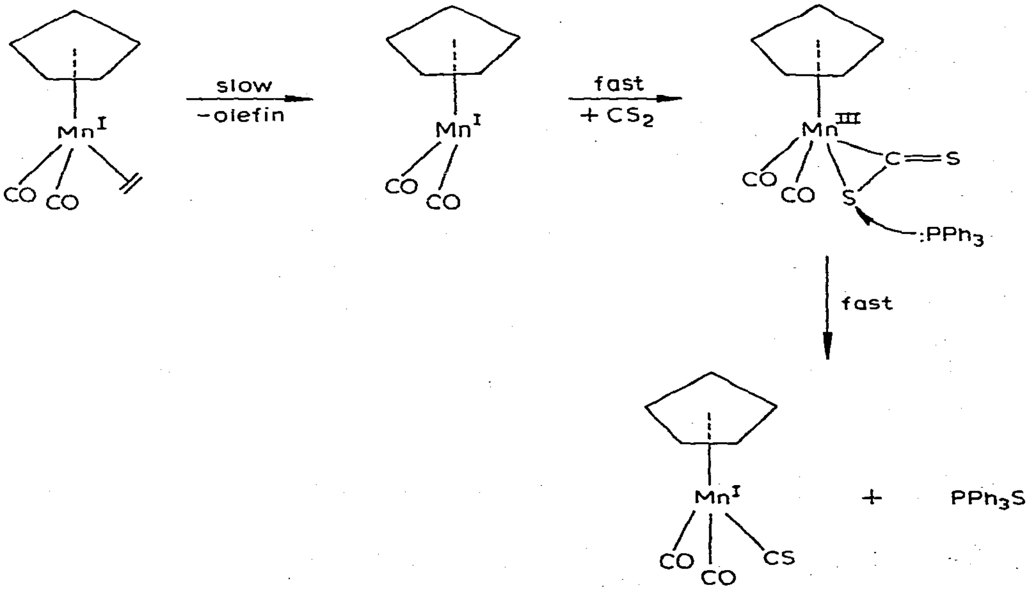
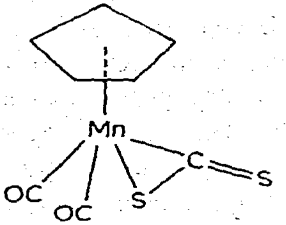


Fig. 3.

The IR data leave little doubt as to the formation of the intermediate $CpMn(CO)_2CS_2$ as a π-CS_2 complex. Moreover, its formation is not unreasonable when one remembers that the syntheses of the Group VIII metal thiocarbonyls also appear to involve π-CS_2 intermediates. Structure XV is proposed [54] for $CpMn(CO)_2(\pi\text{-}CS_2)$. Such a heptacoordinated π-cyclopentadienylmanganese(III) dicarbonyl species is not without precedent because the complexes, $CpMn(CO)_2(SiPh_3)H$ [55], $CpMn(CO)_2(SiCl_3)H$ [56] and $CpMn(CO)_2(SiCl_3)(SnCl_3)$ [57] have been synthesized recently. X-ray data for $CpMn(CO)_2(SiPh_3)H$ suggest the presence of a hydrogen bridge between manganese and silicon, thus forming a three-membered ring similar to that proposed for $CpMn(CO)_2(\pi\text{-}CS_2)$.



(XV)

The mechanism of the reaction in the absence of PPh_3 is difficult to assess. However, there is some evidence [54] that suggests that $CpMn(CO)_2CS$, $CpMn(CO)_3$ and the other products may be formed via thermal decomposition of $CpMn(CO)_2(\pi\text{-}CS_2)$.

Infrared data have also been obtained [54] for the methyl-π-cyclopentadienyl derivative, $(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$.

Both CO groups, but not the CS group, in $CpMn(CO)_2CS$ undergo UV induced substitution with $C^{18}O$ [58], C_8H_{14}, Diphos [54], and various monodentate Group VA ligands such as PPh_3, $SbPh_3$, $P(OMe)_3$ and $P(OPh)_3$ [59] to form $CpMn(CO)(CS)L$ and $CpMn(CS)L_2$. Some of the Group VA derivatives, $CpMn(CO)(CS)L$, exhibit "CO frequency doubling" presumably due to conformational isomerism similar to that observed for various other π-cyclopentadienylmetal carbonyl derivatives, e.g., $CpFe(CO)_2SiMe_2Cl$ [60] and $CpMn(CO)_2S\text{-}n\text{-}Bu_2$ [61]. No splitting of the CS absorptions was detected for any of the thiocarbonyl derivatives.

The *cis*-cyclooctene derivative, $CpMn(CO)(CS)(C_8H_{14})$, has been used as a precursor to $CpMn(CO)(CS)_2$ and $CpMn(CS)_3$ [53].

$$CpMn(CO)_2CS + C_8H_{14} \xrightarrow{h\nu} CpMn(CO)(CS)(C_8H_{14}) + CO$$

$$CpMn(CO)(CS)(C_8H_{14}) + CS_2 \xrightarrow[PPh_3]{} CpMn(CO)(CS)_2 + C_8H_{14} + PPh_3S$$

$$CpMn(CO)(CS)_2 + C_8H_{14} \xrightarrow{h\nu} CpMn(CS)_2(C_8H_{14}) + CO$$

$$\mathrm{CpMn(CS)_2(C_8H_{14}) + CS_2 \xrightarrow[PPh_3]{h\nu} CpMn(CS)_3 + C_8H_{14} + PPh_3S}$$

While the dithiocarbonyl derivative was characterized definitively, the trithiocarbonyl was only identified spectroscopically. These two species are the only known examples of multiple CS groups being attached to a metal atom.

The vibrational spectra of $CpMn(CO)_2CS$ and $CpMn(CO)(CS)_2$ have been assigned [62]. In particular, the ν(CS), ν(Mn—CS) and δ(MnCS) modes have been located in the 1310–1240, 645–473 and 625–448 cm^{-1} regions, respectively. Surprisingly, no Raman lines attributable to the ν(CS) modes were detected in the 1350–1200 cm^{-1} region. This is a particularly remarkable observation because the CS group would be expected to be highly polarizable and hence exhibit strong Raman lines. Whether the lack of CS lines is a general characteristic of thiocarbonyls or just peculiar to the π-cyclopentadienylmanganese thiocarbonyls remains to be established.

The low frequency IR spectra of CpMn(CS)(Diphos) and CpMn(CS)(Triphos) [Triphos = $PPh(CH_2CH_2PPh_2)_2$] have also been studied [63]. The assignments made for the ν(Mn—CS) and δ(MnCS) modes confirm those proposed for $CpMn(CO)_2CS$ and $CpMn(CO)(CS)_2$.

It is of interest that the ν(CS) frequencies for the $CpMn(CS)L_2$ derivatives are lower than those for the related CpMn(CO)(CS)L derivatives [59]. This may imply that the C—S bond in the former has become weaker with concomitant strengthening of the Mn—CS bond. A similar bond-weakening/bond-strengthening effect has been noted for the C—O/Mn—CO bonds in the analogous $CpMn(CO)_2L$ complexes on replacement of CO by L [64].

The mass spectra of $CpMn(CO)_2CS$, $CpMn(CO)(CS)_2$ and several of the CpMn(CO)(CS)L and $CpMn(CS)L_2$ derivatives have been recorded [54, 59]. The proposed fragmentation pathways for the degradation of $CpMn(CO)_2CS$ are shown in Fig. 4. All the spectra exhibit peaks corresponding to the parent molecular ions, as do the spectra of their car-

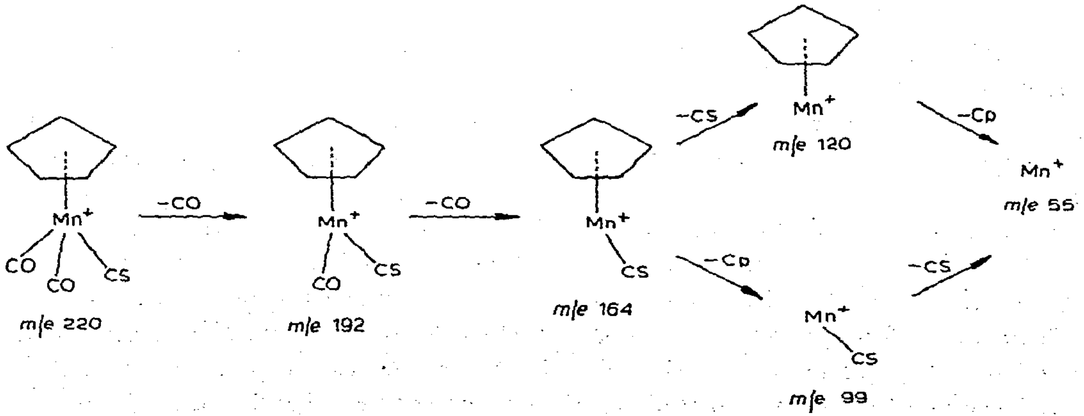


Fig. 4.

bonyl analogues [65]. Moreover, Mn—CS bond cleavage is favoured over C—S bond cleavage; as for CO, the fragmentation of CS from the manganese atom occurs in one step. In contrast to the $CpMn(CO)_2L$ derivatives, for which both CO groups are lost simultaneously from the parent molecular ions, $CpMn(CO)_2CS$ exhibits the stepwise loss of the CO groups followed by the loss of CS. There is a peak at *m/e* 99 in all of the spectra which under high resolution proves to be due to $Mn(CS)^+$. The presence of this peak indicates that, in addition to the pathway leading to $CpMn^+$ (*m/e* 120), the $CpMn(CS)^+$ ion (*m/e* 164) may also lose the π-cyclopentadienyl ring before rupture of the Mn—CS bond. This contrasts to the fragmentation of π-cyclopentadienylmanganese carbonyl complexes where the CO groups and any other ligands present are always lost before the ring [66].

The kinetics and mechanism of the *cis*-cyclooctene substitution in $CpMn(CO)(CS)(C_8H_{14})$ by PPh_3 in methylcyclohexane have been investigated [67]. Over the temperature range employed (50—70°), the rate is approximately four times faster than for the analogous reaction of $CpMn(CO)_2(C_8H_{14})$ with PPh_3. The kinetic data for the thiocarbonyl reaction are in accord with the following S_N1 dissociative mechanism, i.e., a similar mechanism to that proposed by Angelici and Loewen for the reaction of $CpMn(CO)_2(C_8H_{14})$ with PPh_3 [68].

$$CpMn(CO)(CS)(C_8H_{14}) \xrightarrow[-C_8H_{14}]{\text{slow}} CpMn(CO)(CS) \xrightarrow[+PPH_3]{\text{fast}} CpMn(CO)(CS)PPh_3$$

That the thiocarbonyl reaction is significantly faster than that for the carbonyl complex can be explained in terms of the greater π-acceptor capacity of CS compared to CO.

Finally, the absolute integrated infrared intensity of the CS stretching mode in $CpMn(CO)_2CS$ has been measured in CS_2 solution [69]. The value calculated for the associated dipole moment derivative $\mu'(CS)$ is supportive of the similar bonding characteristics of CS and CO.

IV. Conclusion

This review has shown that over the past seven years a great deal of research has been carried out on the activation of CS_2 by transition metal complexes. Nevertheless, this topic remains largely unexplored. In particular, little structural data on the five main types of complexes have been reported and the best synthetic procedures are only just becoming apparent.

In the case of the metal thiocarbonyls, it is obvious that the generation of the CS ligand from CS_2 necessitates the presence of an efficient sulphur acceptor such as PPh_3. The physical and chemical properties of the thiocarbonyl complexes seem to point to the greater stability of these complexes compared to the analogous carbonyl ones, in agreement with the theoretical predictions of Richards [42]. This means that the present scarcity of metal thiocarbonyls is probably due to experimental procedure rather than the inherent instability of the complexes.

In conclusion, it is clear that the use of CS_2 as a solvent for reactions involving transition metal complexes must be carefully considered in future. Carbon disulphide undergoes many more reactions than is often realized. Of the five main types of complexes examined in this review, it is anticipated that in the next few years the study of CS_2 insertion and thiocarbonyl complexes will prove to be two of the most fruitful areas of research in transition metal chemistry.

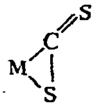
V. Infrared data for carbon disulphide and thiocarbonyl complexes

Infrared spectroscopy provided the chief physical tool used in the studies described in the preceding sections of this review. Consequently, we felt that an analysis of the infrared data collected for the known carbon disulphide and thiocarbonyl complexes would be of importance for future investigations in this field. The frequency ranges for the CS stretching absorptions for the different types of complexes are shown in Table 1; the complete data are listed in Tables 2–4 *.

Of particular interest is the range of the ν(CS) frequencies in metal thiocarbonyls, viz., 1381–1193 cm^{-1}. This is somewhat surprising in view of the similarity in bonding properties of CO and CS. Upon coordination, the CO stretching frequency of free CO decreases from 2143 cm^{-1} to approximately 2000 cm^{-1} (sometimes even as low as 1850 cm^{-1} for terminal CO bonding). However, it appears that the CS stretching frequency can both increase and decrease with respect to the frequency of "free" CS (1274 cm^{-1} when trapped in a CS_2 matrix [70]). Since π-backbonding is almost certainly present in metal–CS bonds, the most probable explanation for this effect lies in the extent of coupling of the CS stretching modes with the low frequency modes (below 700 cm^{-1}) of the molecules.

TABLE 1

ν(CS) FREQUENCY RANGES FOR THE KNOWN TYPES OF TRANSITION METAL CS_2 AND THIOCARBONYL COMPLEXES

Type of complex	ν(CS)(cm^{-1})
	1235–955 [a], 653–632 [b]
M–S=C=S	1520–1503
M–CS_2–M	980, 840 [c]
M–S_2CX [d]	1267–815 [e], 780–612 [f]
M–CS	1381–1193

[a] Out-of-ring ν(C=S) vibration. [b] In-ring ν(C–S) vibration. [c] Data only available for one CS_2 bridging complex viz., $K_6[(CN)_5CoCS_2Co(CN)_5]$ [9, 19]. [d] X = H, alkyl, aryl, or amine. [e] $\nu(CS_2)_{asym}$. [f] $\nu(CS_2)_{sym}$.

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* Note that data are only presented for those complexes whose molecular stoichiometries and probable structures have been reasonably well established.

TABLE 2

CARBON–SULPHUR ABSORPTIONS (cm^{-1}) FOR π-CS_2 AND S-BONDED CS_2 COMPLEXES

Complex	π-CS_2 modes^a				S-bonded CS_2 mode	Medium	Ref.
	ν(C=S)			ν(C–S)	ν(C=S)		
$Cp_2V(\pi$-$CS_2)$	1141s					CS_2	9
$CpMn(CO)_2(\pi$-$CS_2)$	1235s			~ 640m		CS_2	54
$(\pi$-$MeC_5H_4)Mn(CO)_2(\pi$-$CS_2)$	1229s					CS_2	54
$Fe(CO)_2(PPh_3)_2(\pi$-$CS_2)$	1151s	1118s				CS_2	9
$Fe(CO)_2[P(p$-$FC_6H_4)_3]_2(\pi$-$CS_2)$	1148s(br)					CH_2Cl_2	9
	1152(sh)					CS_2	9
$Fe(CO)_2[P(p$-$MeC_6H_4)_3]_2(\pi$-$CS_2)$	1148	1101				CS_2	9
$[RuCl(PPh_3)_3(\pi$-$CS_2)]Cl$	1105s	1055s		850m?		Nujol	11
$RhCl(PPh_3)_2(CS_2)(\pi$-$CS_2)$	1028s				1510	Nujol	8
$[Rh(CO)(PPh_3)_3(\pi$-$CS_2)]BPh_4$	1102m	971m				Nujol	16
$[Rh(CS)(PPh_3)_2(CS_2)(\pi$-$CS_2)]BPh_4$	1101m	955m			1503	Nujol	16
$[Rh(CS)(PPh_3)_2(\pi$-$CS_2)]BPh_4$	1101m	955m				Nujol	16
$[Rh(PPh_3)_3(CS_2)(\pi$-$CS_2)]BPh_4$	1104m	980?			1503	Nujol	16
$[Rh(PPh_3)_3(\pi$-$CS_2)]BPh_4$	1104m	980?				Nujol	16
$Rh(PPh_3)_2(SnCl_3)(\pi$-$CS_2)$	1109s	999m				Nujol	16
$[RhCl(PPh_2Et)_2(\pi$-$CS_2)]_2$	1042^b	1024^b	1000			CS_2	17

$IrCl(CO)(PPh_3)_2(\pi\text{-}CS_2)$	1161	1154				Nujol	8
$IrI(CO)(PPh_3)_2(\pi\text{-}CS_2)$ [c]	1188m	1165s				CS_2	8
$[Ir(CO)(PPh_3)_3(\pi\text{-}CS_2)]BPh_4$	1106m	1012m				Nujol	16
$[Ir(CS)(PPh_3)_2(CS_2)(\pi\text{-}CS_2)]BPh_4$	1106m	1009m			1510	Nujol	16
$[IrCl(C_8H_{12})(\pi\text{-}CS_2)]_2$	1170					*d*	9
$[Ir(CS)(PPh_3)_2(\pi\text{-}CS_2)]BPh_4$	1106m	1009m				Nujol	16
$[Ir(PPh_3)_3(CS_2)(\pi\text{-}CS_2)]BPh_4$	1005m	1000s			1510	Nujol	16
$[Ir(PPh_3)_3(\pi\text{-}CS_2)]BPh_4$	1005m	1000s				Nujol	16
$[Ni(\pi\text{-}CS_2)(PPh_3)]_2$	1122					Nujol	8
	1196	1117				CS_2	8
$Pd(PPh_3)_2(\pi\text{-}CS_2)$	1193					CS_2	8
	1176	1151				Nujol	8
	1190	1177	1152	636		Nujol	6
$Pd(Diphos)(\pi\text{-}CS_2)$	1178	1167	1152	632		Nujol	6
$Pt(PPh_3)_2(\pi\text{-}CS_2)$	1146s			651s		CH_2Cl_2	8,40
	1160s	1141s				Nujol	8
	1179	1163	1145	653		Nujol	6
$Pt(Me)I(PPh_3)_2(CS_2)$					1520	*d*	17

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[a] ν(C=S), out-of-ring vibration; ν(C–S), in-ring vibration. The relative intensities given are those quoted in the various references. In those cases where the π-CS_2 absorptions were not specifically assigned, the assignments given are those of the present authors. [b] Already present but less intense in the parent compound $RhCl_2H(PPh_2Et)_3$. [c] The two ν(C=S) absorptions observed for this complex were attributed to the presence of two isomers differing in the orientation of the π-CS_2 ligand. [d] Medium unspecified.

TABLE 3

CARBON–SULPHUR ABSORPTIONS (cm^{-1}) FOR CS_2 INSERTION COMPLEXES

Complex	$\nu(CS_2)^a$			Medium	Ref.
	asym		sym		
From insertion into metal–hydrogen bonds					
$Mn(CO)_3(Ph_2PCH_2PPh_2)(SSCH)$	818		652?	KBr	25
$Mn(CO)_3(Diphos)(SSCH)$	992		779	KBr	25
$Re(CO)_3(Ph_2PCH_2PPh_2)(SSCH)$	815		645	KBr	25
$Re(CO)_3(Diphos)(SSCH)$	1008		780	KBr	25
$Re(CO)_2(PPh_3)_2(SSCH)$	940			Nujol	24
$PtCl(PPh_3)_2(SSCH)$	1050	930		Nujol	22
$PtCl(PEt_3)_2(SSCH)$	1050	930		Thin film	22
From insertion into metal–carbon bonds					
$Mn(CO)_4(SSCPh)$	1267m		618m	KBr	30
$Mn(CO)_4[SSC(p\text{-}MeC_6H_4)]$	1265m		613m	KBr	30
$Re(CO)_4(SSCMe)$	1146m		616m	KBr	30
$Re(CO)_4(SSCPh)$	1267		613m	KBr	30
$Re(CO)_4[SSC(p\text{-}MeC_6H_4)]$	1264m		612m	KBr	30
$Re(CO)_4[SSC(p\text{-}ClC_6H_4)]$	1258m		616m	KBr	30
$Re(CO)_3(PPh_3)(SSCPh)$	1265m		623m	KBr	30

$RhI_2(PPh_3)_2(SSCMe)\cdot C_6H_6$	1110	630	*c*	17
$Rh(PPh_3)_3(\pi\text{-}CS_2)(SSCPh)$ [b]	1261m		*c*	17
From insertion into metal–nitrogen bonds				
$Ti(SSCNMe_2)_4$	1002		CH_2Cl_2	34
$Ti(SSCNEt_2)_4$	1004		CH_2Cl_2	34
$Ti(SSCN\text{-}n\text{-}Pr_2)_4$	994		CH_2Cl_2	34
$Zr(SSCNMe_2)_4$	998		CH_2Cl_2	34
$Zr(SSCNEt_2)_4$	999		CH_2Cl_2	34
$Zr(SSCN\text{-}n\text{-}Pr_2)_4$	994		CH_2Cl_2	34
$V(SSCNMe_2)_4$	1006		CH_2Cl_2	34
$V(SSCNEt_2)_4$	1000		CH_2Cl_2	34
$Nb(SSCNMe_2)_4$	996		CH_2Cl_2	34
$Nb(SSCNEt_2)_4$	1003		CH_2Cl_2	34
$Ta(SSCNMe_2)_5$	1000		CH_2Cl_2	34
$Ni(SSCN\lhd\ )_2$	1045		Nujol	36
$Ni(SSCN\lhd_{Me})_2$	1045		Nujol	36

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[a] The relative intensities given are those quoted in the various references. In those cases where the $\nu(CS_2)$ absorptions were not specifically assigned, the assignments given are those of the present authors. [b] $\nu(\pi\text{-}CS_2)$ 1003s cm^{-1}. [c] Medium unspecified.

TABLE 4

CARBON–SULPHUR ABSORPTIONS (cm^{-1}) FOR THIOCARBONYL COMPLEXES

Complex	$\nu(CS)^a$	Medium	Ref.
$CpMn(CO)_2CS$	1266s	CS_2	52, 54
	1271s	Nujol	52, 54
$(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$	1262s	CS_2	54
$CpMn(CO)(CS)(C_8H_{14})$	1242s	CS_2	54
$CpMn(CO)(CS)PPh_3$	1231s	CS_2	54
	1236s	n-hexane	54
	1217s	Nujol	54
$CpMn(CO)(CS)AsPh_3$	1231s	CS_2	59
$CpMn(CO)(CS)SbPh_3$	1230s	CS_2	59
	1237s	n-hexane	59
$CpMn(CO)(CS)PMe_2Ph$	1228s	CS_2	59
	1234s	n-hexane	59
$CpMn(CO)(CS)(PCy_3)$	1222s	CS_2	59
	1230s	n-hexane	59
$CpMn(CO)(CS)[P(OMe)_3]$	1239s	CS_2	59
	1245s	n-hexane	59
$CpMn(CO)(CS)[P(OEt)_3]$	1236s	CS_2	59
	1243s	n-hexane	59
$CpMn(CO)(CS)[P(OCH_2CH_2Cl)_3]$	1240s	CS_2	59
	1247s	n-hexane	59
$CpMn(CO)(CS)[P(OPh)_3]$	1254s	CS_2	59
$CpMn(CS)(PPh_3)_2$	1193s	CS_2	59
$CpMn(CS)(PMe_2Ph)_2$	1195s	CS_2	59
$CpMn(CS)[P(OMe)_3]_2$	1218s	CS_2	59
$CpMn(CS)[P(OEt)_3]_2$	1214s	CS_2	59
$CpMn(CS)[P(OCH_2CH_2Cl)_3]_2$	1223s	CS_2	59
$CpMn(CS)[P(OPh)_3]_2$	1219s	CS_2	59
$CpMn(CS)(Diphos)$	1207s	CS_2	54, 63
	1211s	Nujol	54
$CpMn(CS)(Triphos)$	$1203s^b$	CS_2	63
	$1206s^c$	CS_2	63

$CpMn(CS)(Triphos{=}O)$	1203s		CS_2	63
$CpMn(CO)(CS)_2$	1305s	1235vs	CS_2	53, 54
	1308s	1240s	Nujol	54
$CpMn(CS)_2(C_8H_{14})$	1289s	1217vs	CS_2	54
$CpMn(CS)_3$	1338m	1240vs	CS_2	53, 54
$[CpMn(CO)(CS)]_2(Diphos)$	1226s		CS_2	54
	1230s		Nujol	54
$CpMn(CS)(Triphos)Mn(CO)_2Cp$	1204m ^{d}		CS_2	63
	1208m ^{e}		CS_2	63
$CpMn(CS)(Triphos)Cr(CO)_5$	1205m		CS_2	63
	1209m		CS_2	63
$[CpFe(CO)_2CS]PF_6$	1348s		hexachloro-butadiene	43
$CpFe(CO)(CS)(COOMe)$	1316		CS_2	44
$[RuCl_2(CS)(PPh_3)_2]_2$	1290s		f	11
$RuCl_2(CO)(CS)(PPh_3)_2$	1290s		f	11
$RuCl_2(CS)(Py)(PPh_3)_2$	1280s		f	11
$RuCl_2(CS)(Bipy)(PPh_3)\cdot 0.5CH_2Cl_2$	1280s		f	11
$RuCl_2(CS)(Phen)(PPh_3)\cdot 0.5CH_2Cl_2$	1280s		f	11
$Ph_4As[RuCl_3(CS)(PPh_3)_2]$	1272		Nujol	46
trans-$RhCl(CS)(PPh_3)_2$	1299		C_6H_6	9
trans-$RhBr(CS)(PPh_3)_2$	1298		C_6H_6	9
$RhCl_3(CS)(PPh_3)_2$	1362		C_6H_6	9
$RhBr_3(CS)(PPh_3)_2$	1355		C_6H_6	9
trans-$Rh(SCN)(CS)(PPh_3)_2$	1304		C_6H_6	9
$RhCl(CS)(PPh_3)_2(TCNE)$ ^{g}	1355		CH_2Cl_2	45
$[Rh(CS)(PPh_3)_2(CS_2)(\pi\text{-}CS_2)]BPh_4$	1289vs		Nujol	16
$[Rh(CS)(PPh_3)_2(\pi\text{-}CS_2)]BPh_4$	1289vs		Nujol	16
trans-$IrCl(CS)(PPh_3)_2$	1328s		Nujol	16
trans-$IrCl(CS)(PCy_3)_2$	1315s		Nujol	51
$[Ir(CS)(PPh_3)_2(CS_2)(\pi\text{-}CS_2)]BPh_4$	1305vs		Nujol	16
$[Ir(CS)(PPh_3)_2(\pi\text{-}CS_2)]BPh_4$	1305vs		Nujol	16

(continued)

TABLE 4 *(continued)*

Complex	$\nu(CS)$ [a]	Medium	Ref.
$IrCl(CS)(PPh_3)_2(CS_3)$	1360	KBr	46
$IrCl(CO)(CS)(PPh_3)_2$	1289	toluene	16
$IrCl(CS)(SO_2)(PPh_3)_2$	1345	CH_2Cl_2	16
$IrH(CS)(PPh_3)_3$	1252	Nujol	16
$[Ir(CO)_2(CS)(PPh_3)_2]BPh_4$	1321s	$CHCl_3$	51
$[Ir(CO)_2(CS)(PCy_3)_2]BPh_4$	1303s	$CHCl_3$	51
$[IrH_2(CO)(CS)(PCy_3)_2]ClO_4$	1332s	$CHCl_3$	51
$[IrD_2(CO)(CS)(PCy_3)_2]ClO_4$	1322s	$CHCl_3$	51
$Ir(CO)(CS)(PPh_3)_2(COOMe)$	1287s	Nujol	51
$[IrCl(NO)(CS)(PPh_3)_2]BF_4$	1381s	Nujol	51
$[IrCl(NO)(CS)(PCy_3)_2]BF_4$	1340s	Nujol	51
$[Ir(CS)(Diphos)_2]BPh_4$	1263s	Nujol	51
$[Ir(CO)(CS)(PMePh_2)_3]BPh_4$	1297	Nujol	51
$IrCl(CS)(PPh_3)_2 \cdot (BCl_3)_n$	1361	*f*	50
$IrCl(CS)(PPh_3)_2 \cdot (BBr_3)_n$	1377	*f*	50
$IrCl(CS)(PPh_3)_2 \cdot (TCNE)$ [g]	1370	*f*	50
$IrCl(CS)(PPh_3)_2 \cdot (FUM)$ [h]	1350	*f*	50

[a] Absorptions associated with π-CS_2 or S-bonded CS_2 groups are listed in Table 3. The relative intensities given are those quoted in the various references. [b] γ-isomer. [c] ϕ isomer. [d] γ-isomer. [e] ϕ isomer. [f] Medium unspecified. [g] TCNE = tertracyanoethylene, $C_2(CN)_4$. [h] FUM = fumaronitrile, $C_4N_2H_2$.

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Note added in proof

Angelici and co-workers have succeeded in isolating four new metal thiocarbonyls, viz., $M(CO)_5CS$ (M = Cr, Mo, W) and $[PtCl(PPh_3)_2(CS)]^+$ by the following synthetic routes:

$$[M(CO)_5]^{2-} + Cl_2C{=}S \rightarrow M(CO)_5CS + 2Cl^-$$

$$Pt(PPh_3)_4 + Cl(OMe)C{=}S \rightarrow PtCl(PPh_3)_2(CSOMe) \xrightarrow[BF_3]{} [PtCl(PPh_3)_2(CS)]^+$$

For details see R.J. Angelici, B.D. Dombrek and E. Dobrzynski, 6th International Conference on Organometallic Chemistry, Amherst, Mass., U.S.A., August 1973, abstract no. 134.