SYNTHETIC, SPECTROSCOPIC, AND KINETIC STUDIES ON SOME π-CYCLOPENTADIENYLMETAL COMPLEXES

Ph.D. Chemistry Department

Ariel Elie Fenster

ABSTRACT

The first thiocarbonyl complex of manganese, $CpMn(CO)_2CS$, was prepared from the reaction of the *cis*-cyclooctene complex, $CpMn(CO)_2(C_8H_{14})$, with CS_2 in the presence of PPh_3 as sulphur-acceptor. Spectroscopic and kinetic data indicate that the intermediate in the reaction is the π-CS_2 complex, $CpMn(CO)_2(\pi\text{-}CS_2)$. Subsequently, the di- and trithiocarbonyl complexes, $CpMn(CO)(CS)_2$ and $CpMn(CS)_3$ were synthesized in a similar manner from $CpMn(CO)(CS)(C_8H_{14})$ and $CpMn(CS)_2(C_8H_{14})$, respectively. The di- and trithiocarbonyl complexes are the first examples of multiple CS groups attached to a central metal atom. The derivatives, $CpMn(CO)(CS)PPh_3$, $CpMn(CO)(CS)P(OMe)_3$, $[CpMn(CO)(CS)]_2(diphos)$, and CpMn(CS)(diphos), were also prepared.

Synthetic, spectroscopic, and kinetic data seem to indicate that the new thiocarbonyl complexes are indeed more stable than their carbonyl analogues as predicted on theoretical grounds.

The reactions of π-cyclopentadienyl carbonyl complexes of manganese, vanadium, and cobalt with isotopically enriched CO have been followed by i.r. spectroscopy. The observed frequencies associated with the different isotopically CO-substituted species have been assigned with the aid of approximate force constant calculations.

Short Title:

STUDIES ON π-CYCLOPENTADIENYLMETAL COMPLEXES

SYNTHETIC, SPECTROSCOPIC, AND KINETIC STUDIES ON SOME π-CYCLOPENTADIENYLMETAL COMPLEXES

Ariel Elie Fenster

A Thesis Submitted to the Faculty of
Graduate Studies and Research at
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The friendly atmosphere in room 335 made it all possible.

In Memory of my Father

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LIST OF ABBREVIATIONS

Me - methyl

Et - ethyl

Pr^n - *n*-propyl

Bu^t - *tert*-butyl

Cy - cyclohexyl

Ph - phenyl

Cp - π-cyclopentadienyl

en - ethylenediamine

py - pyridine

bipy - 2,2'-bipyridyl

o-phen - *o*-phenanthroline

diphos - 1,2-bis(diphenylphosphino)ethane

TCNE - tetracyanoethylene

THF - tetrahydrofuran

M - a transition metal

L - a monodentate ligand

L-L, L-L-L-L, L-(L)$_3$, etc. - a multidentate ligand

X - a halogen

PART I

CARBON DISULPHIDE AND THIOCARBONYL COMPLEXES OF MANGANESE

CHAPTER I INTRODUCTION

In 1931, Duncan *et al.*[1] reported that carbon disulphide reacts with copper mercaptides to give trithiocarbonates. However, as is often the case in science, this initital report 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 thiocarbonyls of group VIII metals have been prepared by reactions in which CS_2 acts as the source of CS in the formation of the M-CS bonds. These reactions, however, represent only one aspect of the activation of carbon disulphide by transition metal complexes. In fact, reports published over the last five years indicate that CS_2 itself can coordinate to transition metals to form four distinctly different types of complex.

A review on the activation of carbon disulphide by transition metal complexes has not yet appeared in the literature. Therefore, it was thought appropriate to begin this part of the thesis with a survey of the different types of reaction that CS_2 can undergo. This survey is presented in Chapter II. Details of the author's own work on the activation of CS_2 by π-cyclopentadienylmanganese complexes are given in Chapter III. The chemical and physical properties of the new complexes synthesized are also discussed in this chapter, together with a preliminary investigation on the activation of CS_2 by π-cyclopentadienyl complexes of vanadium, cobalt, and iron.

CHAPTER II REVIEW ON THE ACTIVATION OF CARBON DISULPHIDE BY TRANSITION METAL COMPLEXES

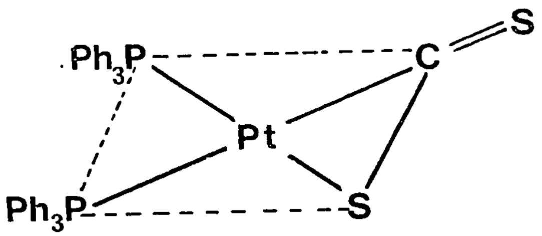
This review is divided into six sections. The first five of these deal with the different types of complex formed in the reactions of CS_2 with transition metal compounds. The last section summarizes in tabular form the infrared data obtained for the various complexes. To the best of the author's knowledge, the literature coverage in the review is complete to January, 1972.

A. π-CARBON DISULPHIDE COMPLEXES

The first examples of complexes to exhibit 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 in turn.

1. Platinum, Palladium, and Nickel

During their investigation of potential methods for the synthesis of thiocarbonyl complexes, Baird and Wilkinson[3] discovered that $Pt(PPh_3)_3$ reacts with CS_2 to form the stable adduct, $Pt(PPh_3)_2CS_2$. They proposed a square-planar structure for the complex in which the CS_2 ligand is coordinated to the platinum(II) ion *via* both a metal-carbon and a metal-sulphur σ-bond:



This structure is similar to that observed for the π-arylacetylene complexes, $Pt(PPh_3)_2$(acetylene)[4]. Moreover, Baird and Wilkinson also obtained $Pt(PPh_3)_2CS_2$ 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].

The π-CS_2 coordination suggested for $Pt(PPh_3)_2CS_2$ has been confirmed by three-dimensional X-ray diffraction of the complex[5,7] (Fig. 1) and 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 $Pt(PPh_3)_2CS_2$ and 1.64 Å for its palladium analogue. The geometry around the central metal atom in the two complexes is essentially similar. The metal and its four neighbours P(1), P(2), C(1), and S(2) are nearly co-planar in both cases.

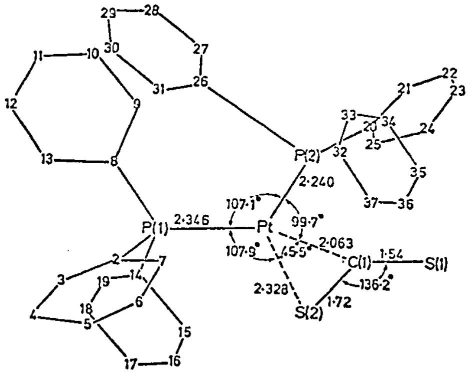
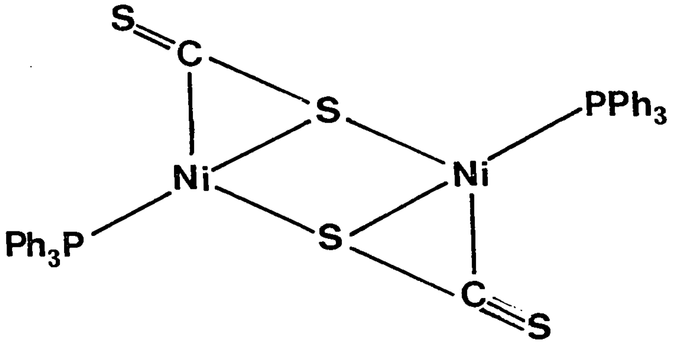


Fig. 1. Molecular structure of $Pt(PPh_3)_2CS_2$[5].

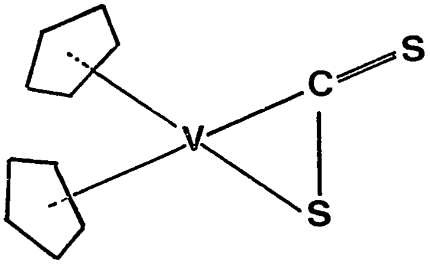
Triphenylstibine displaces the CS_2 group from $Pt(PPh_3)_2(\pi\text{-}CS_2)$ and its palladium analogue to yield the tetracoordinated species, $Pt(PPh_3)_2(SbPh_3)_2$ and $Pd(PPh_3)_2(SbPh_3)_2$[6]. However, with diphos the two triphenylphosphine groups in $Pd(PPh_3)_2(\pi\text{-}CS_2)$ are substituted, resulting in the formation of a new π-CS_2 complex, Pd(diphos)(π-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 in the solid. The structure proposed for the dimer involves sulphur-bridging between the two nickel atoms:



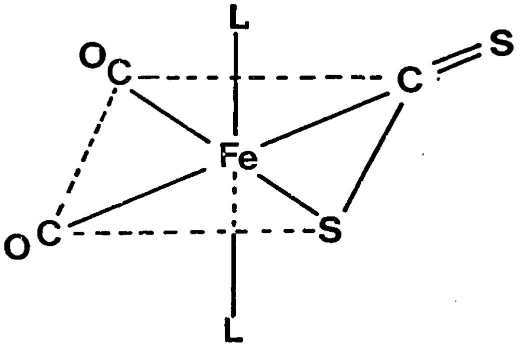
2. Vanadium

Baird *et al.*[9] have reported that CS_2 reacts with the purple complex, Cp_2V, to give a green solution. This solution is very 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 i.r. spctrum 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 proposed structure (shown below) is supported by the fact that an e.s.r. spectrum of the green solution indicates the presence of vanadium(IV).



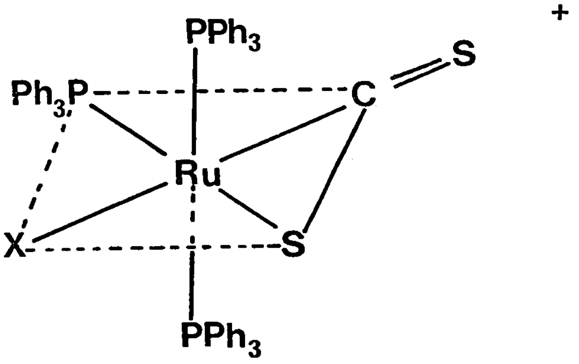
3. Iron and Ruthenium

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



Busetto *et al.*[10] postulated that the intermediate, $[CpFe(CO)_2CS_2]^-$, is formed during the synthesis of the iron thiocarbonyl cation, $[CpFe(CO)_2CS]^+$ (*vide infra*,p. 26). 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]. The suggested structure for the cationic species is:



4. Rhodium and Iridium*

The interaction of CS_2 with a variety of rhodium

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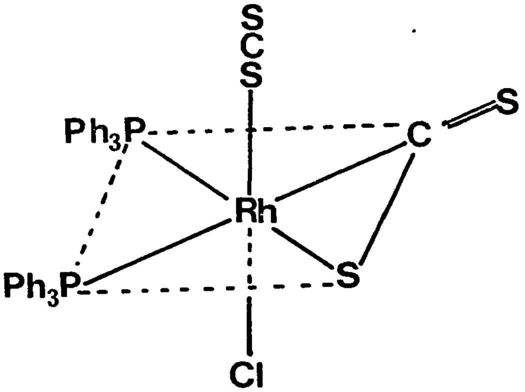
* In 1963, Marko *et al.*[12] reported the preparation of the first cobalt carbon disulphide complex, allegedly $Co_4(CO)_{10}CS_2$. The complex is formed in low yield from the reaction of $Co_2(CO)_8$ with CS_2. In a subsequent publication[13], the same authors indicated that an isomer of the above 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.

and iridium complexes has been investigated. Details of some of these reactions are given in Fig. 2a.

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 i.r. 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 $Pt(PPh_3)_2(\pi-CS_2)$ and $Pd(PPh_3)_2(\pi-CS_2)$. 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:



Yagupsky and Wilkinson[16] have prepared several cationic $\pi-CS_2$ 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 $[Rh(PPh_3)_3(CS_2)(\pi-CS_2)]^+$. This cation is believed to contain an S-bonded CS_2 group similar to that shown above for $RhCl(PPh_3)_2(CS_2)(\pi-CS_2)$. This CS_2

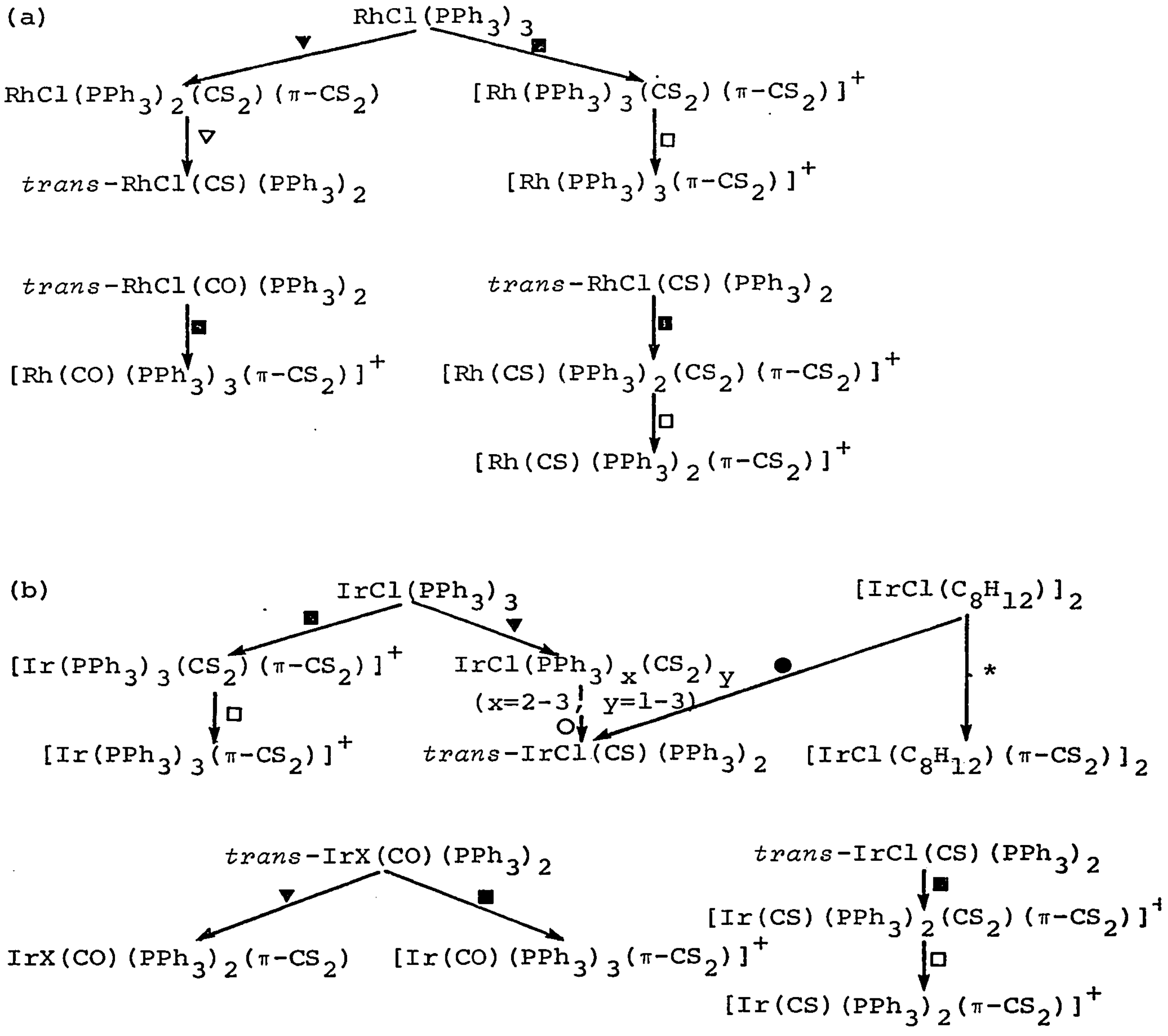
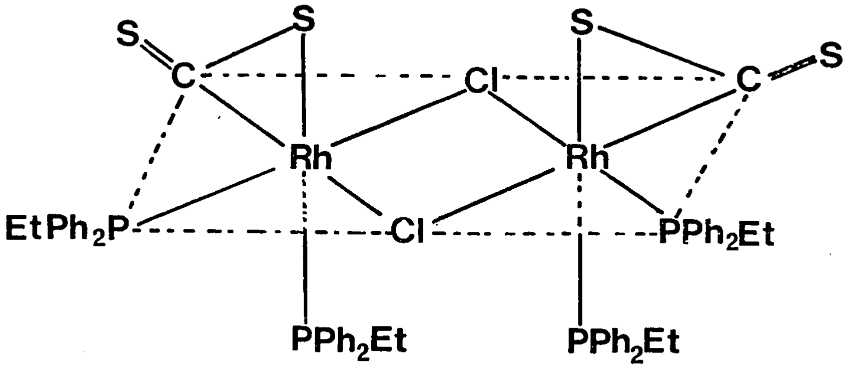


Fig. 2. Typical reactions of rhodium and iridium complexes with CS_2[8,9,16]. The symbols shown signify the following: ▼, in CS_2; ■ , in CS_2 and in the presence of PPh_3 and MeOH; ▽, in $CHCl_3$ followed by addition of MeOH; □ , *in vacuo*; ○, upon heating in $CHCl_3$; ● , in CS_2 and in the presence of PPh_3 and $CHCl_3$; *, in CS_2 and CH_2Cl_2.

group is readily lost from the complex to yield the stable cation, $[Rh(PPh_3)_3(\pi-CS_2)]^+$.

Addition of CS_2 to *trans*-$RhCl(CO)(PPh_3)_2$ in MeOH and in the presence of excess PPh_3 produces a blue solution. Treatment of this blue solution with sodium tetraphenylborate results in precipitation of $[Rh(CO)(PPh_3)_3(\pi-CS_2)]BPh_4$. The thiocarbonyl analogue, *trans*-$RhCl(CS)(PPh_3)_2$ (*vide infra*, p. 32), also reacts with CS_2 in the presence of MeOH and excess PPh_3 to give $[Rh(CS)(PPh_3)_2(CS_2)(\pi-CS_2)]^+$ and $[Rh(CS)(PPh_3)_2(\pi-CS_2)]^+$.

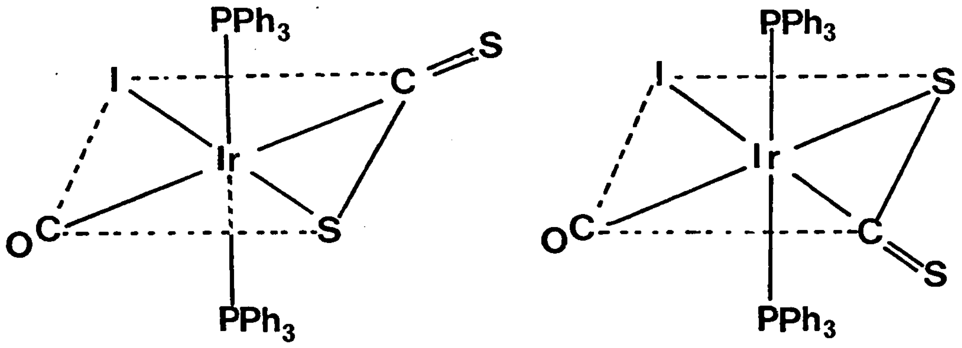
A complex, analysing as $RhCl(CS)_2(PPh_2Et)_2$, can be obtained from the reaction of the rhodium(III) hydride, $RhCl_2H(PPh_2Et)_3$, with CS_2[17]. Infrared data for this complex are compatible with the following structure:



Addition of $SnCl_2$ in ethanol to a CS_2 solution of $RhCl(PPh_3)_3$ and PPh_3 affords the complex, $Rh(PPh_3)_2(\pi-CS_2)(SnCl_3)$[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. 2b).

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$_3$)$_2$(π-CS$_2$)[8]. All attempts to separate the two complexes failed. However, when the iodo-analogue, *trans*-IrI(CO)(PPh$_3$)$_2$, was used instead, the pure complex, IrI(CO)(PPh$_3$)$_2$(π-CS$_2$), could be isolated. Its infrared spectrum in CS$_2$ solution exhibits <u>two</u> bands in the π-CS$_2$ region at 1188m and 1165s cm^{-1}. Consequently, it was proposed that the complex is in fact a mixture of two isomers which differ in the orientation of the π-bonded CS$_2$ group:



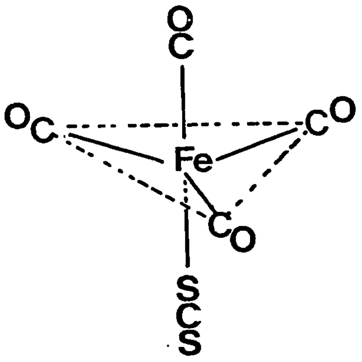
Deeming and Shaw[18] have isolated the analogous dimethylphenylphosphine complex, IrCl(CO)(PPhMe$_2$)$_2$(π-CS$_2$). The n.m.r. spectrum of the complex consists of two 1:2:1 triplets. However, because two triplets would be expected for each of the two possible π-CS$_2$ isomers, it was suggested that only one isomer is present in solution. Furthermore, this must be true also 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 CARBON DISULPHIDE 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 i.r. data, in the CO stretching region, a complex with the structure shown below allegedly results from the reaction of $Fe_2(CO)_9$ with CS_2[9].

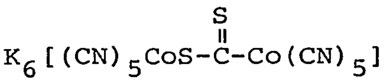


A complex of stoichiometry, $Pt(Me)I(PPh_3)_2CS_2$, has been isolated from the reaction of $Pt(Me)I(PPh_3)_2$ with CS_2[17]. The strong band in the spectrum at 1520 cm^{-1} was taken to be indicative of an S-bonded CS_2 molecule. The ease of CS_2 dissociation from the complex supports this suggestion.

C. COMPLEXES WITH BRIDGING CARBON DISULPHIDE 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 workers suggest a structure 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:

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



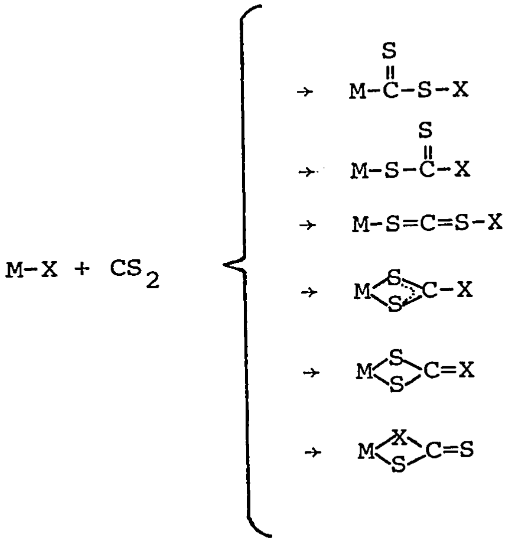
$K_6[(CN)_5CoS\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}Co(CN)_5]$

Direct reaction of $IrCl(PPh_3)_3$ with CS_2 leads to green solutions from which complexes of stoichiometry, $IrCl(PPh_3)_x(CS_2)_y$ ($x = 2\text{-}3$, $y = 1\text{-}3$), can be obtained[16]. The actual composition of the complexes formed depends critically on the experimental conditions employed. Owing to their instability, the exact nature of these compounds was not determined. However, from i.r. 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. CARBON DISULPHIDE INSERTION COMPLEXES

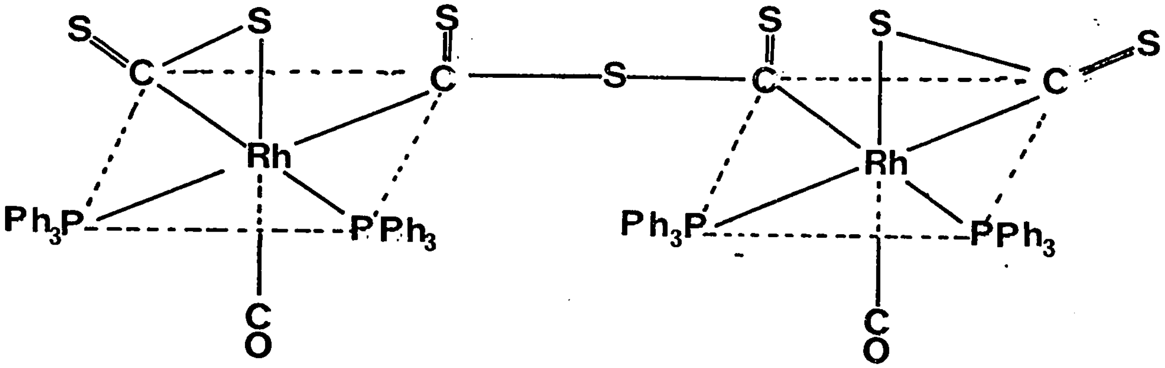
Although insertion reactions between main group metal complexes and CS_2 have been known for some time, very little work had been reported until recently on similar reactions with transition metal complexes[21]. Potentially, the insertion of a CS_2 molecule into an M-X bond (M = transition metal, X =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



The known CS_2 insertion reactions of transition metal complexes will now 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 i.r. 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 n.m.r. spectroscopy. The structure shown below was suggested for the complex; it can be arrived at by coupling together two molecules of the insertion product, $Rh(CO)(PPh_3)_2(\pi\text{-}CS_2)(CSSH)$, with the elimination of H_2S:



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

$$IrH(CO)(PPh_3)_3 + CS_2 \rightarrow PPh_3 + IrH(CO)(PPh_3)_2(\pi\text{-}CS_2)$$

$$\downarrow H^- \text{ transfer}$$

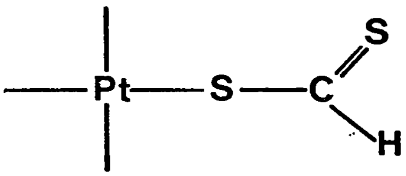
$$Ir(CO)(PPh_3)_2(CSSH)$$

Owing to the lack of documentation of the chemical shift of the SH proton no distinction between a -CSSH or HCSS- type of bonding in the insertion product was made.

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 n.m.r. signal attributable to -CSSH or HCSS- protons was observed.

The interaction of CS_2 with the π-cyclopentadienyl hydride complexes, Cp_2WH_2 and Cp_2ReH, has also been studied but no definite products have been 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 i.r. spectrum at 1050 and 930 cm^{-1} but no Pt-H absorption. The structure preferred for the complex is shown below. The basis for



this choice was the fact 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 $PtCl(PPh_3)_2(SSCH)$. First, S-coordination of CS_2 to produce a labile species; second, intramolecular hydrogen migration in a four-centre transition state to form the insertion product.

The only 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 an H 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 (*vide infra*, p. 21).

On the basis of the results for $Re(CO)_2(PPh_3)_2(SSCH)$, it has been suggested[23] that the iridium complex, $Ir(CO)(PPh_3)_2(CSSH)$, described earlier must also contain a chelated dithioformato- group.

2. Metal-Carbon Bonds

Complexes of the type, $M(CO)_4(SSCR)$ (M = Mn, Re; R = Ph, CF_3), have been prepared by reaction of the appropriate free dithioacid with $M(CO)_5X$[25,26]. An alternative synthetic route to $Re(CO)_4(SSCPh)$ and a variety of new dithiocarboxylato-complexes of manganese and rhenium have been reported by Lindner *et al.*[27-29]. The reactions involve direct CS_2 insertion into metal-carbon bonds:

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

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

An X-ray diffraction study of $Re(CO)_4(SSCPh)$ indicates[30] that the dithio- group acts as bidentate ligand and the coordination around the central metal is pseudo-octahedral. The vibrational spectra of the manganese and rhenium complexes are in agreement with the observed pseudo-C_{2v} molecular symmetry[27,29].

Lindner *et al.*[29] 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 pentacarbonyl-manganese(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 the complex contains a dithiomethyl ester group -CSSMe. However, in view of the CS_2 insertion reactions described earlier, it seems to this author that the $MeCS_2$ group in the complex is more likely to be 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 a 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.*[31,32] 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 and Gitlitz[33]. In particular, complexes of Ti(IV), V(IV), and Zr(IV) give the hitherto unknown tetrakis(N,N-dialkyldithiocarbamato)-complexes:

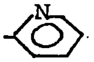
$$M(NR_2)_4 + 4CS_2 \longrightarrow M(SSCNR_2)_4$$

$$(M = Ti,\ Zr,\quad R = Me,\ Et,\ Pr^n;$$
$$M = V,\quad R = Me,\ Et)$$

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[34] 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 $[Ni(amp)_3]Cl_2$ (amp = H_2NCH_2-).

Carbon disulphide also gives insertion products with $[Ni(aziridine)_4]^{2+}$ and $[Ni(2\text{-methylaziridine})_4]^{2+}$ [35]. 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, e.g. with $Ni(OMe)_2$, nickel methylxanthate, $Ni(SSCOMe)_2$, is formed[36].

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 $[CpM(CO)_2SR]_2$[37]. 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)[38].

During their investigation of the reaction of $Pt(PPh_3)_2O_2$ with various unsaturated molecules, Hayward *et al.*[39] 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[40] *viz.*, the formation of $[Pt(PPh_3)_2(SSCF)]HF_2$ from the reaction of $[PtF(PPh_3)_3]HF_2$ with CS_2. The crystal structure of this complex displays pseudo-square-planar coordination around the metal with the FCSS group bonded through the two sulphur atoms.

E. 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 only for certain group VIII metals. Furthermore, in sharp contrast to metal carbonyls, only thiocarbonyl complexes with a single CS group attached to a central metal have thus far been isolated.

1. Iron

The cation 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 i.r. 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[41] by the following reaction sequence:

$$[CpFe(CO)_2]^- + ClC(S)OR \longrightarrow CpFe(CO)_2C(S)OR \xrightarrow{HCl}$$

$$(R = Me, Et)$$

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

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.*[42] 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:

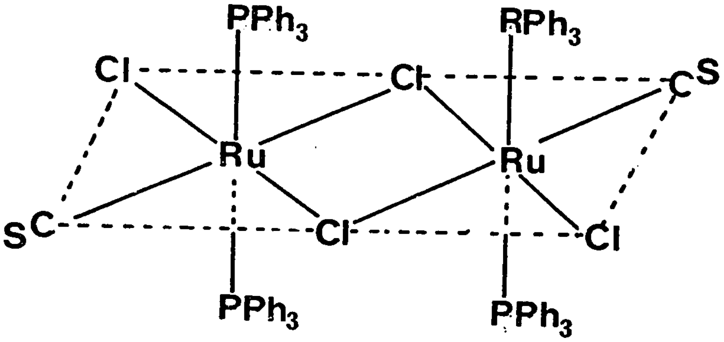
$$[CpFe(CO)_2CS]^+ \left\{ \begin{array}{ll} \xrightarrow{N_3^-} & CpFe(CO)_2NCS + N_2 \\ \xrightarrow{NH_2\text{-}NH_2} & CpFe(CO)_2NCS + NH_3 + H^+ \\ & \\ \xrightarrow{RO^-} & CpFe(CO)_2C(S)OR \ (R = Me, Et) \\ \xrightarrow{NH_2R} & CpFe(CO)_2C(S)NHR + H^+ \ (R = Me, Et) \\ & \\ \xrightarrow{NCO^-} & CpFe(CO)_2CN + COS \\ \xrightarrow{NCS^-} & CpFe(CO)_2CN + CS_2 \end{array} \right.$$

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.

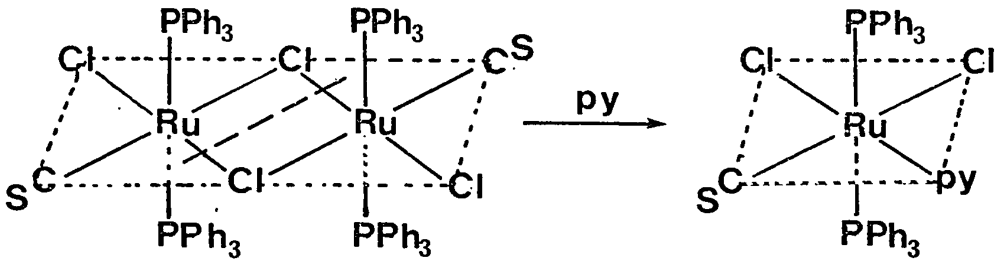
2. Ruthenium

As mentioned already (*vide supra*, p. 8), 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 i.r. evidence the structure shown below (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.



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[43]. This complex is as yet the only example of a thiocarbonylmetallate.

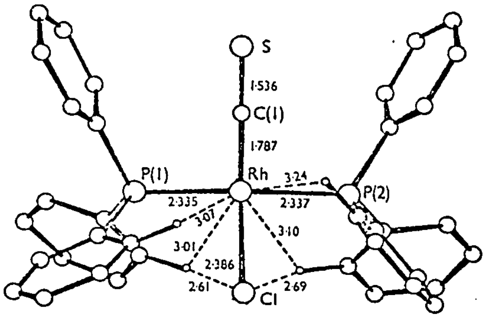
3. Cobalt

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. 9) 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 then 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 Boer *et al.*[44]. Although there is a slight distortion, the structure contains the expected square-planar coordination around the rhodium atom together with a very nearly linear thiocarbonyl ligand (Fig. 3). 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.



Angle	
Rh-C(1)-S	177.2°
P(1)-Rh-Cl	89.4
P(2)-Rh-Cl	87.3
P(1)-Rh-C(1)	91.6
P(2)-Rh-C(1)	92.0
Cl-Rh-C(1)	174.5
P(1)-Rh-P(2)	175.6

Fig. 3. Molecular structure of *trans*-RhCl(CS)$(PPh_3)_2$[44].

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 be indicative of a lowered non-bonding electron density on the metal resulting from the better π-acceptor character of CS. That it has proved experimentally impossible to replace the thiocarbonyl ligand in the complex by CO (1 atm., 25°) and that the complex decomposes following attack by MeI and $HgCl_2$ was also explained in terms of CS π-acidity.

Treatment of *trans*-RhCl(CS)(PPh_3) with LiSCN gives the S-bonded thiocyanato- complex, *trans*-Rh(CS)(SCN)$(PPh_3)_2$[9].

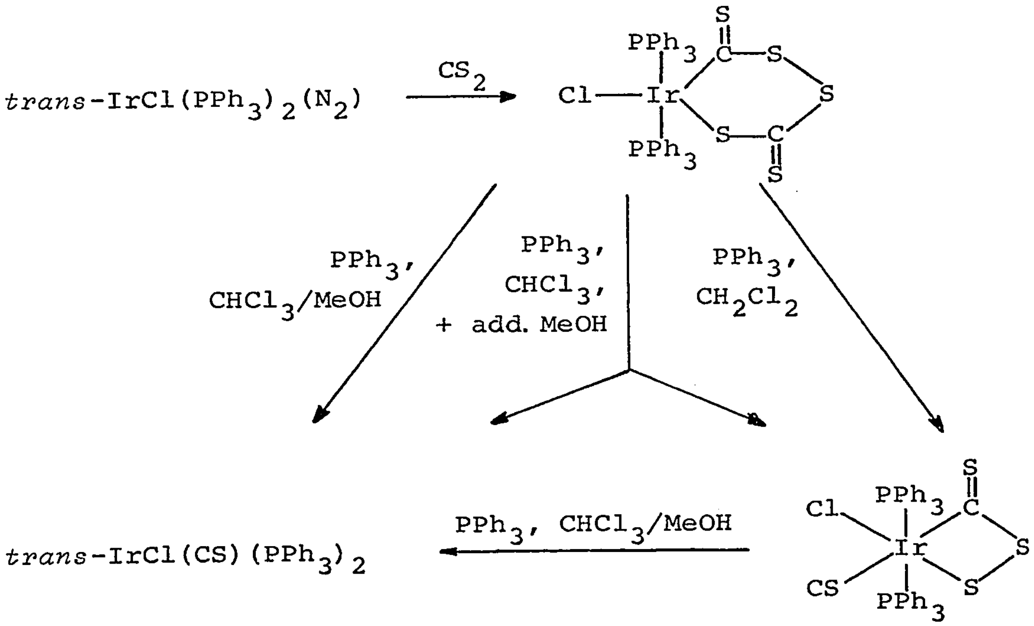
The complex, *trans*-RhCl(CS)$(PPh_3)_2$, reacts easily with tetracyanoethylene (TCNE) to give RhCl(CS)$(PPh_3)_2$(TCNE)[45]. Infrared data seem to support a hexacoordinated structure with TCNE bonded to the rhodium atom *via* metal-carbon σ-bonds.

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 (*vide supra,* p. 11).

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[46] 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 (shown at the top of next page) 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 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 the above scheme.

Because of low yields in their synthetic methods and experimental difficulties, Yagupsky and Wilkinson[16] restricted their investigation of the chemistry of *trans*-$IrCl(CS)(PPh_3)_2$ 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 n.m.r. spectrum indicated a trigonal-bipyramidal structure with equivalent equatorial PPh_3 groups.

The cationic thiocarbonyls of iridium, $[Ir(CO)_2(CS)L_2]^+$ (L = PPh_3, PCy_3), were prepared recently by Mays and Stefanini[47] 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. By analogy with the tricarbonyl cations, $[Ir(CO)_3L_2]^+$ (L = tertiary phosphine or arsine), it was suggested that the thiocarbonyls derivatives have trigonal bipyramidal structures with the phosphines in mutually *trans* positions.

Some of 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. For instance, whereas 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. It was this result that 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 dideutride 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 with respect 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*-$IrCl(CS)(PPh_3)_2$ (*vide supra*, p. 34).

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*-$IrCl(CO)L_2$.

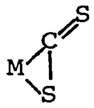
Reaction of $[CpFe(CO)_2CS]^+$ with MeO^- in anhydrous MeOH leads to the formation of the thioester, $CpFe(CO)_2C(S)OMe$ (*vide supra*, p. 27). However, in the case of $[Ir(CO)_2(CS)(PPh_3)_2]^+$, nucleophilic attack takes place at the carbon atom of a coordinated carbonyl rather than at that of the 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 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 $[Ir(CO)(diphos)_2]^+$.

F. INFRARED DATA FOR CARBON DISULPHIDE AND THIOCARBONYL COMPLEXES

Infrared spectroscopy was the chief physical tool used in the studies described in the preceding sections of this review. Consequently, it was felt than an analysis of the infrared data collected so far 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 I; the complete data are listed in Tables II-IV.

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

Type of Complex	ν(CS) (cm^{-1})
	1180-950[a], 655-635[b]
M-S=C=S	1520-1500
M-CS_2-M	980, 840[c]
M-S_2CX[d]	1270-950[e], 650-600[f]
M-CS	1380-1250

[a] Out-of-ring ν(C=S) vibration.

[b] In-ring ν(C-S) vibration; reported for only three compounds.

[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] $\nu(CS_2)_{sym}$

TABLE II. 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)		
$Cp_2V(\pi\text{-}CS_2)$	1141s			CS_2	9
$Fe(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$	1151s 1118s			CS_2	9
$[RuCl(PPh_3)_3(\pi\text{-}CS_2)]Cl$	1105s 1055s	850m?		Nujol	11
$RhCl(PPh_3)_2(CS_2)(\pi\text{-}CS_2)$	1028s		1510	Nujol	8
$[Rh(CO)(PPh_3)_3(\pi\text{-}CS_2)]BPh_4$	1102m 971m			Nujol	16
$[Rh(CS)(PPh_3)_2(CS_2)(\pi\text{-}CS_2)]BPh_4$	1101m 955m		1503	Nujol	16
$[Rh(CS)(PPh_3)_2(\pi\text{-}CS_2)]BPh_4$	1101m 955m			Nujol	16
$[Rh(PPh_3)_3(CS_2)(\pi\text{-}CS_2)]BPh_4$	1104m 980?		1503	Nujol	16
$[Rh(PPh_3)_3(\pi\text{-}CS_2)]BPh_4$	1104m 980?			Nujol	16
$Rh(PPh_3)_2(SnCl_3)(\pi\text{-}CS_2)$	1109s 999m			Nujol	16
$[RhCl(PPh_2Et)_2(\pi\text{-}CS_2)]_2$	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

TABLE II (Cont'd)

$[Ir(CS)(PPh_3)_2(\pi-CS_2)]BPh_4$	1106m 1009m			Nujol	16
$[Ir(PPh_3)_3(CS_2)(\pi-CS_2)]BPh_4$	1005m 1000s		1510	Nujol	16
$[Ir(PPh_3)_3(\pi-CS_2)]BPh_4$	1005m 1000s			Nujol	16
$Pd(PPh_3)_2(\pi-CS_2)$	1193			CS_2	8
	1176 1151			Nujol	8
	1190 1177 1152	636		Nujol	6
$Pd(diphos)(\pi-CS_2)$	1178 1167 1152	632		Nujol	6
$Pt(PPh_3)_2(\pi-CS_2)$	1146s	651s		CH_2Cl_2	8,39
	1160s 1141s			Nujol	8
	1179 1163 1145	653		Nujol	6
$Pt(Me)I(PPh_3)_2(CS_2)$			1520	d	17

[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 $\pi-CS_2$ absorptions were not specifically assigned, the assignments given are those of the present author.

[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 $\pi-CS_2$ ligand.

[d] Medium unspecified.

TABLE III. CARBON-SULPHUR ABSORPTIONS (cm^{-1}) FOR CS_2 INSERTION COMPLEXES

Complex	$\nu(CS_2)^a$ asym	$\nu(CS_2)^a$ sym	Medium	Ref.
$Re(CO)_2(PPh_3)_2(SSCH)$	940		Nujol	24
$PtCl(PPh_3)_2(SSCH)$	1050 930		Nujol	22
$Mn(CO)_4(SSCPh)$	1267m	618m	KBr	29
$Mn(CO)_4[SSC(p\text{-}MeC_6H_4)]$	1265m	613m	KBr	29
$Re(CO)_4(SSCMe)$	1146m	616m	KBr	29
$Re(CO)_4(SSCPh)$	1267	613m	KBr	29
$Re(CO)_4[SSC(p\text{-}MeC_6H_4)]$	1264m	612m	KBr	29
$Re(CO)_4[SSC(p\text{-}ClC_6H_4)]$	1258m	616m	KBr	29
$Re(CO)_3(PPh_3)(SSCPh)$	1265m	623m	KBr	29
$RhI_2(PPh_3)_2(SSCMe)\cdot C_6H_6$	1110	630	c	17
$Rh(PPh_3)_3(\pi\text{-}CS_2)(SSCPh)^b$	1261m		c	17
$Ti(SSCNMe_2)_4$	1002		CH_2Cl_2	33
$Ti(SSCNEt_2)_4$	1004		CH_2Cl_2	33
$Ti(SSCNPr^n{}_2)_4$	994		CH_2Cl_2	33
$Zr(SSCNMe_2)_4$	998		CH_2Cl_2	33
$Zr(SSCNEt_2)_4$	999		CH_2Cl_2	33
$Zr(SSCNPr^n{}_2)_4$	994		CH_2Cl_2	33

$V(SSCNMe_2)_4$	1006	CH_2Cl_2	33
$V(SSCNEt_2)_4$	1000	CH_2Cl_2	33
$Nb(SSCNMe_2)_4$	996	CH_2Cl_2	33
$Nb(SSCNEt_2)_4$	1003	CH_2Cl_2	33
$Ta(SSCNMe_2)_5$	1000	CH_2Cl_2	33
$Ni(SSCN\triangleleft)_2$	1045	Nujol	35
$Ni(SSCN\triangleleft_{Me})_2$	1045	Nujol	35

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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 author.

[b] $\nu(\pi\text{-}CS_2)$ 1003s cm^{-1}.

[c] Medium unspecified.

TABLE IV. CARBON-SULPHUR ABSORPTIONS (cm^{-1}) FOR THIOCARBONYL COMPLEXES

Complex	$\nu(CS)^{a}$	Medium	Ref.
$[CpFe(CO)_2CS]PF_6$	1348s	hexachlorobutadiene	41
$CpFe(CO)(CS)(COOMe)$	1316	CS_2	42
$[RuCl_2(CS)(PPh_3)_2]_2$	1290s	b	11
$RuCl_2(CO)(CS)(PPh_3)_2$	1290s	b	11
$RuCl_2(CS)(py)(PPh_3)_2$	1280s	b	11
$RuCl_2(CS)(bipy)(PPh_3)\cdot 0.5CH_2Cl_2$	1280s	b	11
$RuCl_2(CS)(phen)(PPh_3)\cdot 0.5CH_2Cl_2$	1280s	b	11
$Ph_4As[RuCl_3(CS)(PPh_3)_2]$	1272	Nujol	43
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
$RhCl(CS)(PPh_3)_2(TCNE)$	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	47

TABLE IV (Cont'd)

$[Ir(CS)(PPh_3)_2(CS_2)(\pi\text{-}CS_2)]BPh_4$	1305vs	Nujol	16
$[Ir(CS)(PPh_3)_2(\pi\text{-}CS_2)]BPh_4$	1305vs	Nujol	16
$IrCl(CS)(PPh_3)_2(CS_3)$	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	$CHCl_3$	47
$Ir(CO)_2(CS)(PCy_3)_2]BPh_4$	1303s	$CHCl_3$	47
$[IrH_2(CO)(CS)(PCy_3)_2]ClO_4$	1332s	$CHCl_3$	47
$[IrD_2(CO)(CS)(PCy_3)_2]ClO_4$	1322s	$CHCl_3$	47
$Ir(CO)(CS)(PPh_3)_2(COOMe)$	1287s	Nujol	47
$[IrCl(NO)(CS)(PPh_3)_2]BF_4$	1381s	Nujol	47
$[IrCl(NO)(CS)(PCy_3)_2]BF_4$	1340s	Nujol	47
$[Ir(CS)(diphos)_2]BPh_4$	1263s	Nujol	47
$[Ir(CO)(CS)(PMePh_2)_3]BPh_4$	1297	Nujol	47

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[a] Absorptions associated with $\pi\text{-}CS_2$ or S-bonded CS_2 groups are listed in Table III. The relative intensities given are those quoted in the various references.

[b] Medium unspecified: in Nujol or Vaseline mulls or in CS_2 or C_6H_6 solution.

CHAPTER III RESULTS AND DISCUSSION

An almost spectroscopically pure sample of the mono-$C^{18}O$ substituted species, $CpMn(CO)_2(C^{18}O)$, can be obtained by maintaining an *n*-hexane solution of the *cis*-cyclooctene complex, $CpMn(CO)_2(C_8H_{14})$, under an atmosphere of ^{18}O-enriched CO for several days (*vide infra*, p. 153). The work described in this part of the thesis was initiated accidentally following the decision to repeat the same olefin substitution reaction in CS_2 solution. This solvent was thought to be ideally suited for a low-frequency infrared study of the mono-$C^{18}O$ species. However, monitoring the reaction by i.r. spectroscopy showed that under these conditions the species, $CpMn(CO)_2(C^{18}O)$, is not formed. Instead, the appearance of new absorptions and dramatic colour changes of the solution indicated that $CpMn(CO)_2(C_8H_{14})$ reacted with CS_2 rather than with $C^{18}O$. This observation was felt intriguing enought to warrant a detailed investigation of the possible activation of CS_2 by some π-cyclopentadienylmanganese carbonyl complexes.

A. ACTIVATION OF CARBON DISULPHIDE BY π-CYCLOPENTADIENYL-MANGANESE CARBONYL COMPLEXES

1. Reactions of $CpMn(CO)_2$(*cis*-Cyclooctene) with CS_2

The reactions between $CpMn(CO)_2(C_8H_{14})$ and CS_2 are very complex; the number and nature of the compounds formed depends upon the actual experimental conditions employed. Furthermore, some of the compounds are extremely unstable rendering their characterization difficult.

a. In the Absence of PPh_3*

When a 2×10^{-3}M solution of $CpMn(CO)_2(C_8H_{14})$ in CS_2 is heated at 40° for about four days, the colour of the solution changes gradually from yellow to orange. The two strong infrared-active CO stretching absorptions characteristic of the olefin complex disappear and are replaced by a new set of absorptions attributable to a complex, (I), (Fig. 4). This complex appears to be particularly unstable in the absence of CS_2 because all attempts to isolate it in the solid state failed.

A more concentrated solution (1.5×10^{-2}M) of the olefin complex in CS_2 undergoes a different series of colour changes when maintained at reflux temperature (∿45°) for about two days. The solution turns red within a few hours, then dark-purple, and finally, dark-green. The i.r. spectra of samples taken from the reaction mixture at different times indicate that initially the absorptions characteristic of complex (I) begin to appear. However, as the reaction proceeds,

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* A preliminary report of the work described in this section has already been published[48].

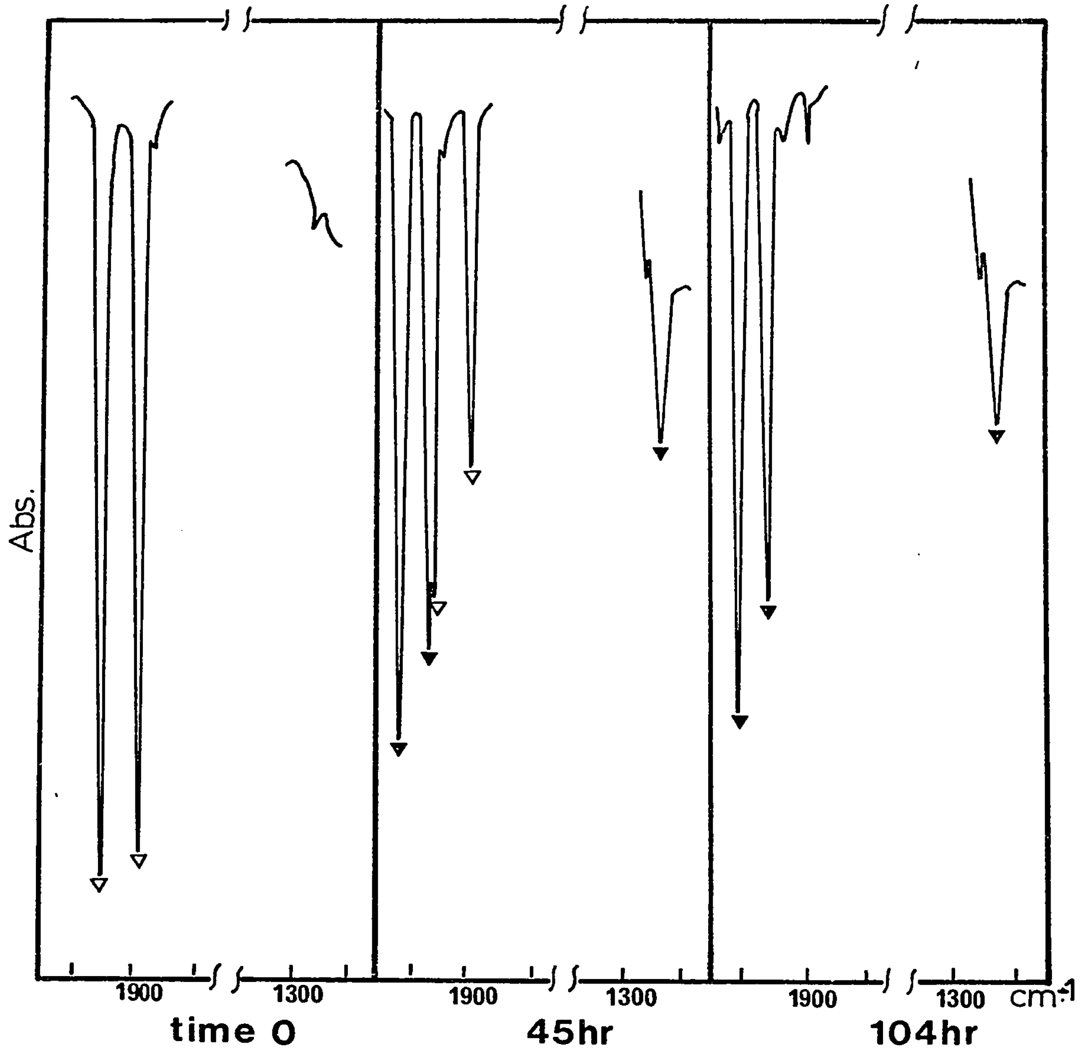


Fig. 4. Infrared spectral changes occurring in the 2100-1900 and 1300-1200 cm^{-1} regions during the reaction of CpMn(CO)$_2$(C$_8$H$_{14}$) with CS$_2$ at 40°; [CpMn(CO)$_2$(C$_8$H$_{14}$)], 2 x 10^{-3}M. The symbols ▽ and ▼ refer to the absorptions of CpMn(CO)$_2$(C$_8$H$_{14}$) and complex (I), respectively (see Table V for actual frequencies).

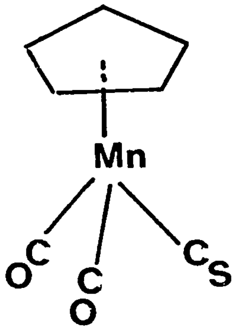
TABLE V. INFRARED FREQUENCIES OBSERVED DURING THE REACTION OF $CpMn(CO)_2(C_8H_{14})$ WITH CS_2

Complex	Symbol designation (Figs. 4-7)	Frequencies (cm^{-1})	
$CpMn(CO)_2(C_8H_{14})$	▽	1956 1893	
(I)	▼	2012 1962	1235
(II)	■	2006 1954	1266
(III)	□	2022 1938	
(IV)[a]			
(V)		2009 1959 1940(sh) 1925(sh)	
(VI)		2038	1260
(VII)	●	2022 1976 1932 1878	1195

[a] This unstable green complex decomposed before its spectrum could be recorded.

these bands (together with a number of other new bands which have also appeared) eventually vanish and are replaced by yet another set of absorptions (Fig. 5). The complexity of the reaction is underscored by thin layer chromatography which shows that there are at least four species present at the end of the reaction. The colours of the species on the t.l.c. plate are light-yellow (II), yellow (III), green (IV), and purple (V).

Filtration of the dark-green solution at the end of the reflux temperature reaction reveals a large amount of a gummy black deposit. This decomposition product is insoluble in all common solvents and its spectrum in Nujol does not exhibit any noticeable absorption in the 4000-400 cm^{-1} region. Only species (II), (III), and (V) could be isolated by column chromatography of the filtrate; the green band corresponding to complex (IV) fades away as it travels down the column. The front-running light-yellow species (II) affords air-stable crystals. Elemental analysis, molecular weight determination, and spectroscopic data indicate that (II) is the first thiocarbonyl complex of manganese, $CpMn(CO)_2CS$:



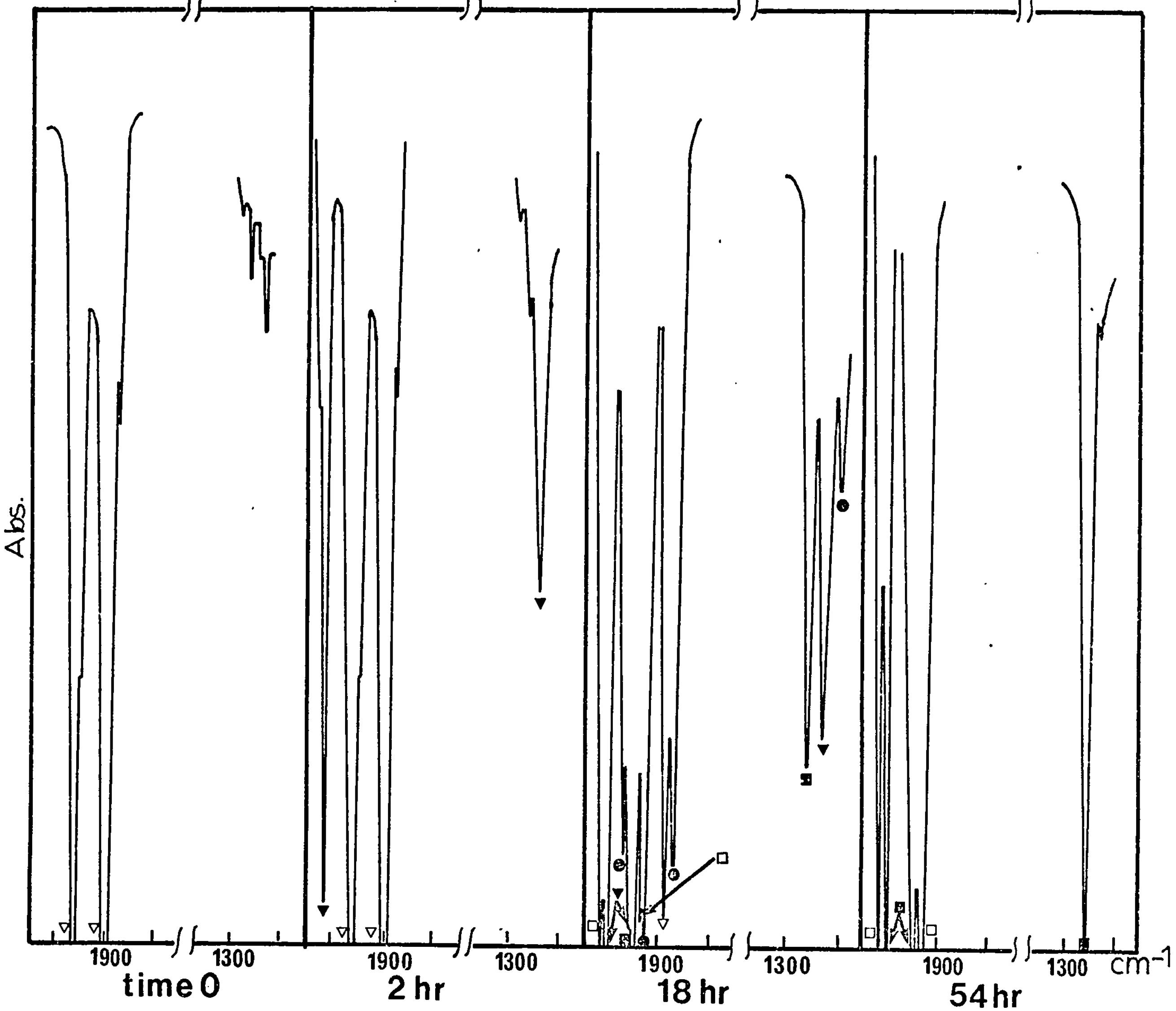


Fig. 5. Infrared spectral changes occurring in the 2100-1900 and 1300-1200 cm^{-1} regions during the reaction of CpMn(CO)$_2$(C$_8$H$_{14}$) with CS$_2$ at reflux temperature (∿45°); [CpMn(CO)$_2$(C$_8$H$_{14}$)], 1.5 x 10^{-2}M. The frequencies associated with the complexes designated by the different symbols are given in Table V.

The other yellow product (III) is the tricarbonyl complex $CpMn(CO)_3$. The complexes, $CpMn(CO)_2CS$ and $CpMn(CO)_3$, are obtained in very low yield (∿5% based on the amount of the original olefin complex). The purple species (V) is produced in even more minute quantities and only spectroscopic data could be obtained for it. This complex exhibits two strong i.r. absorptions at 2009 and 1959 cm^{-1} together with medium-intense shoulders at 1940 and 1925 cm^{-1}. The fragmentation pattern observed in its mass spectrum suggests the presence of four CO groups. Since the starting material, $CpMn(CO)_2(C_8H_{14})$ has only two CO groups, these data hint that complex (V) could possibly be a dimer. The identity of the unstable green complex (IV) is not known.

At any given time, the ratio of the amount of complex (I) to that of the other species formed during the reaction under reflux conditions depends upon the initial concentration of $CpMn(CO)_2(C_8H_{14})$ in CS_2 solution (e.g., see Fig. 6). The same effect is noted for the reaction at 40°. When the initial concentration of the olefin complex in CS_2 solution is $2 \times 10^{-3}M$, complex (I) is produced with little apparent decomposition, and the i.r. spectrum of the reaction mixture after 104 hr (Fig. 4) indicates that this complex is the only carbonyl-containing species formed in any significant amount. However, when the initial concentration of olefin complex is

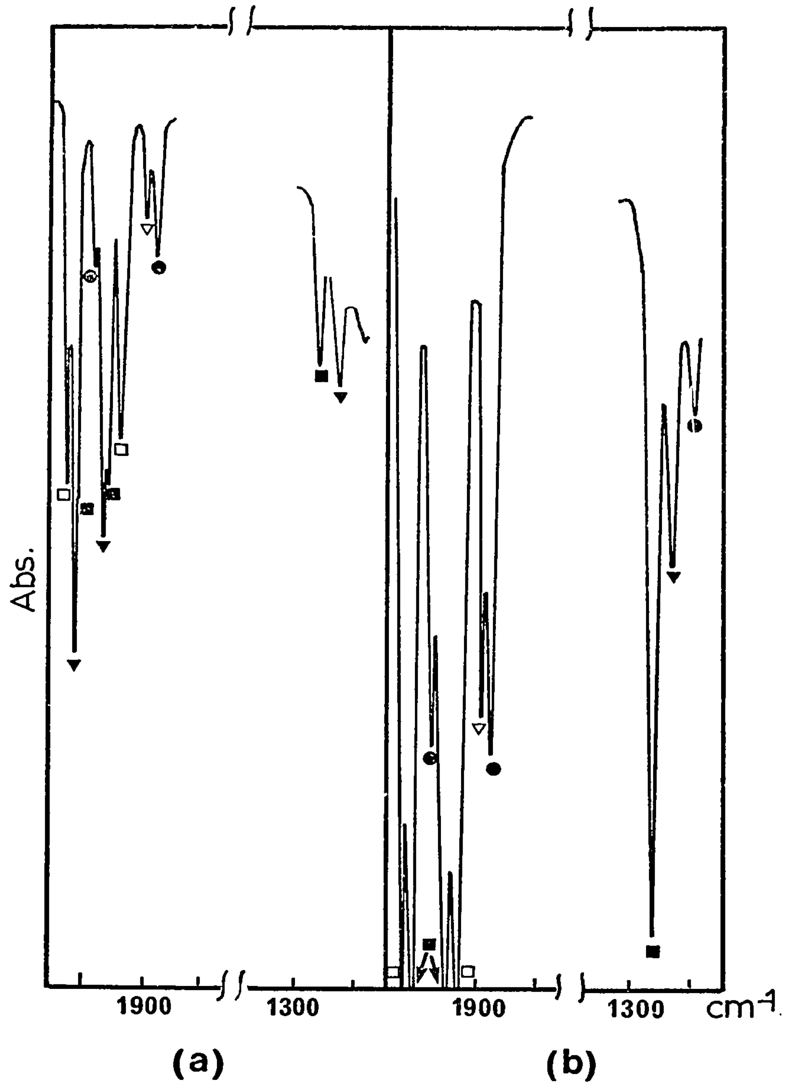


Fig. 6. Effect of the concentration of $CpMn(CO)_2(C_8H_{14})$ on its reaction with CS_2 under reflux conditions (i.r. spectra taken after 32 hr); (a) $[CpMn(CO)_2(C_8H_{14})]$, $2 \times 10^{-3}M$, (b) $[CpMn(CO)_2(C_8H_{14})]$, $1.5 \times 10^{-2}M$. ▽ $CpMn(CO)_2(C_8H_{14})$, ▼ complex (I), ■ $CpMn(CO)_2CS$, □ $CpMn(CO)_3$, ● complex (VII) (see Table V for the actual frequencies of the absorptions for each of these species.

increased ten-fold, the reaction at 40° proceeds in a similar manner to the reaction under reflux conditions.

When the dilute solution of (I) in CS_2 is left to stand at 40°, it slowly decomposes. However, an i.r. spectrum taken after three weeks indicates that only an insignificant amount of $CpMn(CO)_2CS$ has been produced by comparison with the amount formed in the reaction under reflux conditions. Moreover, the appearance of two new bands at 2038 and 1260 cm^{-1} suggests that another carbonyl-thiocarbonyl complex (VI) is formed instead.

Spectra taken during the first part of the reaction under reflux conditions (Fig. 5) show the appearance and subsequent disappearance of a set of absorptions at 1976, 1932, 1878, and 1195 cm^{-1}. In an attempt to determine the identity of the species responsible for these bands, the reaction was terminated when the intensities of the absorptions were at a maximum relative to the other absorptions in the spectrum. Following removal of CS_2, purple, green, and yellow materials settle successively at the bottom of the reaction flask. Washing this mixture of coloured materials with *n*-pentane affords a green solution which almost instantly turns yellow! The i.r. spectrum of this yellow solution shows that it contains $CpMn(CO)_2CS$ and $CpMn(CO)_3$ as well as some unreacted $CpMn(CO)_2(C_8H_{14})$. The solid residue which is insoluble in *n*-pentane dissolves readily in benzene. Following filtration, and subsequent removal of the benzene solvent, a purple-black solid (VII) is obtained in minute quantities. Only infrared data could be obtained for this complex: 2022s, 1976s, 1932s, 1878s, 1195m (CS_2 solution). It should be noted that the 2022 and 1932 cm^{-1} bands of (VII) are obscured in Figs. 5 and 6 by the CO stretching absorptions of $CpMn(CO)_3$.

When the CS_2 solution of complex (VII) is left to stand for several hours at room temperature, the colour changes gradually from purple to orange. At the same time, its CO absorptions are replaced by new ones characteristic of complex (I).

Ultraviolet light irradiation of $CpMn(CO)_2(C_8H_{14})$ in CS_2 solution affords a mixture of $CpMn(CO)_2CS$, $CpMn(CO)_3$, and complex (VII) (identified by their CO stretching absorptions). The presence in the reaction mixture also of the same unidentified green species (IV) that is formed in the thermal reaction can be shown by t.l.c. The photochemical reaction leads to even more extensive decomposition than occurs in the thermal process.

b. In the Presence of PPh_3*

It is known that the presence of PPh_3 is essential to the formation in good yield of the thiocarbonyl complexes,

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* A preliminary report on this and related reactions has already been published[49].

trans-$MCl(CS)(PPh_3)_2$ (M = Rh, Ir) (*vide supra*, pp. 30, 32). Consequently, it was felt worthwhile repeating the thermal reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the presence of PPh_3. Under these conditions and irrespective of the concentration of the olefin complex and the reaction temperature, $CpMn(CO)_2CS$ is formed in almost quantitative yield. Moreover, at reflux temperature, the reaction reaches completion after only about a day. In sharp contrast to the reaction under reflux conditions in the absence of PPh_3, there is no appreciable decomposition and no other carbonyl-containing products are formed (Fig. 7). The only side-products present in any significant amount in the reaction mixture are PPh_3S and C_8H_{14} (identified by i.r. spectroscopy and v.p.c. analysis).

The synthesis of $CpMn(CO)_2CS$ from $CpMn(CO)_2(C_8H_{14})$ and PPh_3 in CS_2 solution dramatically illustrates the dual role played by CS_2 as a solvent and as a reactant in the reaction. In other solvents (e.g., methylcyclohexane and nitromethane), $CpMn(CO)_2(C_8H_{14})$ undergoes olefin substitution with PPh_3 to produce only $CpMn(CO)_2PPh_3$[50].

2. Mechanisms for the Reactions of $CpMn(CO)_2$(*cis*-Cyclooctene) with CS_2

a. In the Presence of PPh_3

Because of the apparent simplicity of the synthesis

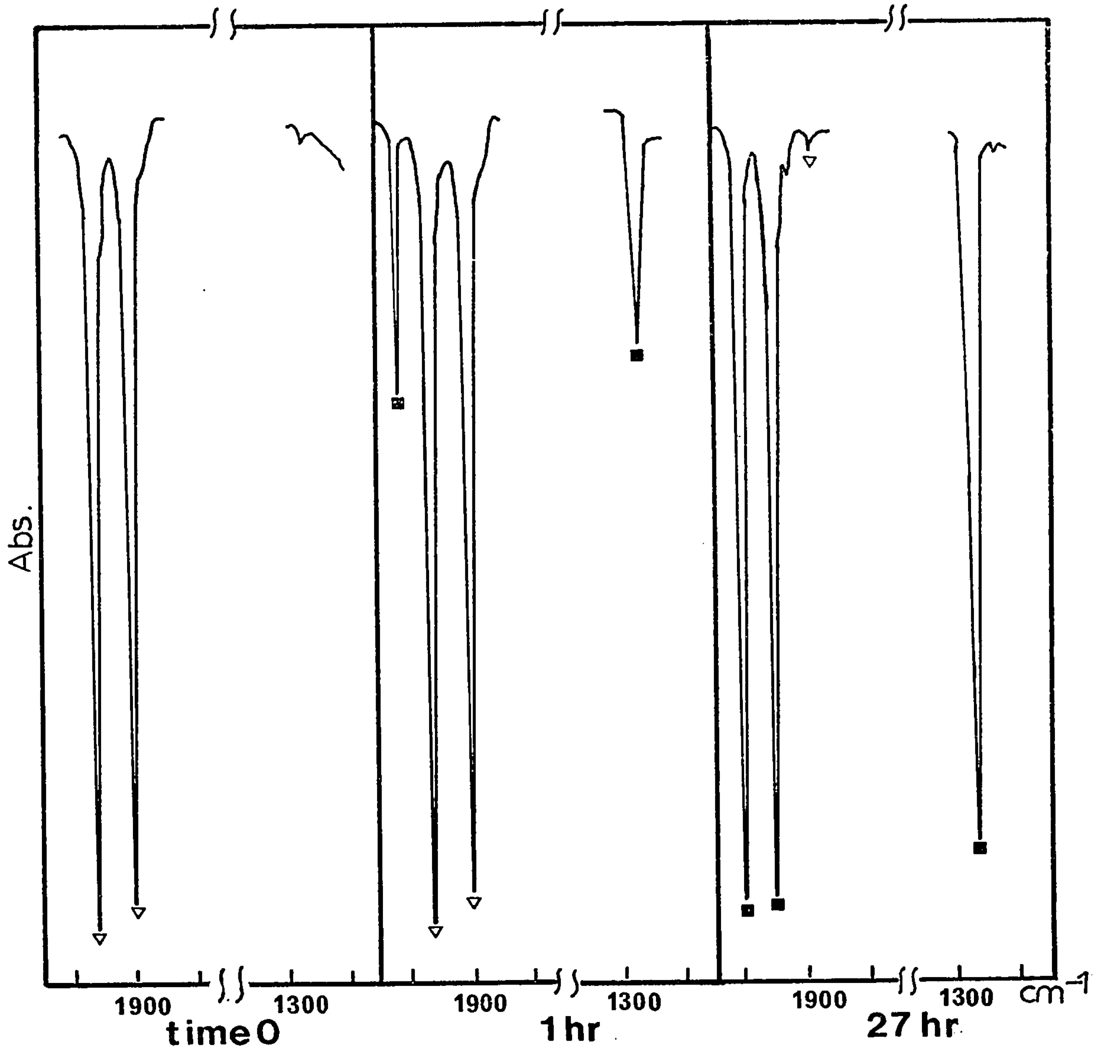

Fig. 7. Infrared spectral changes observed in the CO and CS stretching regions during the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the presence of PPh_3 under reflux conditions. ▽, $CpMn(CO)_2(C_8H_{14})$; ■, $CpMn(CO)_2CS$ (see Table V).

of $CpMn(CO)_2CS$ from $CpMn(CO)_2(C_8H_{14})$ and CS_2 in the presence of PPh_3, the mechanism for this reaction will be discussed first.

$$CpMn(CO)_2(C_8H_{14}) + PPh_3 \xrightarrow{CS_2} CpMn(CO)_2CS + PPh_3S + C_8H_{14} \qquad (1)$$

Neither PPh_3 nor C_8H_{14} reacts thermally with CS_2, even after 24 hr at reflux temperature.* This suggests that one of the steps in reaction 1 must be the formation of a reactive intermediate from which sulphur can be abstracted by PPh_3 to give PPh_3S and $CpMn(CO)_2CS$. Moreover, $CpMn(CO)_2(C_8H_{14})$ reacts with a <u>stoichiometric</u> amount of PPh_3 in CS_2 to give $CpMn(CO)_2CS$ in almost quantitative yield (85%).** Analysis of the final reaction mixture by v.p.c. indicates that all the PPh_3 has reacted and that the only other products present in any significant amount are C_8H_{14} and PPh_3S. Thus, it seems reasonable to suggest the stoichiometry, $CpMn(CO)_2(CS_2)$, for the sulphur-containing intermediate.

That reaction 1 proceeds *via* the fast abstraction of a sulphur atom from a CS_2-containing intermediate and that this intermediate is complex (I), formed during the reaction of

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* It is of interest to note that uv irradiation of PPh_3 in CS_2 solution does afford PPh_3S in low yield (<10%). A dark red solid is also formed which is probably the same product noted by other workers[51] and attributed to the polymerization of CS.

** Some losses occur during purification.

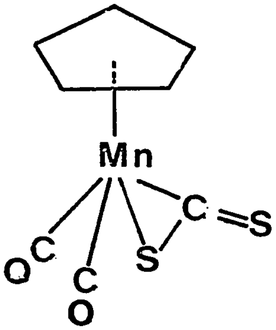
$CpMn(CO)_2(C_8H_{14})$ with CS_2 in the absence of PPh_3, is supported by the following experimental evidence.

(i) Addition of PPh_3 to a solution of (I) [prepared by maintaining a 2×10^{-3}M solution of $CpMn(CO)_2(C_8H_{14})$ in CS_2 at 40° for four days] results in the <u>instantaneous</u> formation of $CpMn(CO)_2CS$ and PPh_3S.

(ii) Monitoring reaction 1 by i.r. spectroscopy when it is carried out at 40° for a 2×10^{-3}M solution of $CpMn(CO)_2(C_8H_{14})$ and <u>less than a stoichiometric</u> amount of PPh_3 shows that $CpMn(CO)_2CS$ is formed only as long as there is still some unreacted PPh_3 left in solution. After all the PPh_3 has been converted into PPh_3S, the absorptions characteristic of $CpMn(CO)_2CS$ stop increasing in intensity and the bands associated with complex (I) appear and continue to grow until the reaction is complete.

The i.r. data leave little doubt that complex (I) of stoichiometry, $CpMn(CO)_2(CS_2)$, is the first example of a π-CS_2 complex of manganese. The strong absorption at 1235 cm^{-1} is assigned to the out-of-ring $\nu(C{=}S)$ mode and a medium intense band present at $\sim$640 cm^{-1} to the in-ring $\nu(C{-}S)$. That $CpMn(CO)_2(CS_2)$ should be a π-CS_2 complex is particularly reasonable when one remembers that the syntheses of group VIII metal thiocarbonyl complexes also appear to involve the formation of π-CS_2 complexes (*vide supra*, IIE.).

In the proposed structure of $CpMn(CO)_2(\pi\text{-}CS_2)$ shown below, the manganese is formally heptacoordinated and in the oxidation state +3. Such a π-cyclopentadienylmanganese(III) dicarbonyl species is not without precedent because the complexes, $CpMn(CO)_2(SiPh_3)H$[52], $CpMn(CO)_2(SiCl_3)H$[53], and $CpMn(CO)_2(SiCl_3)(SnCl_3)$[54] have been synthesized recently. An X-ray structure determination[52] of $CpMn(CO)_2(SiPh_3)H$ suggests the presence of a hydrogen bridge between manganese and silicon; thus forming a three-membered ring similar to that proposed for $CpMn(CO)_2(\pi\text{-}CS_2)$. Moreover, the CO stretching frequencies observed for the $\pi\text{-}CS_2$ complex (at 2012 and 1962 cm^{-1} in CS_2 solution) fall in the same range as those reported for the π-cyclopentadienylmanganese(III) silyl complexes [$\nu(CO)_{sym}$ 2025-1990 cm^{-1}, $\nu(CO)_{asym}$ 1980-1930 cm^{-1} in *n*-hexane solution].



Angelici and Loewen[50] have investigated the kinetics and mechanism of reaction 2 in methylcyclohexane solution

$$CpMn(CO)_2(olefin) + L \longrightarrow CpMn(CO)_2L + olefin \qquad (2)$$

(at 50-95°) in which various olefins (including *cis*-cyclooctene) are replaced by monodentate ligands such as PPh_3. They proposed that reaction 2 proceeds by an S_N1 dissociative mechanism involving the slow loss of the olefin in the rate-determining step to form the intermediate $CpMn(CO)_2$, followed by the rapid entry of L. In an attempt to ascertain the role played by *cis*-cyclooctene in the formation of $CpMn(CO)_2CS$ from $CpMn(CO)_2(C_8H_{14})$, kinetic data were obtained at 40° for reactions 1, 2 (olefin = C_8H_{14}, L = PPh_3), and 3. The rate for these reactions

$$CpMn(CO)_2(C_8H_{14}) \xrightarrow{CS_2} CpMn(CO)_2(\pi\text{-}CS_2) + C_8H_{14} \qquad (3)$$

were determined by monitoring the rate of disappearance of the infrared-active CO stretching absorption of $CpMn(CO)_2(C_8H_{14})$ at *ca.* 1900 cm^{-1}. Linear first-order plots of $\ln(A - A_\infty)$ *vs.* time where A is the absorbance at time t and A_∞ the absorbance at infinite time were obtained. All the reactions went to completion and typical first-order plots for each of them are shown in Fig. 8. The observed pseudo-first-order rate constants (k_{obsd}) for the reactions are given in Table VI.

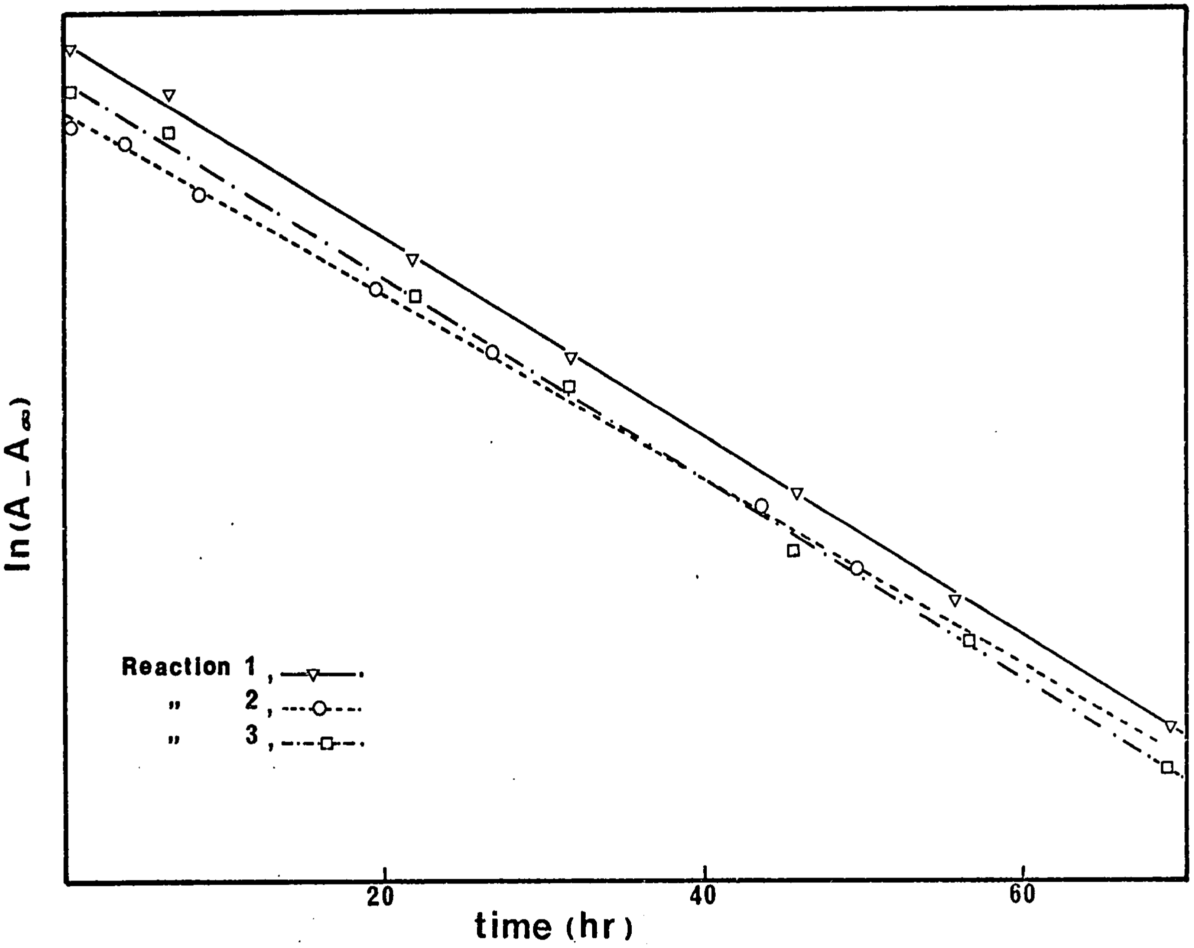


Fig. 8. First-order plots for the reactions at 40° of $CpMn(CO)_2(C_8H_{14})$ with CS_2 and PPh_3 (1), with PPh_3 in methylcyclohexane solution (2), and with CS_2 in the absence of PPh_3 (3).

TABLE VI. PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTIONS AT 40° OF $CpMn(CO)_2(C_8H_{14})$ WITH CS_2 AND PPh_3, WITH PPh_3 IN METHYLCYCLOHEXANE SOLUTION, AND WITH CS_2 IN THE ABSENCE OF PPh_3

Reaction		$[PPh_3]^a$ (M)	$10^5 k_{obsd}$ (sec^{-1})
$CpMn(CO)_2(C_8H_{14}) + PPh_3 \xrightarrow{CS_2} CpMn(CO)_2CS + PPh_3S + C_8H_{14}$	(1)	0.02	7.4
		0.05	7.9
		0.1	7.6
$CpMn(CO)_2(C_8H_{14}) + PPh_3 \xrightarrow{\text{methyl-cyclohexane}} CpMn(CO)_2(PPh_3) + C_8H_{14}$	(2)	0.02	6.4^b
$CpMn(CO)_2(C_8H_{14}) \xrightarrow{CS_2} CpMn(CO)_2(\pi\text{-}CS_2) + C_8H_{14}$	(3)		7.8^b

[a] $[CpMn(CO)_2(C_8H_{14})]$, 2×10^{-3}M

[b] Average of several identical runs; reproducibility ±6%.

The data indicate that when the concentration of $CpMn(CO)_2(C_8H_{14})$ is 2×10^{-3}M the rates for reactions 1 and 3 at 40° are identical*; moreover, the rate of reaction 1 is independent of $[PPh_3]$. The observed rates for reactions 1 and 3 are also essentially equal to the rate determined for reaction 2. The small discrepancy is within the range noted by Angelici and Loewen for reaction 2 when the nature of either the solvent or the incoming ligand is changed.

On the basis of the kinetic results, it seems likely that the <u>same</u> rate-determining step is operative in all three reactions *viz.*, the slow dissociation of *cis*-cyclooctene from $CpMn(CO)_2(C_8H_{14})$ to form the intermediate, $CpMn(CO)_2$. This suggestion receives some support from the results obtained for the reaction of the norbornadiene derivative, $CpMn(CO)_2(C_7H_8)$, with CS_2 and PPh_3 under reflux conditions. The reaction again leads to $CpMn(CO)_2CS$ but is extremely slow. This observation is in accord with Angelici and Loewen's results for reaction 2 which indicate that the rate of dissociation of norbornadiene is appreciably slower than that for *cis*-cyclooctene.

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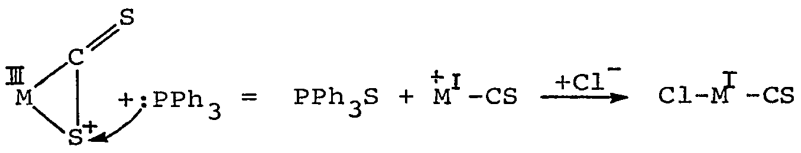
* It should be emphasized that these results are valid only when the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 affords the π-CS_2 complex as the <u>only</u> carbonyl-containing species. At a higher temperature or with an increased concentration of $CpMn(CO)_2(C_8H_{14})$, when the reaction yields $CpMn(CO)_2CS$, $CpMn(CO)_3$, and other products, the observed rate for reaction 3 is approximately half that for reaction 1.

On the basis of the results discussed above, the general reaction scheme shown in Fig. 9 is proposed for the formation of $CpMn(CO)_2CS$ from $CpMn(CO)_2(olefin)$, CS_2, and PPh_3. The last step in the mechanism is very similar to that proposed by Yagupsky and Wilkinson[16] for the formation of rhodium and iridium thiocarbonyls:



Their mechanism involves the formation of cationic species and they suggested that some positive charge could be located on the in-ring sulphur making it susceptible to nucleophilic attack. However, the existence of a cationic species does not appear to be essential for the abstraction of sulphur by PPh_3 because the perthiocarbonato- anion, $[Ni(CS_4)_2]^{2-}$, reacts readily with PPh_3 to give $[Ni(CS_3)_2]^{2-}$ and PPh_3S[55].

b. In the Absence of PPh_3

Owing to its complexity, the mechanism of the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the absence of PPh_3 appears more difficult to assess, particularly as some of the complexes formed could not be identified. Nevertheless, it is possible to make a few comments.

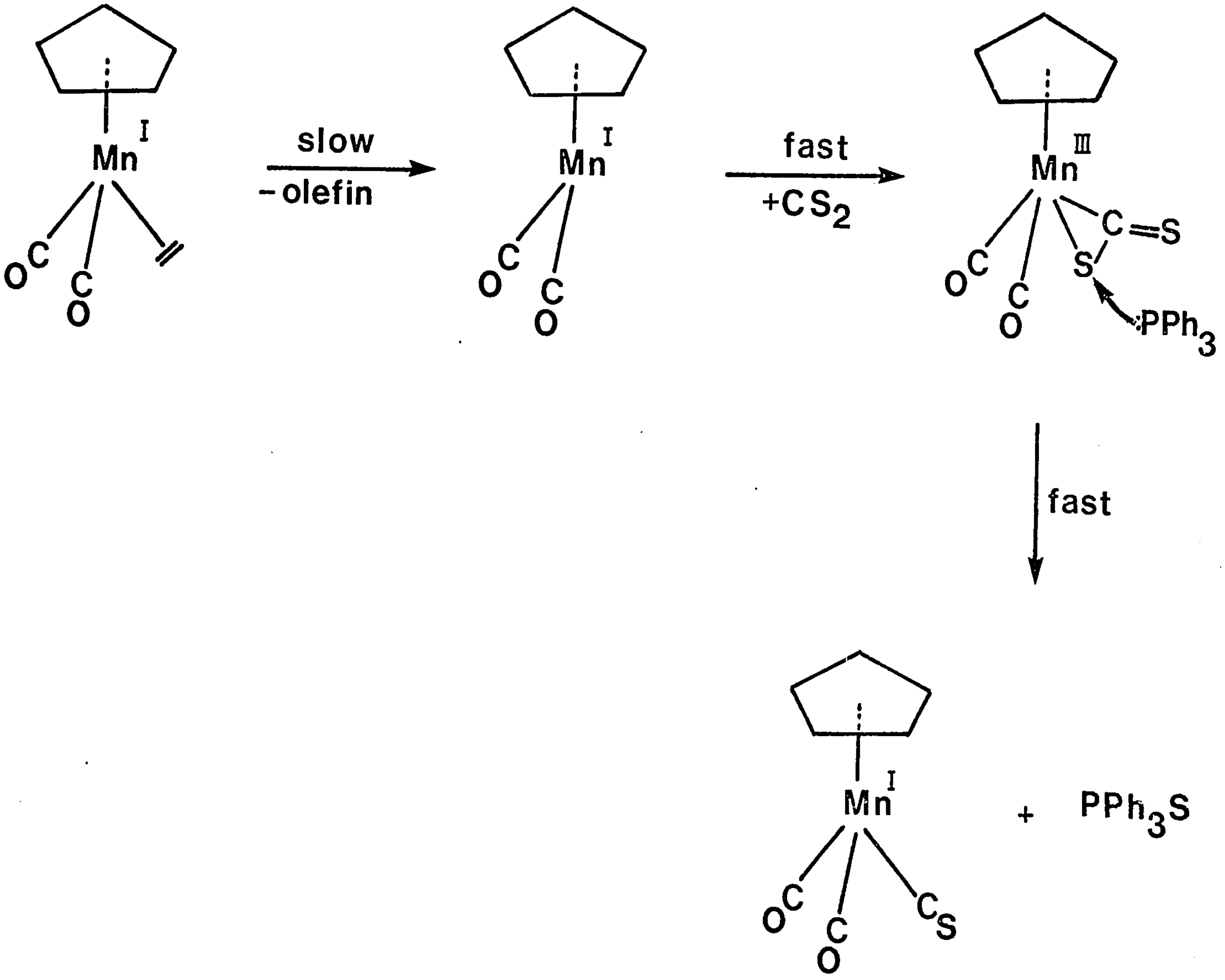
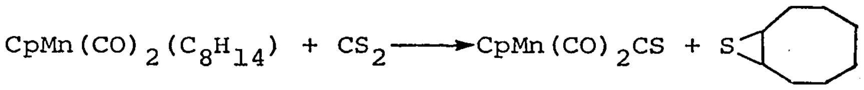


Fig. 9. Proposed reaction scheme for the formation of CpMn(CO)$_2$CS from CpMn(CO)$_2$(olefin), CS$_2$, and PPh$_3$.

It was shown earlier that $CpMn(CO)_2(\pi\text{-}CS_2)$ is formed alone, only for low concentrations of $CpMn(CO)_2(C_8H_{14})$ in CS_2 solution and at temperatures below reflux. An increase in either or both of these factors brings about the formation, apparently from $CpMn(CO)_2(\pi\text{-}CS_2)$, of $CpMn(CO)_2CS$, $CpMn(CO)_3$, other carbonyl-containing species, and a black decomposition product. The amounts of $CpMn(CO)_2CS$ and $CpMn(CO)_3$ present in the reaction mixture at any given time relative to the amount of $CpMn(CO)_2(\pi\text{-}CS_2)$ also appear to be dependent on the concentration of $CpMn(CO)_2(C_8H_{14})$ and the temperature. These observations suggest that, in the absence of PPh_3, the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 leads to the formation of the products mentioned above *via* the thermal decomposition of $CpMn(CO)_2(\pi\text{-}CS_2)$. In partial support of this hypothesis is the fact that $RhCl(PPh_3)_2(CS_2)(\pi\text{-}CS_2)$ decomposes thermally in chloroform solution to give *trans*-$RhCl(CS)(PPh_3)_2$[8].

The approximate rate for the thermal decomposition process leading to $CpMn(CO)_2CS$ is half that for the reaction in the presence of PPh_3 but under otherwise identical experimental conditions. This suggests that some of the complexes formed may react with intermediates in the reaction mixture. A similar rate decrease is noted for the thermal decomposition of $CpMn(CO)_2(C_8H_{14})$ in methylcyclohexane solution (to give $CpMn(CO)_3$ and a brown precipitate) when compared to the reaction with PPh_3 affording $CpMn(CO)_2PPh_3$.

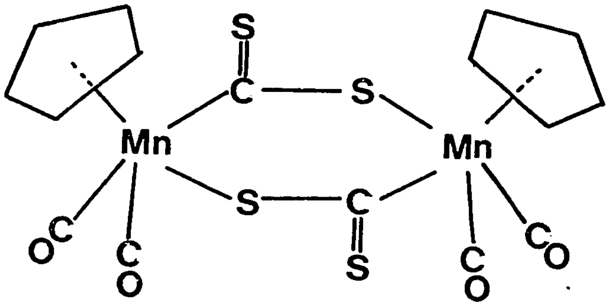
It was thought originally[48] that the liberated olefin might play the role of sulphur-acceptor in the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the absence of PPh_3. Moreover, in doing so, it would be converted into an episulfide:



$$CpMn(CO)_2(C_8H_{14}) + CS_2 \longrightarrow CpMn(CO)_2CS + S$$

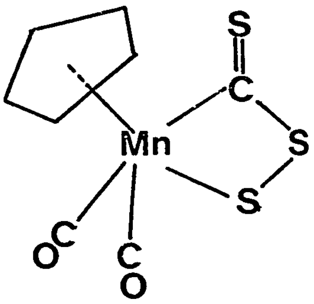
However, further investigation failed to give any evidence for the formation of $C_8H_{14}S$[56]. In particular, the i.r. spectrum of the reaction mixture did not exhibit the absorptions characteristic of $C_8H_{14}S$ at 1038s and 1110m cm^{-1}.

Unfortunately, the experimental data allow only speculation as to the nature of some of the other complexes formed in the reaction. The purple complex (VII) is formed, and disappears, in step with $CpMn(CO)_2(\pi-CS_2)$ provided that the concentration of $CpMn(CO)_2(C_8H_{14})$ or the reaction temperature is high enough. Once isolated, complex (VII) can be converted into $CpMn(CO)_2(\pi-CS_2)$ by addition of CS_2. Thus, it is felt that (VII) could possibly be the dimeric form of $CpMn(CO)_2(\pi-CS_2)$ containing two CS_2 bridges:



Similar structures containing CS_2 bridges have been proposed by Yagupsky and Wilkinson for the materials of composition, $IrCl(PPh_3)_x(CS_2)_y$ (x = 2-3, y = 1-3), which are formed during the reaction of $IrCl(PPh_3)_3$ with CS_2 in the absence of PPh_3 (*vide supra*, p. 15).

The green species (IV) formed during the thermal decomposition of $CpMn(CO)_2(\pi\text{-}CS_2)$ could possibly be a π-cyclopentadienylmanganese(III) complex such as:



Similar -S-S-C(S)- linkages have been proposed by Kubota and Carey for iridium(III) intermediates in the synthesis of *trans*-$IrCl(CS)(PPh_3)_2$ from *trans*-$IrCl(PPh_3)_2(N_2)$ and CS_2 (*vide supra*, p. 32).

3. Miscellaneous Reactions

Following the synthesis of $CpMn(CO)_2CS$ from $CpMn(CO)_2(C_8H_{14})$, the reactions of CS_2 with a variety of π-cyclopentadienylmanganese complexes were investigated spectroscopically. The purpose of the study was to determine whether or not $CpMn(CO)_2CS$ and related thiocarbonyl complexes could be prepared using other complexes in place of $CpMn(CO)_2(C_8H_{14})$. The results of this investigation are presented below.

a. Reaction of $CpMn(CO)_3$ with CS_2

The tricarbonyl complex, $CpMn(CO)_3$, is relatively inert towards CO substitution and this may be achieved usually only under intense uv light. When a CS_2 solution of $CpMn(CO)_3$ is irradiated for 1 hr, its colour changes from yellow to red. In addition, a large amount of a black decomposition product is formed which eventually coats the walls of the reaction vessel in the form of an opaque film so that no further reaction occurs. Nevertheless, an i.r. spectrum of the red solution shows the presence of small amounts of $CpMn(CO)_2CS$. In contrast to the uv irradiation of a CS_2 solution of $Fe(CO)_5$ and PPh_3 which affords $Fe(CO)_2(PPh_3)_2(\pi\text{-}CS_2)$[9], there was no spectral evidence for the formation of a $\pi\text{-}CS_2$ species. The nature of the complex responsible for the red colour of the solution remains unknown.

b. Reaction of $CpMn(CO)_2PPh_3$ with CS_2

The thermal reaction of $CpMn(CO)_2PPh_3$ with CS_2 is of particular interest because the starting complex already contains the sulphur-acceptor group, PPh_3. However, $CpMn(CO)_2PPh_3$ appears to be extremely inert towards ligand substitution because even after 3 days at reflux temperature, a CS_2 solution of $CpMn(CO)_2PPh_3$ does not exhibit any noticeable change in either its appearance or its i.r. spectrum. Curiously, when the reaction is repeated without prior distillation of the solvent under nitrogen, different results are obtained. An i.r. spectrum of the solution recorded after 3 days at reflux temperature shows that the characteristic absorptions of the triphenylphosphine complex have decreased slightly. Moreover, the appearance of weak bands at 2006, 1954, and 1266 cm^{-1} indicates that some $CpMn(CO)_2CS$ has been formed. In contrast to the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 alone, $CpMn(CO)_2CS$ is the only carbonyl-containing compound produced. The presence of brown particles in the solution indicates that the process involves decomposition of $CpMn(CO)_2PPh_3$.

c. Reaction of π-$MeC_5H_4Mn(CO)_2$(*cis*-Cyclooctene) with CS_2

The replacement of a hydrogen atom in the π-cyclopentadienyl ring of $CpMn(CO)_2(C_8H_{14})$ by a methyl group does not appear to bring about any significant change in reactivity. The complex, π-$MeC_5H_4Mn(CO)_2(C_8H_{14})$, does react with CS_2 to produce the following species (among others) which can be identified by their i.r. spectra in CS_2 solution: π-$MeC_5H_4Mn(CO)_2(\pi$-$CS_2)$ [ν(CO) 2009, 1959; ν(CS) 1229 cm^{-1}], π-$MeC_5H_4Mn(CO)_2CS$

[ν(CO) 2004, 1952; ν(CS) 1261 cm^{-1}], and π-$MeC_5H_4Mn(CO)_3$ [ν(CO) 2019, 1933 cm^{-1}].

d. Reaction of $CpMn(CO)_2$(*cis*-Cyclooctene) with Me_2S_2

The result of a preliminary spectroscopic investigation of the reaction between $CpMn(CO)_2(C_8H_{14})$ and Me_2S_2 is included in this chapter because it appears that the olefin complex undergoes oxidative-addition reactions to form π-cyclopentadienylmanganese(III) complexes much more readily than it was previously thought. Therefore, the formation of $CpMn(CO)_2$(π-CS_2) and π-$MeC_5H_4Mn(CO)_2$(π-CS_2) is in fact quite feasible.

Dimethyl disulphide contains a weak sulphur-sulphur bond. When the ligand reacts with metal carbonyl complexes, the S-S bond is cleaved and monomeric or polymeric mercaptides are formed[57]. Various monomeric and dimeric π-cyclopentadienylmetal complexes containing methylthio- groups have been prepared by this method. For example, $CpMo(CO)_3H$ reacts with Me_2S_2 to form a mixture of isomers of the sulphur-bridged dimer, $[CpMo(CO)_2SMe]_2$[58]. A similar reaction with the analogous tungsten hydride was also thought to yield a dimer; however a subsequent study[59] has shown that the properties of the complex are more compatible with the monomeric species, $CpW(CO)_3SMe$. The thermal reaction of $[CpFe(CO)_2]_2$ with Me_2S_2 yields the dimer, $[CpFe(CO)SMe]_2$[60]. The related monomeric species, $CpFe(CO)_2SMe$, can be obtained either thermally from $CpFe(CO)_2H$ or photochemically from $[CpFe(CO)_2]_2$[61]. Controlled thermal decomposition of the iron monomer gives variable mixtures of two isomers of the dimer[62].

In the present work, it was found that $CpMn(CO)_2(C_8H_{14})$ also reacts with Me_2S_2. When an *n*-hexane solution of these two compounds is refluxed for 6 hr, there is a colour change from yellow to purple and extensive decomposition takes place. The i.r. spectrum in the CO stretching region of the final reaction mixture shows that the characteristic absorptions of the olefin complex have vanished. Instead, there are six new CO absorptions at 2028, 1992, 1947, 1933, 1887, and 1879 cm^{-1} (Fig. 10). Analysis of the reaction mixture by t.l.c. indicates that three species (yellow, green, and purple in order of decreasing movement on the plate) are present. The yellow species is $CpMn(CO)_3$[ν(CO) 2028, 1947 cm^{-1} in *n*-hexane solution]. The green and purple species are somewhat air-sensitive and efforts to obtain these complexes in any significant amounts failed. However, spectroscopic data afford some clues as to their possible identity.

The purple species and $CpMn(CO)_3$ co-sublime. An i.r. spectrum of the sublimate in *n*-hexane solution indicates that the bands at 1992 and 1933 cm^{-1} can be assigned exclusively to the purple species. Thus, by elimination, the absorptions at 1887 and 1879 cm^{-1} are associated with the green species.

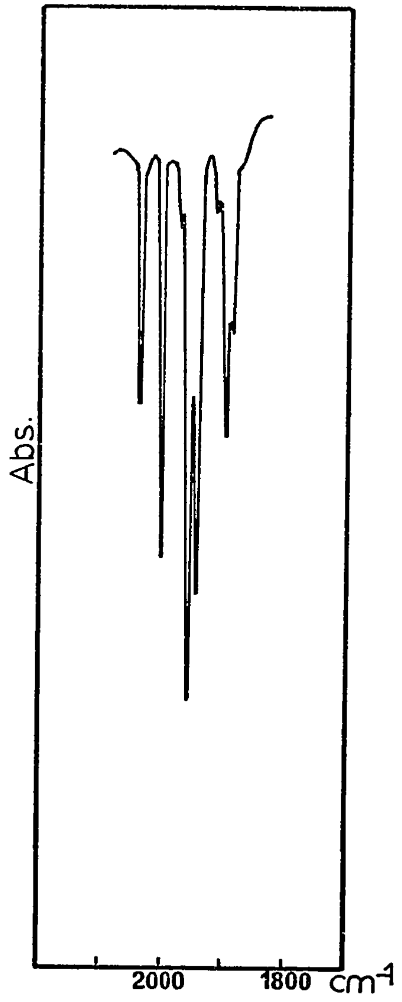


Fig. 10. Infrared spectrum in the CO stretching region of the mixture formed in the reaction of $CpMn(CO)_2(C_8H_{14})$ with Me_2S_2.

The major peaks present in the mass spectrum of the original reaction mixture are given in Table VII. The highest mass peak of any appreciable abundance is at m/e 270 which can be assigned to $CpMn(CO)_2(SMe)_2^+$. The fragmentation pattern observed at lower mass is very similar to that reported by King[63] for the degradation of $CpFe(CO)_2SMe^+$ and is consistent with the presence of a second non-bridging methylthio- group.

Two CO groups are lost simultaneously from $CpMn(CO)_2(SMe)_2^+$ (m/e 270) to give $CpMn(SMe)_2^+$ (m/e 214). The simultaneous loss of two CO groups has also been observed for the degradation of the molecular ions, $CpMn(CO)_2L^+$ (L = cycloolefin, phosphine, amine, $SO(CH_3)_2$, etc.)[64]. It seems unlikely that $CpMn(CO)_2(SMe)_2^+$ could result from the prior fragmentation of a binuclear complex with bridging methylthio- groups because the first step in the degradation of such metal carbonyl dimers always appears to be the stepwise loss of the CO ligands[65]. The rupture of the sulphur-bridges only occurs later and is preceeded by the loss of the methyl groups.

Although these results certainly do suggest that the Mn(III) complex, $CpMn(CO)_2(SMe)_2$, is formed in the reaction of $CpMn(CO)_2(C_8H_{14})$ with Me_2S_2, further experimental data are needed to confirm this. Complexes such as $Cp_2M(SR)_2$[66] (M = Mo, W; R = Me, Et) are known but to the author's knowledge there are no examples in the literature of π-cyclopentadienylmetal carbonyls containing <u>two</u> non-bridging mercapto- groups.

TABLE VII. MASS SPECTRUM AND TENTATIVE ASSIGNMENT OF FRAGMENT IONS FOR THE MIXTURE OBTAINED FROM THE REACTION OF $CpMn(CO)_2(C_8H_{14})$ WITH Me_2S_2

m/e	Ion	Rel. abund.	m/e	Ion	Rel. abund.
344	$(CpMnCO)_2(SMe)H^+$	0.2	97	CpS^+	25
288	$(CpMn)_2(SMe)H^+$	0.2	85	$C_3H_3SCH_2{}^+$	11
270	$CpMn(CO)_2(SMe)_2{}^+$	2.0	83	$C_6H_9{}^+$	16
224	$CpMn(CO)_2(SMe)H^+$	8.5	82	$C_6H_8{}^+$	10
214	$CpMn(SMe)_2$	14	79	$C_6H_7{}^+$	13
182	$CpMnMe(SMe)^+$	6.5	78	$C_6H_6{}^+$	10
177	$CpMn(CO)_2H^+$	7.0	77	$C_6H_5{}^+$	10
176	$CpMn(CO)_2$	7.5	66	$C_5H_6{}^+$	24
151	$CpMnMe_2H^+$	9.5	65	Cp^+	16
129	$C_{10}H_9{}^+$	19	61	$MeSCH_2{}^+$	15
128	$C_{10}H_8{}^+$	15	55	Mn^+	23
121	$CpMnH^+$	19	47	MeS^+	11
120	$CpMn^+$	19	39	$C_3H_3{}^+$	18
112	$CpSMe^+$	100			

The complex, $CpMn(CO)_2(SMe)_2$, would probably have a great tendency to dimerize owing to the availability of the lone pairs on the sulphur atoms. One such process would be that leading to $[CpMn(CO)(SMe)_2]_2$ with the elimination of two CO molecules, i.e. similar to the dimerization of $CpFe(CO)_2SMe$[62]. Thus, it is possible that either the green or the purple species could be $[CpMn(CO)(SMe)_2]_2$. The mass spectrum of the reaction mixture does exhibit two small peaks (rel. abund. 0.2) at m/e 344 and 288 which could well be fragment ions of $[CpMn(CO)(SMe)_2]_2^+$ *viz.*, $(CpMnCO)_2(SMe)H^+$ and $(CpMn)_2(SMe)H^+$, respectively.

B. PROPERTIES OF CpMn(CO)$_2$CS AND ITS DERIVATIVES

1. Stability of Thiocarbonyls

The discovery of the first transition metal thiocarbonyls prompted Richards[67] 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. Thus, this is a similar situation to 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 -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 little affected 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 (*vide supra*, IIE.) and so presumably should be more strongly bound to a transition metal than is CO.

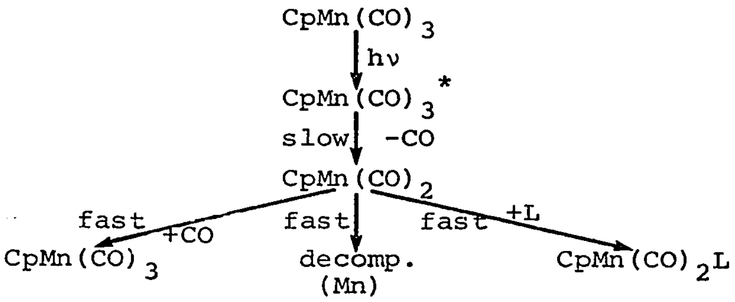
In the next sections of this part of the thesis the results of an investigation of some of the properties of $CpMn(CO)_2CS$ and its derivatives will be discussed in relation to their "stability" relative to that of their carbonyl analogues. It was hoped that these results would provide some evidence for or against the validity of Richards' conclusion in the case of π-cyclopentadienylmanganese thiocarbonyl complexes.

2. Chemical Studies

In order to facilitate a comparison of the chemistry of $CpMn(CO)_2CS$ with that of its tricarbonyl analogue, $CpMn(CO)_3$, a brief review of the CO substitution reactions of the latter will be given initially.

a. Carbonyl Substiution Reactions of $CpMn(CO)_3$

Usually, $CpMn(CO)_3$, is inert to CO substitution except under the influence of intense uv irradiation. A large number of derivatives of the type, $CpMn(CO)_2L$, have been prepared in this way[68]. The photochemical reaction is believed to proceed by an S_N1 dissociative mechanism:[69]



Absorption of a light quantum by the $CpMn(CO)_3$ molecule in solution affords a short-lived excited species, $CpMn(CO)_3^*$. De-excitation of this molecule takes place by the slow expulsion of a CO group and the formation of a reactive 16-electron intermediate to which L adds rapidly. The recombination and decomposition processes can be minimized by appropriate experimental conditions *viz.*, high concentration of L and removal of the evolved CO.

Photochemical replacement of a second CO group to give monocarbonyls, $CpMn(CO)L_2$, has been achieved only with certain strong σ-donors[68]. Irradiation of the tricarbonyl in the presence of bidentate ligands, L-L can afford either monocarbonyls, CpMn(CO)(L-L), or bridged species, $[CpMn(CO)_2](L\text{-}L)$, depending on the nature of the ligands and/or the experimental conditions[68]. The last remaining CO group is remarkably inert towards replacement. Even the photochemical reactions of $CpMn(CO)_3$ with linear L-L-L-L or branched $L\text{+}(L)_3$ tetratertiary phosphines afford the bidentate derivatives, CpMn(CO)L-L-L-L and $CpMn(CO)L\text{+}(L)_3$, respectively[70]. In fact, the only example in which all three CO groups have been replaced is the mixed-sandwich complex, $CpMn(\pi\text{-}C_6H_6)$, which is obtained in 2% yield by uv irradiation of a benzene solution of the tricarbonyl complex[69].

b. Reactions of $CpMn(CO)_2CS$

The thiocarbonyl complex, $CpMn(CO)_2CS$, also appears to be relatively inert towards carbonyl, and for that matter thiocarbonyl, thermal replacement. For instance, when an *n*-hexane solution of $CpMn(CO)_2CS$ is maintained under a $C^{18}O$ atmosphere for about a week at 40°, there are no apparent changes in the i.r. spectrum. Similarly, no reaction occurs when the thiocarbonyl complex is refluxed for 48 hours in *n*-hexane solution by itself or in the presence of excess *cis*-cyclooctene.

Owing to the relative thermal stability of $CpMn(CO)_2CS$, its reactions with C_8H_{14}, $P(OMe)_3$, PPh_3, and THF were investigated under photochemical conditions.

The isolation of substitution products in any significant yield appears to be more difficult experimentally for $CpMn(CO)_2CS$ than for $CpMn(CO)_3$. Much more extensive decomposition occurs even in the presence of a large excess of ligand. Thus, whereas fairly concentrated solutions of $CpMn(CO)_3$ can be used for the large scale preparation of CO-substituted derivatives, it is essential to work with only dilute solutions of $CpMn(CO)_2CS$ in order to minimize the extent of decomposition. Even then, a quantitative amount of a substitution product could be obtained only with *cis*-cyclooctene.

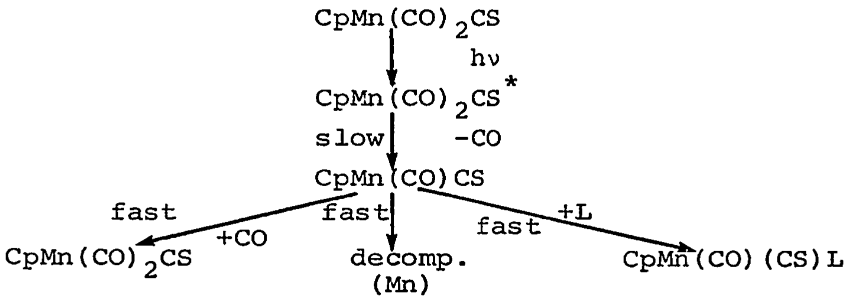
After uv irradiation, an *n*-hexane solution of $CpMn(CO)_2CS$ and excess C_8H_{14} exhibits a single new i.r. absorption in the CO stretching region at 1958 cm^{-1}. The reaction proceeds with extensive decomposition and the air-sensitive complex, CpMn(CO)(CS)(C_8H_{14}) [ν(CO) 1951; ν(CS) 1242 cm^{-1} in CS_2 solution], is obtained as an impure oil. This oil can be used as CpMn(CO)(CS)(C_8H_{14}) for most practical purposes. Further purification results in additional decomposition and a reasonably analytically pure solid sample of the olefin complex is obtained in only *ca.* 5% yield.

Extensive decomposition occurs in the photochemical reactions of CpMn$(CO)_2$CS with PPh_3 and P$(OMe)_3$ in *n*-hexane solution and no products could be isolated. However, i.r. spectra recorded in the 2000 cm^{-1} region during the reactions show that as the CO stretching absorptions of CpMn$(CO)_2$CS decrease new CO absorptions initially appear. In the case of the reaction with PPh_3, the two new bands at 1939 and 1929 cm^{-1} can be assigned to the thiocarbonyl complex, CpMn(CO)(CS)PPh_3; while for the P$(OMe)_3$ reaction, a new peak at 1943 cm^{-1} characterizes the phosphite derivative, CpMn(CO)(CS)P$(OMe)_3$ (*vide infra*, p. 85).

A better synthetic route to the monosubstituted derivatives, CpMn$(CO)_2$L (L = tertiary phosphine, olefin, amine), is the uv irradiation of CpMn$(CO)_3$ in THF solution to produce CpMn$(CO)_2$(THF) from which the coordinated THF ligand is readily displaced by L at room temperature to give the required CpMn$(CO)_2$L product[69,71]. Attempts in the present study to extend this method to the synthesis of thiocarbonyl-containing derivatives were unsuccessful and resulted only in decomposition. However, a new i.r. absorption at 1916 cm^{-1} is initially present in the CO stretching region of a THF solution of $CpMn(CO)_2CS$ during the uv irradiation. The CS stretching region is obscured by solvent absorption, but it appears likely that the 1916 cm^{-1} absorption is due to the thiocarbonyl complex, CpMn(CO)(CS)(THF).

In all four of the reactions above there is no evidence for the formation of $CpMn(CO)_2L$. This suggests that under the photochemical conditions employed one of the CO groups in $CpMn(CO)_2CS$ is replaced preferentially to the CS group. This is clearly the case in the photochemical reaction of $CpMn(CO)_2CS$ with $C^{18}O$ (*vide infra*, p. 158).

The most likely mechanism for the reactions of $CpMn(CO)_2CS$ with monodentate ligands, L, is shown below [*cf.* $CpMn(CO)_3$]. Initially, there is an S_N1 dissociative



step to form the highly reactive 16-electron intermediate, CpMn(CO)CS. This can then react with L or undergo decomposition.

The fact that the majority of the CpMn(CO)(CS)L complexes could not be isolated suggests that they are probably unstable under the photochemical conditions employed.

The thiocarbonyl complex, $CpMn(CO)_2CS$, does not react thermally with $NaNO_2$ and HCl as does $CpMn(CO)_3$ and so efforts to obtain a "spectroscopist's dream", $[CpMn(CO)(CS)(NO)]^+$, the thiocarbonyl analogue of $[CpMn(CO)_2(NO)]^+$[72], failed. A possible explanation for this is that CS requires a larger share of the electrons available for backbonding than does CO. The resultant lowering of the electron density on the manganese atom would thus destabilize a cationic state with respect to a neutral one.

c. Reactions of $CpMn(CO)(CS)(C_8H_{14})$

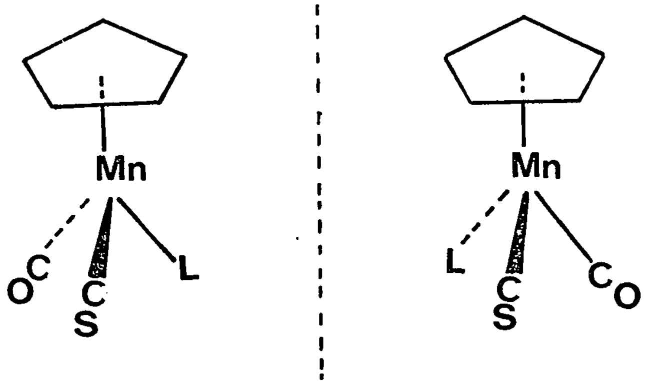
Owing to low yield obtained in the synthesis of $CpMn(CO)(CS)(C_8H_{14})$, only its reactions with PPh_3, $P(OMe)_3$, diphos, and CS_2 were investigated.

i. Reactions of $CpMn(CO)(CS)(C_8H_{14})$ with PPh_3 and $P(OMe)_3$

The synthetic aspect of the olefin replacement reactions of $CpMn(CO)_2$(olefin) investigated kinetically by Angelici and Loewen (*vide supra*, p. 60) can be extended to the synthesis of thiocarbonyl derivatives from $CpMn(CO)(CS)(C_8H_{14})$.

Reaction of crude CpMn(CO)(CS)(C_8H_{14}) [from the photochemical reaction of $CpMn(CO)_2CS$ with C_8H_{14}] with PPh_3 in *n*-hexane solution affords the air-stable complex, $CpMn(CO)(CS)PPh_3$.* Similarly, with $P(OMe)_3$ the phosphite derivative, $CpMn(CO)(CS)P(OMe)_3$, is formed.

The thiocarbonyl complexes, CpMn(CO)(CS)L [L = C_8H_{14}, PPh_3, $P(OMe)_3$], are the first examples of a π-cyclopentadienylmanganese moiety with three different two-electron ligands attached to the central manganese atom. Since these complexes presumably have pseudo-tetrahedral structures, enantiomeric pairs are expected:



Two similar enantiomers of the optically active nitrosyl cation, $[CpMn(CO)(NO)PPh_3]^+$, have been prepared recently by acid hydrolysis of the separated diastereomers of $CpMn(NO)(PPh_3)[C(O)OC_{10}H_{19}]$ ($OC_{10}H_{19}$ = *l*-mentholate)[73]. Therefore, it is feasible that it

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[*] The kinetics and mechanism of this reaction are discussed in Section B4, p. 116 of this chapter.

might be possible to resolve the two enantiomers of CpMn(CO)(CS)L when L is an optically active ligand, e.g. P(Me)(Ph)(Bu^t)[74].

ii. Reaction of CpMn(CO)(CS)(C_8H_{14}) with diphos

Angelici and Loewen[50] investigated the thermal replacement of olefins in $CpMn(CO)_2$(olefin) only with monodentate ligands. However, as expected, similar reactions can also be carried out with bidentate ligands. For instance, $CpMn(CO)_2(C_8H_{14})$ reacts with diphos in *n*-hexane solution to give the known bridged complex, $[CpMn(CO)_2]_2$(diphos). Even in the presence of excess diphos, there is no evidence for the formation of the chelated complex, CpMn(CO)(diphos). However, when a similar reaction is carried out for crude CpMn(CO)(CS)(C_8H_{14}), both the bridged complex, $[CpMn(CO)(CS)]_2$(diphos), and the chelated complex, CpMn(CS)(diphos), are readily produced. This illustrates the dramatic effect that changing a CO group to a CS one has on the reactivity of the resulting *cis*-cyclooctene complex. The formation of CpMn(CS)(diphos) is remarkable in view of the fact that thermal replacement of a CO group in $CpMn(CO)_3$ or in one of its derivatives is extremely unusual. One of the few examples of this type of reaction is the thermal (250°) synthesis of $CpMn(CO)_2PPh_3$[75].

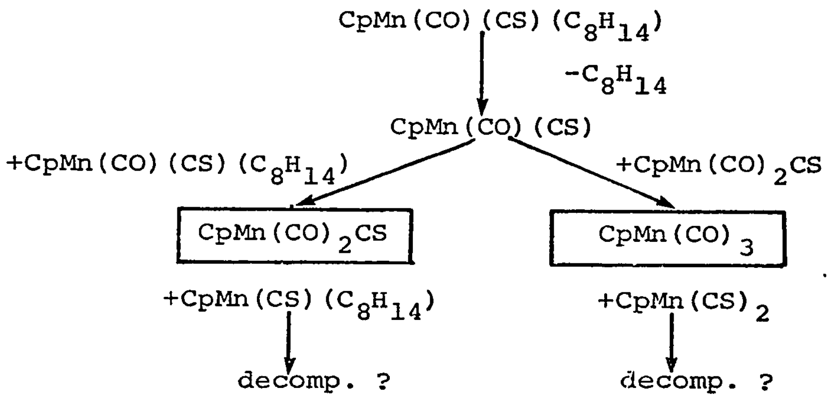
The facile thermal replacement of the CO group in CpMn(CO)(CS)(C_8H_{14}) by diphos may be interpreted in terms of the better π-acceptor ability of CS compared to that of CO.

Such a situation would result in a weakening of the Mn-CO bond in the thiocarbonyl complex compared to those in $CpMn(CO)_2(C_8H_{14})$, as is observed. However, CpMn(CS)(diphos) certainly must also be stabilized by the "chelate effect"[76] of diphos.

The proposed structures for the diphos complexes are shown in Fig. 11. It should be noted that the binuclear complex $[CpMn(CO)(CS)]_2$(diphos) contains two assymetric centres and so three isomers are expected for it.

iii. Thermal Decomposition of $CpMn(CO)(CS)(C_8H_{14})$

It was mentioned earlier (*vide supra*, p. 67) that $CpMn(CO)_2(C_8H_{14})$ decomposes thermally in methylcyclohexane solution to form $CpMn(CO)_3$ and a brown precipitate. The analogous thermal decomposition reaction of $CpMn(CO)(CS)(C_8H_{14})$ is more complex - $CpMn(CO)_2CS$, $CpMn(CO)_3$, and a brown precipitate being formed (Fig. 12). The thermal decomposition reactions possibly involves steps such as those shown below:[77,78]



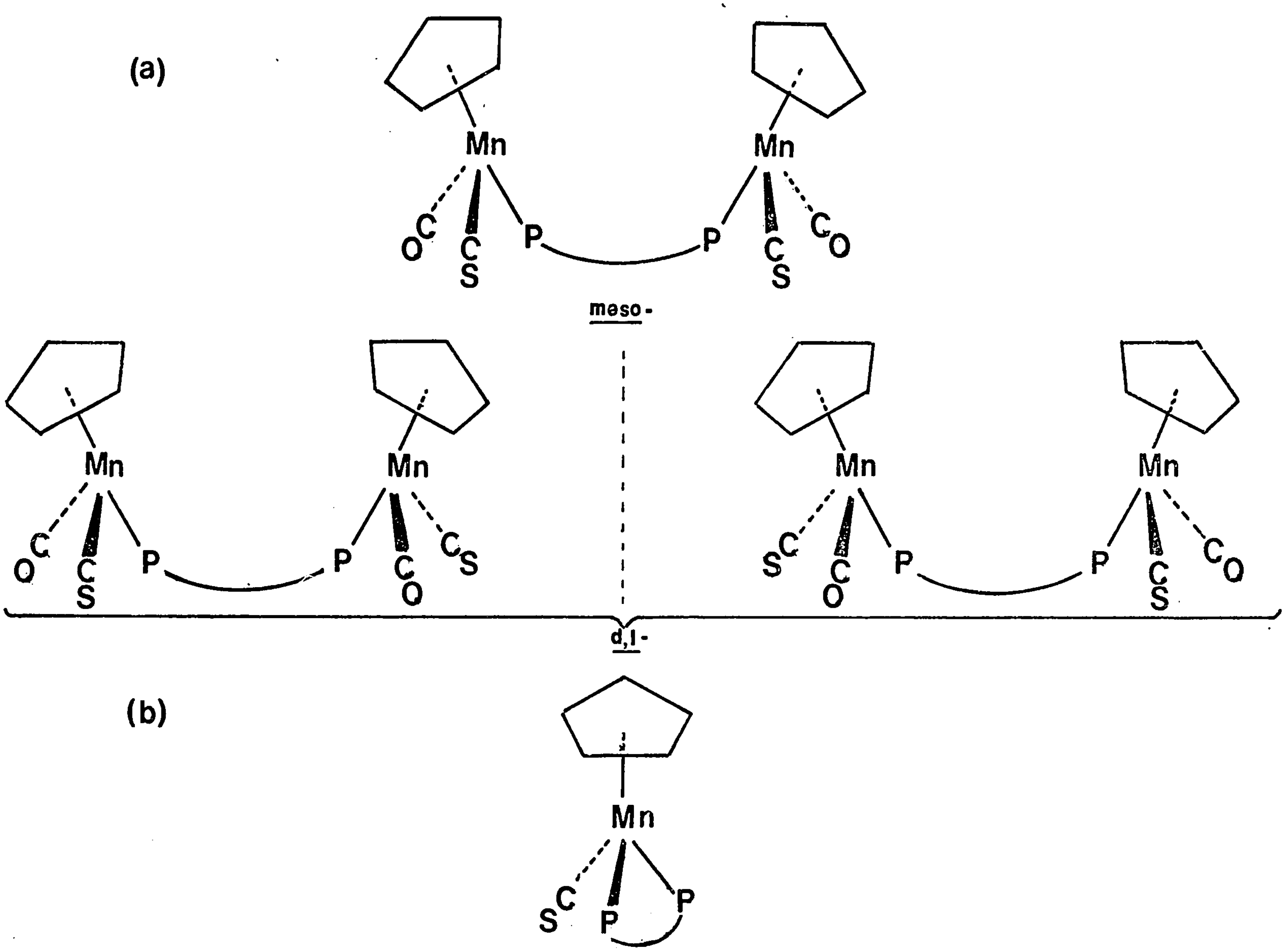


Fig.11. Proposed structures for the diphos complexes; (a) $[CpMn(CO)(CS)]_2(diphos)$, (b) CpMn(CS)(diphos). The Ph and CH_2 groups have been omitted for the sake of clarity.

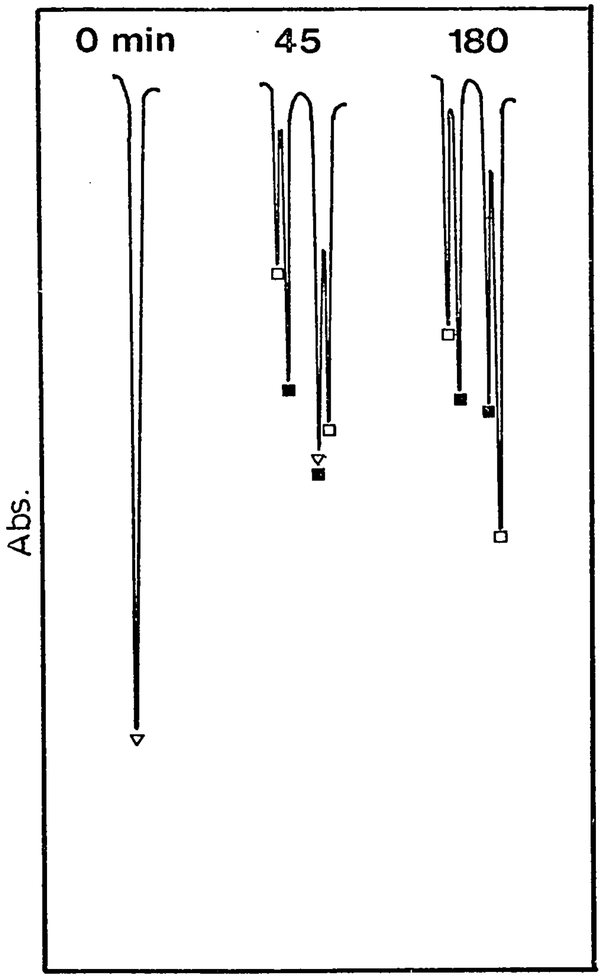
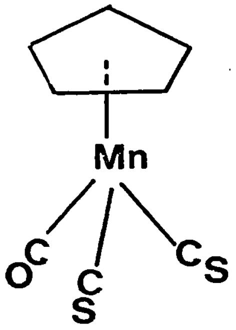


Fig. 12. Infrared spectral changes occurring in the CO stretching region during the thermal decomposition of $CpMn(CO)(CS)(C_8H_{14})$ in methylcyclohexane solution at 70°. The bands marked, ▽ □, and ■ , refer to the complexes $CpMn(CO)(CS)(C_8H_{14})$, $CpMn(CO)_3$, $CpMn(CO)_2CS$, respectively.

iv. Reaction of $CpMn(CO)(CS)(C_8H_{14})$ with CS_2

To date, only thiocarbonyl complexes containing a single CS group attached to a transition metal have been synthesized. The quantitative synthesis of $CpMn(CO)_2CS$ from the thermal reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the presence of PPh_3 suggests that $CpMn(CO)(CS)(C_8H_{14})$ should be an appropriate starting material for the synthesis of $CpMn(CO)(CS)_2$. This indeed proves to be true. The thermal reaction of $CpMn(CO)(CS)(C_8H_{14})$ with CS_2 in the presence of PPh_3 affords the expected dithiocarbonyl complex, $CpMn(CO)(CS)_2$:



The reaction proceeds without apparent decomposition and, as in the synthesis of $CpMn(CO)_2CS$, the only side-products present in the reaction mixture are PPh_3S and C_8H_{14}.

The mechanism proposed below for the reaction is similar to that discussed for the synthesis of $CpMn(CO)_2CS$.

$$\begin{tikzcd}
CpMn(CO)(CS)(C_8H_{14}) \arrow[r, "slow", "-C_8H_{14}"'] & CpMn(CO)CS \arrow[r, "fast", "+CS_2"'] & CpMn(CO)(CS)(\pi\text{-}CS_2) \arrow[d, "fast"', "+PPh_3"] \\
 & & CpMn(CO)(CS)_2 + PPh_3S
\end{tikzcd}$$

That the first step in the reaction is the slow dissociation of the olefin to give the reactive 16-electron intermediate, CpMn(CO)CS, is supported by the kinetic data obtained for the reaction of CpMn(CO)(CS)(C_8H_{14}) with PPh_3 to be discussed later (p. 116). In contrast to the reactions leading to CpMn$(CO)_2$CS [and π-MeC_5H_4Mn$(CO)_2$CS], there is no i.r. evidence for the formation of a π-CS_2 species. The reaction of CpMn(CO)(CS)(C_8H_{14}) with CS_2 in the absence of PPh_3 results in extensive decomposition, even for dilute concentrations, suggesting that the thiocarbonyl π-CS_2 complex, CpMn(CO)(CS)(π-CS_2), is appreciably more unstable thermally than its dicarbonyl analogue. However, i.r. data indicate that a little CpMn(CO)$(CS)_2$ is also formed in this reaction.

d. Reaction of CpMn(CO)$(CS)_2$ with *cis*-Cyclooctene; Synthesis of CpMn$(CS)_3$

Because of the experimental difficulties in preparing CpMn(CO)(CS)(C_8H_{14}), the thiocarbonyl complex, CpMn(CO)$(CS)_2$, could be obtained only in small quantities. Therefore, the investigation of its chemical properties was restricted to its potential as a precursor for the synthesis of the trithiocarbonyl complex, CpMn$(CS)_3$.

The thermal replacement of CO and C_8H_{14} in CpMn(CO)(CS)(C_8H_{14}) by diphos to give CpMn(CS)(diphos) appears to indicate that substitution of CO by CS in metal carbonyls results in a weakening of the remaining metal-CO bonds. Thus, it was thought that CpMn(CO)$(CS)_2$ would readily lose its lone CO group on reaction with *cis*-cyclooctene in refluxing *n*-hexane solution. However, an i.r. spectrum of the reaction mixture (after *ca*.12 hr) shows that the thiocarbonyl complex does not react under these conditions.

The experimental difficulties encountered already during the photochemical preparation of derivatives of CpMn$(CO)_2$CS appear to be even more acute for the reaction of CpMn(CO)$(CS)_2$ with C_8H_{14}. In order to achieve the replacement of the CO group without complete decomposition, the reaction has to be carried out for an even lower concentration of the thiocarbonyl complex and in the presence of a larger excess of the olefin. When eventually prepared, CpMn$(CS)_2(C_8H_{14})$ is only obtained in minute quantities and appears to be significantly more "unstable" than its monocarbonyl analogue, CpMn(CO)(CS)(C_8H_{14}). All attempts to isolate CpMn$(CS)_2(C_8H_{14})$ from the reaction mixture, which also contains unreacted CpMn(CO)$(CS)_2$ and C_8H_{14}, result in complete decomposition. Thus, CpMn$(CS)_2(C_8H_{14})$ can be identified only by its i.r. spectrum [ν(CS) 1289s, 1217vs cm^{-1} in CS_2 solution] and its subsequent reaction with CS_2.

When a CS_2 solution of the crude CpMn$(CS)_2(C_8H_{14})$ and PPh_3 is refluxed for 5 hr, the i.r. spectra of the reaction mixture exhibit changes in the CS stretching region consistent with the formation of the trithiocarbonyl complex, CpMn$(CS)_3$ (Fig. 13). The decrease in intensity of the two

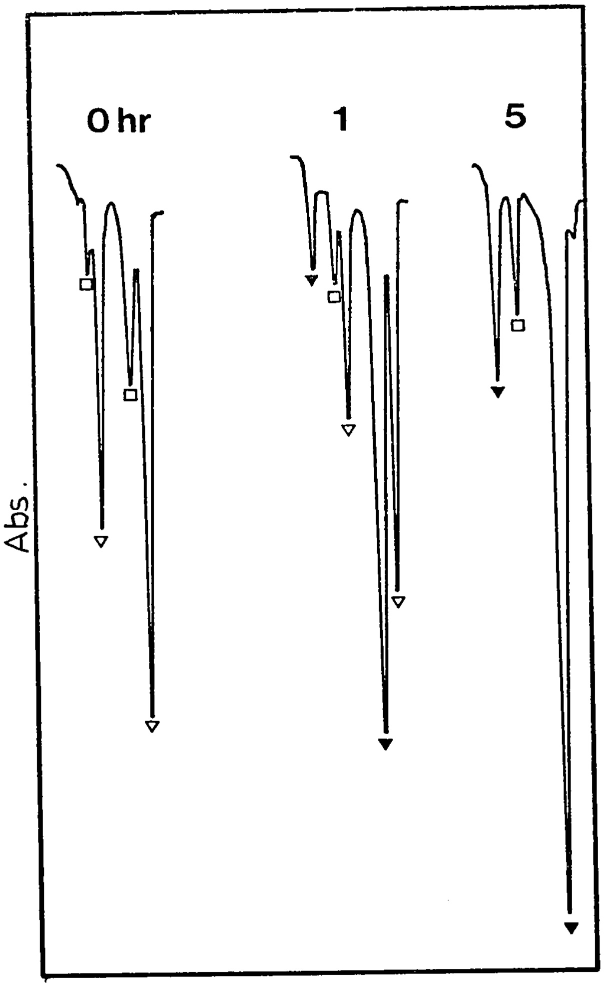
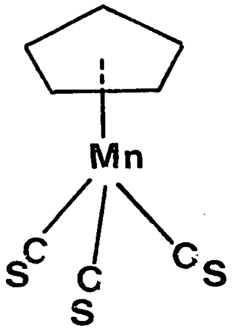


Fig. 13. Spectral changes occurring in the CS stretching region during the reaction of $CpMn(CS)_2(C_8H_{14})$ with CS_2 and PPh_3. The bands marked, ▽ and ▼ , refer to the complexes $CpMn(CS)_2(C_8H_{14})$ and $CpMn(CS)_3$, respectively. The bands associated with $CpMn(CO)(CS)_2$, present as an impurity, are marked □ . The actual frequencies are given in Table VIII.

strong CS absorptions of $CpMn(CS)_2(C_8H_{14})$ at 1289 and 1217 cm^{-1} is accompanied by the concomitant appearance of two new CS absorptions at 1338m and 1240vs cm^{-1}. As is the case for the syntheses of $CpMn(CO)_2CS$ and $CpMn(CO)(CS)_2$, the reaction also involves the formation of PPh_3S and presumably proceeds *via* the π-CS_2 intermediate, $CpMn(CS)_2(\pi\text{-}CS_2)$.

Owing to the low yield syntheses of its precursors, $CpMn(CS)_3$ is obtained only in minute quantities so that it can be identified only by its i.r. spectrum. In addition to the two bands expected in the CS stretching region, there is also an out-of-plane C-H deformation mode at *ca.* 825 cm^{-1} characteristic of the Cp moiety. Finally, it should also be mentioned that the trithiocarbonyl sublimes readily under high vacuum at room temperature. This is also true for $CpMn(CO)_3$, $CpMn(CO)_2CS$, and $CpMn(CO)(CS)_2$.

The trithiocarbonyl complex, $CpMn(CS)_3$, is presumably isostructural with $CpMn(CO)_3$:



Its synthesis completes the series of complexes, $CpMn(CO)_{3-x}(CS)_x$ (x = 1, 2, 3) sought in this work. The trithiocarbonyl and $CpMn(CS)_2(C_8H_{14})$ are unique in that they are the first examples of derivatives of $CpMn(CO)_3$ containing three non-carbonyl two-electron ligands.

3. Spectroscopic Studies

a. Infrared Spectra

The i.r. spectra of all the complexes identified in this work exhibit the anticipated number of CO and CS stretching absorptions in CS_2 solution (Table VIII) *viz.*, di-CO (or CS) complexes, two CO (or CS) stretching absorptions; mono-CO (or CS) complexes, one CO (or CS) stretching absorption; $CpMn(CS)_3$, two CS stretching absorptions. Typical spectra are shown in Figs. 14-18.

The 1235 cm^{-1} absorption associated with the out-of-ring C=S group in $CpMn(CO)_2(\pi\text{-}CS_2)$ (Fig. 15) occurs in the same region as the 1266 cm^{-1} terminal CS stretching frequency of $CpMn(CO)_2CS$ (Fig. 14b). However, when compared to the respective CO absorptions of the complexes, the π-CS_2 absorption is broader and significantly weaker than the terminal CS absorption.

The i.r. spectrum of the triphenylphosphine derivative, $CpMn(CO)(CS)PPh_3$, in CS_2 solution exhibits

TABLE VIII. CHARACTERISTIC INFRARED ABSORPTIONS (cm^{-1}) OF THE MANGANESE π-CS_2 AND THIOCARBONYL COMPLEXES IDENTIFIED IN THIS WORK

Complex	ν(CO)		ν(CS)		Medium
$CpMn(CO)_2(\pi\text{-}CS_2)$	2012s	1962s	1235s[a]	∿640m[b]	CS_2
$\pi\text{-}MeC_5H_4Mn(CO)_2(\pi\text{-}CS_2)$	2009s	1959s	1229s[a]		CS_2
$CpMn(CO)_2CS$[c]	2006s	1954s	1266s		CS_2
	2010s	1959s	1271s		Nujol
$\pi\text{-}MeC_5H_4Mn(CO)_2CS$	2004s	1952s	1262s		CS_2
$CpMn(CO)(CS)(C_8H_{14})$	1951s		1242s		CS_2
$CpMn(CO)(CS)PPh_3$	1925s		1231s		CS_2
	1939s	1929s	1236s		*n*-hexane
	1913s		1217s		Nujol
$CpMn(CO)(CS)P(OMe)_3$	1934s		1238s		CS_2
$[CpMn(CO)(CS)]_2(diphos)$	1920s		1226s		CS_2
	1922s	1903sh	1230s		Nujol
$CpMn(CS)(diphos)$			1208s		CS_2
			1211s		Nujol
$CpMn(CO)(CS)_2$	1991s		1305s	1235vs	CS_2
	1996s		1308s	1240s	Nujol
$CpMn(CS)_2(C_8H_{14})$			1289s	1217vs	CS_2
$CpMn(CS)_3$			1338m	1240vs	CS_2

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[a] Out-of-ring ν(C=S) mode.

[b] In-ring ν(C-S) mode.

[c] The frequencies observed for the isoelectronic and presumably isostructural cationic species, $[CpFe(CO)_2CS]^+$, are: 2093s, 2064s, and 1348s cm^{-1} in Nujol mull[41].

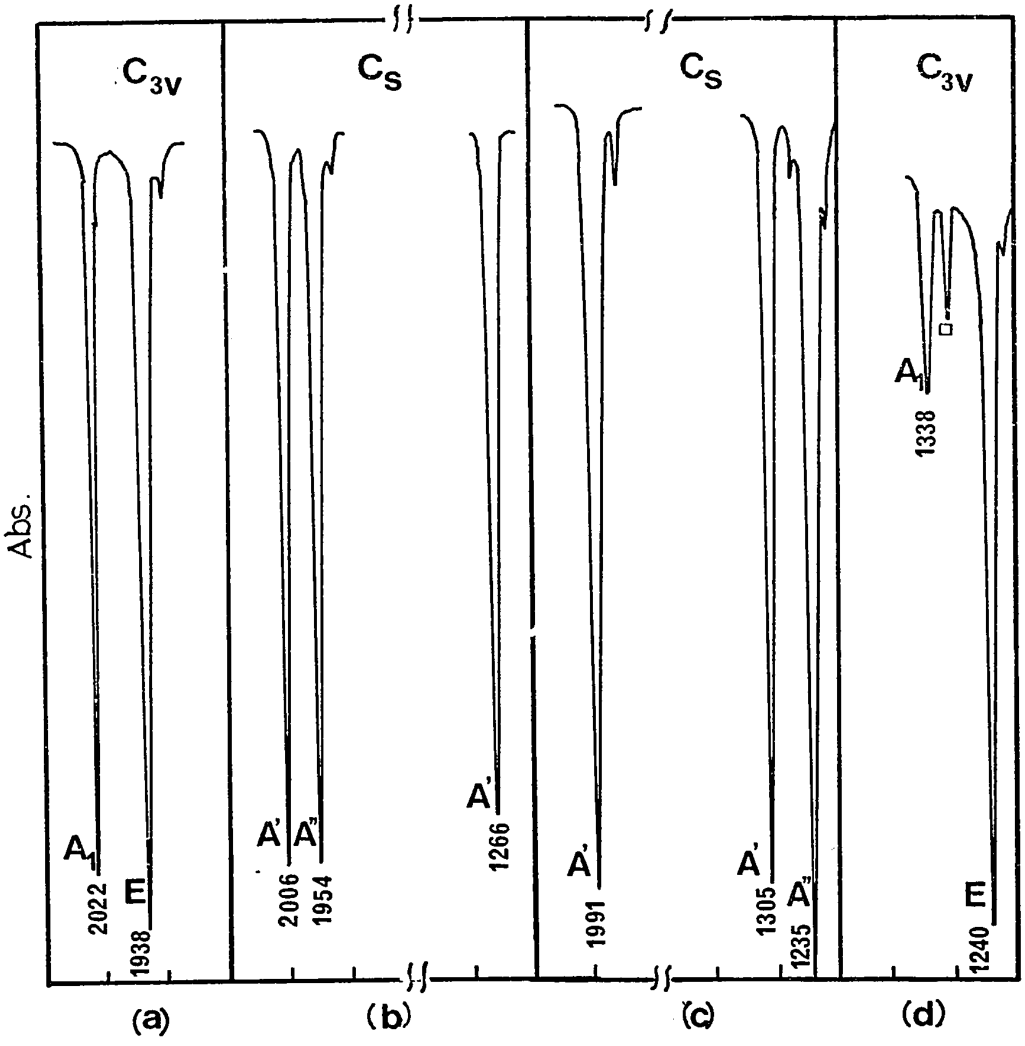


Fig. 14. Infrared spectra (cm^{-1}) in the CO and/or CS stretching regions (in CS_2) of the complexes $CpMn(CO)_3$ and $CpMn(CO)_{3-x}(CS)_x$ (x = 1-3). (a) $CpMn(CO)_3$, (b) $CpMn(CO)_2CS$, (c) $CpMn(CO)(CS)_2$, (d) $CpMn(CS)_3$. The band assignments shown are based on the local symmetry indicated at the top of each spectrum of the appropriate manganese carbonyl-thiocarbonyl moiety. The band marked □ in spectrum (d) is due to a small amount of $CpMn(CO)(CS)_2$ present as an impurity.

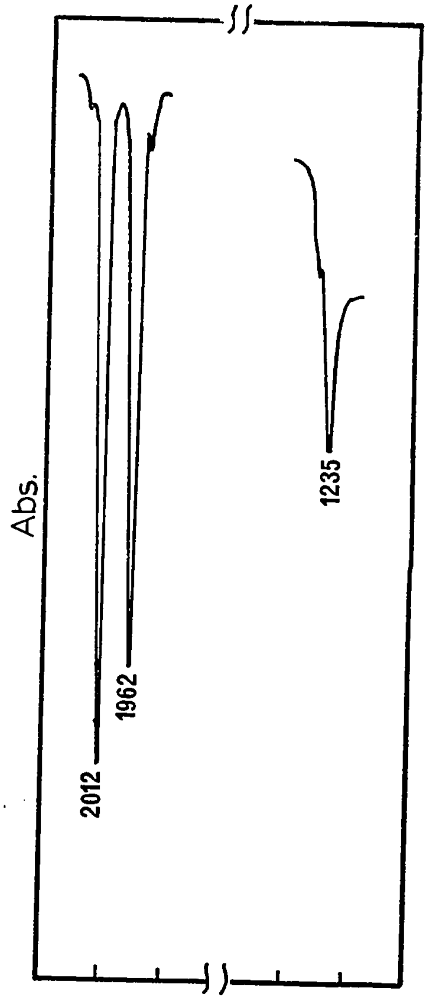


Fig. 15. Infrared spectrum (cm^{-1}) in the CO and CS stretching regions (in CS_2) of the complex $CpMn(CO)_2(\pi\text{-}CS_2)$.

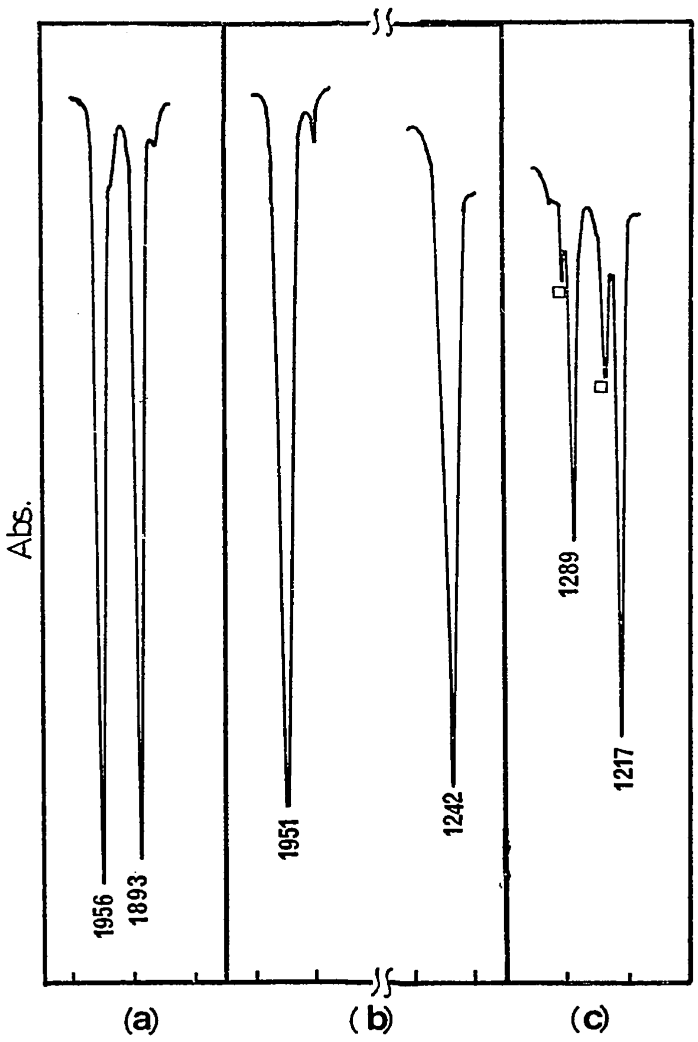


Fig. 16. Infrared spectra (cm^{-1}) in the CO and/or CS stretching regions (in CS_2) of the complexes $CpMn(CO)_{3-x}(CS)_{x-1}(C_8H_{14})$ (x = 1-3). (a) $CpMn(CO)_2(C_8H_{14})$, (b) $CpMn(CO)(CS)(C_8H_{14})$, (c) $CpMn(CS)_2(C_8H_{14})$. The bands marked □ in the spectrum of $CpMn(CS)_2(C_8H_{14})$ are due to a small amount of $CpMn(CO)(CS)_2$ present as an impurity.

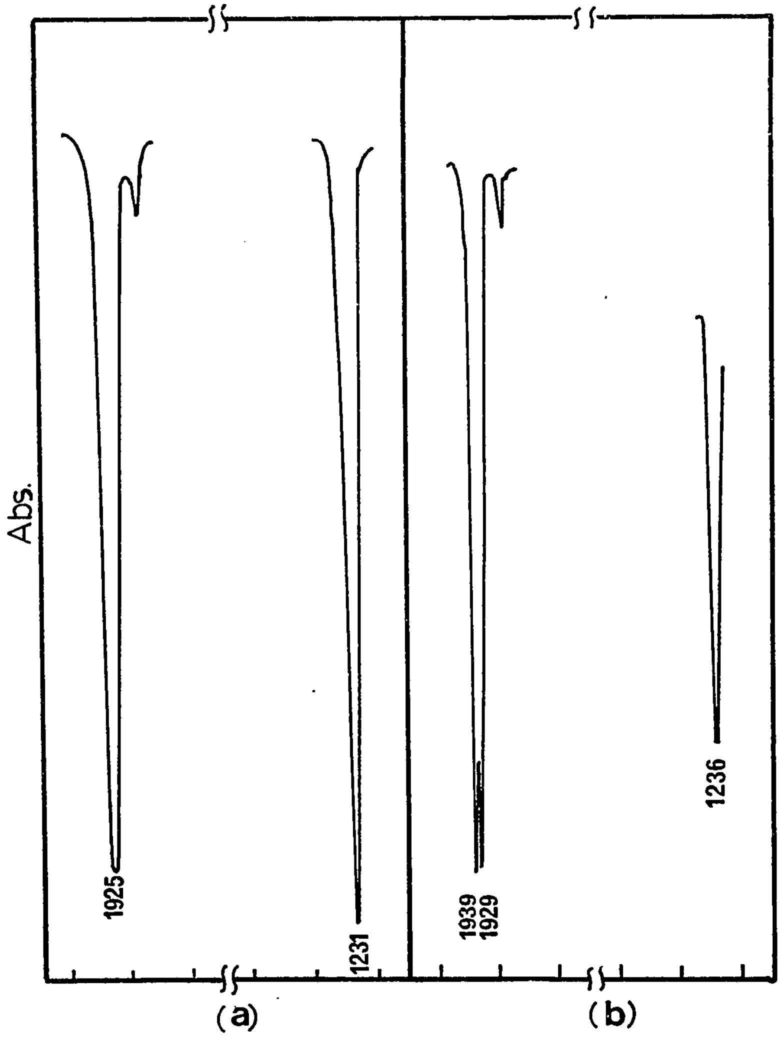


Fig. 17. Infrared spectra (cm^{-1}) in the CO and CS stretching regions of the complex CpMn(CO)(CS)PPh$_3$, (a) in CS$_2$, (b) in *n*-hexane.

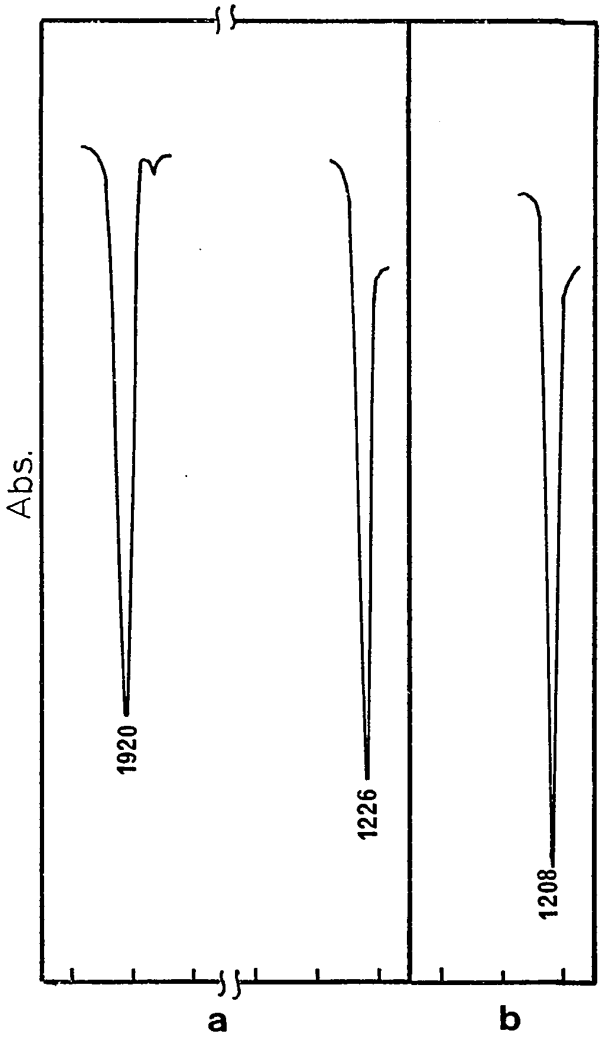


Fig. 18. Infrared spectra (cm^{-1}) in the CO and/or CS stretching regions (in CS_2) of the diphos-thiocarbonyl carbonyl complexes, (a) [CpMn(CO)(CS)]$_2$(diphos), (b) CpMn(CS)(diphos).

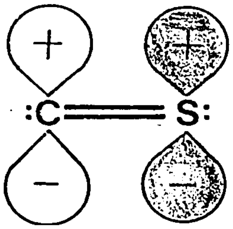
one CO and one CS absorption, as expected. However, in *n*-hexane solution, the CO absorption is resolved into two components of approximately the same intensity; there is no splitting observed for the CS band (Fig. 17). Similar "CO frequency doubling" has been observed in the i.r. spectra of a number of π-cyclopentadienylmetal carbonyl complexes such as $CpFe(CO)_2SiCl_2Me$ and π-$MeC_5H_4Mn(CO)_2P(OMe)_3$ in hydrocarbon solvents[79,80]. The phenomenon has been attributed to conformational isomerism either about the metal-ligand bond (i.e. Fe-Si, Mn-P, etc.) or within the ligand itself. Although the appearance of two CO bands in the i.r. spectrum of $CpMn(CO)(CS)(PPh_3)$ could also be caused by conformational isomerism, it should be emphasized that no such splitting occurs in the i.r. spectra of $CpMn(CO)(CS)P(OMe)_3$ and $CpMn(CO)_2PPh_3$ in *n*-hexane solution. An alternative explanation of the splitting is that it arises because of Fermi resonance between the CO stretching fundamental at 1939 cm^{-1} with a combination band of the same symmetry at 1929 cm^{-1}. The combination band could be the summation of the CS stretching fundamental at 1236 cm^{-1} and the strong triphenylphosphine absorption at $\sim$690 cm^{-1}.

It is of interest to compare the CO and CS stretching frequencies of $CpMn(CO)_2CS$ with those given in footnote c, Table VIII for the isoelectronic and presumably isostructural iron complex, $[CpFe(CO)_2CS]^+$. The absence of positive charge on the manganese complex would be expected to result in an increase in the extent of backbonding between the metal and the CO and CS groups. Consequently, the CO and CS stretching frequencies of $CpMn(CO)_2CS$ would be expected to be lower than those of the iron complex, as is observed.

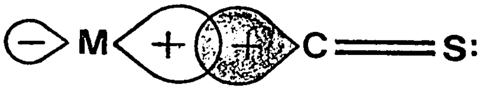
The CS stretching absorptions for the π-cyclopentadienylmanganese thiocarbonyls listed in Table VIII lie between 1338 and 1208 cm^{-1}, i.e. almost within the range observed previously for the known metal thiocarbonyl complexes *viz.*, 1350-1250 cm^{-1} (*vide supra*, p. 39). Thus, the new range for ν(CS) frequencies of thiocarbonyl complexes is 1350-1208 cm^{-1}. A comparison of this range with the CS stretching frequency [ν(CS) 1274 cm^{-1}] for the CS molecule trapped in a CS_2 matrix[81] indicates that, in sharp contrast to CO, the stretching frequency of CS is not always lowered upon coordination. A possible explanation for this dichotomy lies in the apparently large double-bond character of the CS bond in the uncoordinated ligand. On the basis of microwave data for the CS molecule, Mockler and Bird[51] proposed that structures (a) and (b) shown below contribute 60 and 40%, respectively to the total structure

(a) (b)

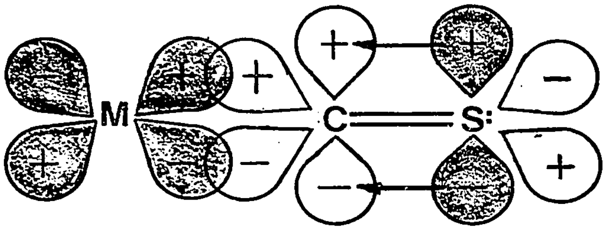
of the molecule. Mockler and Bird's results can be expressed in molecular orbital formulation chiefly in term of a largely filled p_π orbital on sulphur and a largely vacant p_π orbital of the same symmetry on the carbon:



The formation of a metal-carbon σ-bond* (shown below) results in a lowering of the electron density on the carbon atom and this can be expected to favour <u>two</u> different effects concurrently.



The first one is backbonding between a filled metal d_π orbital and an empty π^* antibonding orbital of CS; the second effect consists of electron transfer from the sulphur p_π orbital to the carbon p_π orbital:



A decrease in the CS bond order would result from electron transfer from the metal to the CS ligand whereas electron transfer within the ligand would have the opposite effect.

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*Although it has been shown only for *trans*-RhCl(CS)(PPh$_3$)$_2$ that CS bonds through the carbon atom[44], this is assumed to be the case in all thiocarbonyl complexes.

Thus, because of competition between these two effects, it is not unreasonable to find CS stretching absorptions for coordinated CS groups both above and below the CS stretching frequency for the free CS molecule..

The observed increase in the Cotton-Kraihanzel type[82] CO stretching force constant (k_{CO}) (Table IX) when the CO groups in $CpMn(CO)_3$ are replaced successively by CS can be taken as an indication of the better π-acceptor capacity of CS compared to CO.* It is questionable whether the small decrease observed in the CS stretching force constant (k_{CS}), when the CS groups in $CpMn(CS)_3$ are replaced successively by CO, is meaningful because the high frequency separation used for their calculation may not be applicable. A comparison between the values of the various interaction force constants (k'_{CO}, k'_{CS}) is pointless because they were calculated using a non-rigorous force field.

TABLE IX. CALCULATED COTTON-KRAIHANZEL CO AND/OR CS STRETCHING FORCE CONSTANTS (mdyn/Å) FOR THE COMPLEXES $CpMn(CO)_3$ AND $CpMn(CO)_{3-x}(CS)_x$ (x = 1-3)

Complex	k_{CO}	k'_{CO}	k_{CS}	k'_{CS}
$CpMn(CO)_3$	15.61	0.45		
$CpMn(CO)_2CS$	15.83	0.41	8.24	
$CpMn(CO)(CS)_2$	16.00		8.30	0.47
$CpMn(CS)_3$			8.33	0.43

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*Although in absolute terms the values of the primary force constants given are almost certainly not significant to the number of figures quoted, it is felt that nevertheless the trend is in the direction indicated.

b. Raman Spectra

To date, no Raman data for thiocarbonyl complexes have been reported in the literature. In the present work, partial laser Raman spectra were obtained for $CpMn(CO)_2CS$ (Fig. 19), $CpMn(CO)(CS)_2$ and $CpMn(CO)(CS)PPh_3$; the spectra of the last two compounds are of extremely poor quality and are not shown here. Nevertheless, all three spectra exhibit lines attributable to the CO stretching modes [$CpMn(CO)_2CS$, 1986(a'), 1953(a") cm^{-1}; $CpMn(CO)(CS)_2$, 1978(a') cm^{-1}; and $CpMn(CO)(CS)PPh_3$, 1913 cm^{-1}]. Surprisingly, no lines attributable to the CS stretching 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.

c. Mass Spectra

The mass spectra of transition metal carbonyls have been investigated extensively over the past few years[65]. The outstanding feature of the fragmentation patterns for these complexes is the stepwise loss of the CO groups. The successive

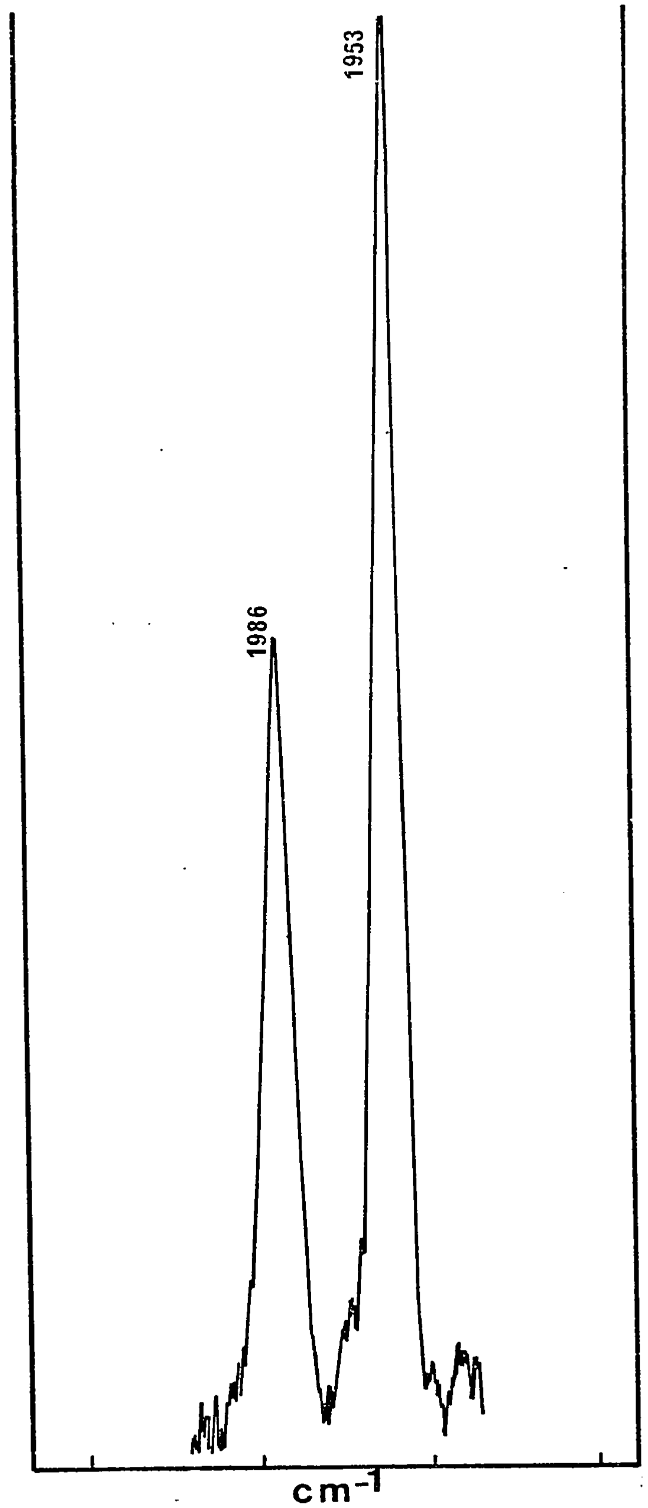

Fig. 19. Raman spectrum of $CpMn(CO)_2CS$ in the CO stretching region (slit width 5 cm^{-1}, laser power 45 mW).

cleavage of the metal-CO bonds has been attributed to a strengthening of the remaining metal-CO bonds because the electron density available on the metal for backbonding is being shared between fewer carbonyl groups. The simultaneous loss of two CO groups has been observed for complexes with particularly strong metal-CO bonds. In these cases, it has been suggested that as the metal-CO bonds become stronger, the difference in the amount of energy required to remove successive CO groups decreases[65].

Müller and Herberhold[64] have investigated the mass spectra of complexes of the types, $CpMn(CO)_2L$ (L = CO, cyclo-olefin, isonitrile, amine, tertiary phosphine, sulfoxide, maleic anhydride, etc.). Whereas the primary fragmentation of $CpMn(CO)_3^+$ is the stepwise loss of the three CO groups, the initial fragmentation step of $CpMn(CO)_2L^+$ is the simultaneous loss of both CO groups. When L is an olefin, $CpMn(CO)_2L^+$ may lose either the olefin or the two CO groups in the primary fragmentation process.

In contrast to the wealth of data available for transition metal carbonyls, there are as yet no data in the literature on the behaviour of transition metal thiocarbonyl complexes upon electron impact. Consequently, in order to determine whether or not thiocarbonyl complexes exhibit similar fragmentation patterns to their carbonyl analogues, the mass spectra of $CpMn(CO)_2CS$, $CpMn(CO)(CS)_2$, and

$CpMn(CO)(CS)(C_8H_{14})$ were recorded for comparison with those reported [64] for $CpMn(CO)_3$ and $CpMn(CO)_2(C_8H_{14})$.

The mass spectra of all three thiocarbonyl complexes exhibit peaks corresponding to their parent molecular ions as do the spectra of their carbonyl analogues (Tables X, XI). Moreover, Mn-CS bond cleavage is favoured over C-S bond cleavage and, as for CO, the fragmentation of CS from the manganese atom occurs in one step. All three complexes lose CO and CS in the first steps following ionization of the parent species.

The most probable fragmentation pathways to the bare metal ion, Mn^+, for $CpMn(CO)_2(CS)^+$, $CpMn(CO)(CS)_2^+$, and $CpMn(CO)(CS)(C_8H_{14})^+$ are shown in Figs. 20 and 21. Some of these proposed pathways are supported by the appearance of metastable ions in the spectra. In contrast to the $CpMn(CO)_2L$ derivatives investigated by Müller and Herberhold, where the two CO groups are lost simultaneously from the parent molecular ions, $CpMn(CO)_2CS$ exhibits stepwise loss of the CO groups in the mass spectrometer. Thus, if the suggestion[65] that the simultaneous loss of two CO groups indicates strong metal-CO bonds is valid, then the observed weakening of these bonds in the case of $CpMn(CO)_2CS$ may mean that CS is a better π-acceptor than any of the ligands, L, in the $CpMn(CO)_2L$ series mentioned above.

The degradation of the parent molecular ion, $CpMn(CO)(CS)(C_8H_{14})^+$, as for its dicarbonyl analogue, may follow two pathways. However, the CO and CS groups are lost successively in one of these.

TABLE X. MASS SPECTRA AND ASSIGNMENT OF FRAGMENT IONS FOR $CpMn(CO)_3$, $CpMn(CO)_2CS$ AND $CpMn(CO)(CS)_2$

$CpMn(CO)_3$			$CpMn(CO)_2CS$			$CpMn(CO)(CS)_2$		
m/e	Ion[a,b]	Rel. abund.	m/e	Ion[c]	Rel. abund.	m/e	Ion[d]	Rel. abund.
204	$CpMn(CO)_3^{+}$	33	220	$CpMn(CO)_2(CS)^{+}$	31	236	$CpMn(CO)(CS)_2^{+}$	58
176	$CpMn(CO)_2^{+}$	1.5	192	$CpMn(CO)(CS)^{+}$	1.4	208	$CpMn(CS)_2^{+}$	60
148	$CpMn(CO)^{+}$	31	164	$CpMn(CS)^{+}$	55	164	$CpMn(CS)^{+}$	91
120	$CpMn^{+}$	100	120	$CpMn^{+}$	100	120	$CpMn^{+}$	100
93	$MnC_3H_2^{+}$	4.4	99	$Mn(CS)^{+}$	6.5	99	$Mn(CS)^{+}$	14
80	MnC_2H^{+}	4.3	93	$MnC_3H_2^{+}$	4.5	93	$MnC_3H_2^{+}$	3.5
66	$C_5H_6^{+}$[e]	2.5	91	MnC_3^{+}	2.1	88	$MnSH^{+}$	1.7
65	Cp^{+}[e]	2.0	80	MnC_2H^{+}	6.2	87	MnS^{+}	1.7
56	MnH^{+}	2.0	66	$C_5H_6^{+}$	2.7	80	MnC_2H^{+}	5.4
55	Mn^{+}	60	65	Cp^{+}	2.4	66	$C_5H_6^{+}$	6.3
39	$C_3H_3^{+}$[e]	3.6	56	MnH^{+}	2.1	65	Cp^{+}	4.0
			55	Mn^{+}	65	56	MnH^{+}	2.0
			39	$C_3H_3^{+}$	6.5	55	Mn^{+}	77
						39	$C_3H_3^{+}$	5.4

[a] From ref. 64 unless otherwise specified. [b] $CpMn(CO)^{++}$, rel. abund. 3.6; $CpMn^{++}$, rel. abund. 2.5. [c] $CpMn(CS)^{++}$, rel. abund. 2.1. [d] $CpMn(CS)_2^{++}$, rel. abund. 1.8; $CpMn(CS)^{++}$, rel. abund. 6.1.

[e] Not reported in ref. 64.

TABLE XI. MASS SPECTRA AND ASSIGNMENT OF FRAGMENT IONS FOR $CpMn(CO)_2(C_8H_{14})$ AND $CpMn(CO)(CS)(C_8H_{14})$

$CpMn(CO)_2(C_8H_{14})$			$CpMn(CO)(CS)(C_8H_{14})$		
m/e	Ion[a,b]	Rel. abund.	m/e	Ion	Rel. abund.
286	$CpMn(CO)_2(C_8H_{14})$	8.4	302	$CpMn(CO)(CS)(C_8H_{14})^+$	16
230	$CpMn(C_8H_{14})^+$	42	274	$CpMn(CS)(C_8H_{14})^+$	1.1
176	$CpMn(CO)_2^+$	0.2	230	$CpMn(C_8H_{14})^+$	9.7
148	$CpMn(CO)^+$, $CpMnC_2H_4^+$	6.9	192	$CpMn(CO)(CS)^+$	1.3
120	$CpMn^+$	100	164	$CpMn(CS)^+$	137
110	$C_8H_{14}^+$	10	120	$CpMn^+$	100
95	$MnC_3H_4^+$	4.2	110	$C_8H_{14}^+$	5.4
82	$MnC_2H_3^+$	16	99	$Mn(CS)^+$	4.7
81	$MnC_2H_2^+$	11	82	$MnC_2H_3^+$	11
69	$C_5H_9^+$[c]	3.5	81	$MnC_2H_2^+$	8
68	$C_5H_8^+$[c]	8.8	69	$C_5H_9^+$	3.2
67	$C_5H_7^+$[c]	19	68	C_5H_8	5.9
66	$C_5H_6^+$[c]	18	67	$C_5H_7^+$	16
65	Cp^+[c]	7.3	66	$C_5H_6^+$	7.8
56	MnH^+	3.1	65	Cp^+	4.6
55	Mn^+	31	56	MnH^+	6.0
54	$C_4H_6^+$[c]	18	55	Mn^+	67
41	$C_3H_5^+$[c]	14	54	$C_4H_6^+$	12
40	$C_3H_4^+$[c]	5.3	41	$C_3H_5^+$	19
39	$C_3H_3^+$[c]	11	40	$C_3H_4^+$	4.0
			39	$C_3H_3^+$	16

[a] From ref. 64 unless otherwise specified.

[b] $CpMn(C_8H_{14})^{++}$, rel. abund. 2.6. [c] Not reported in ref. 64.

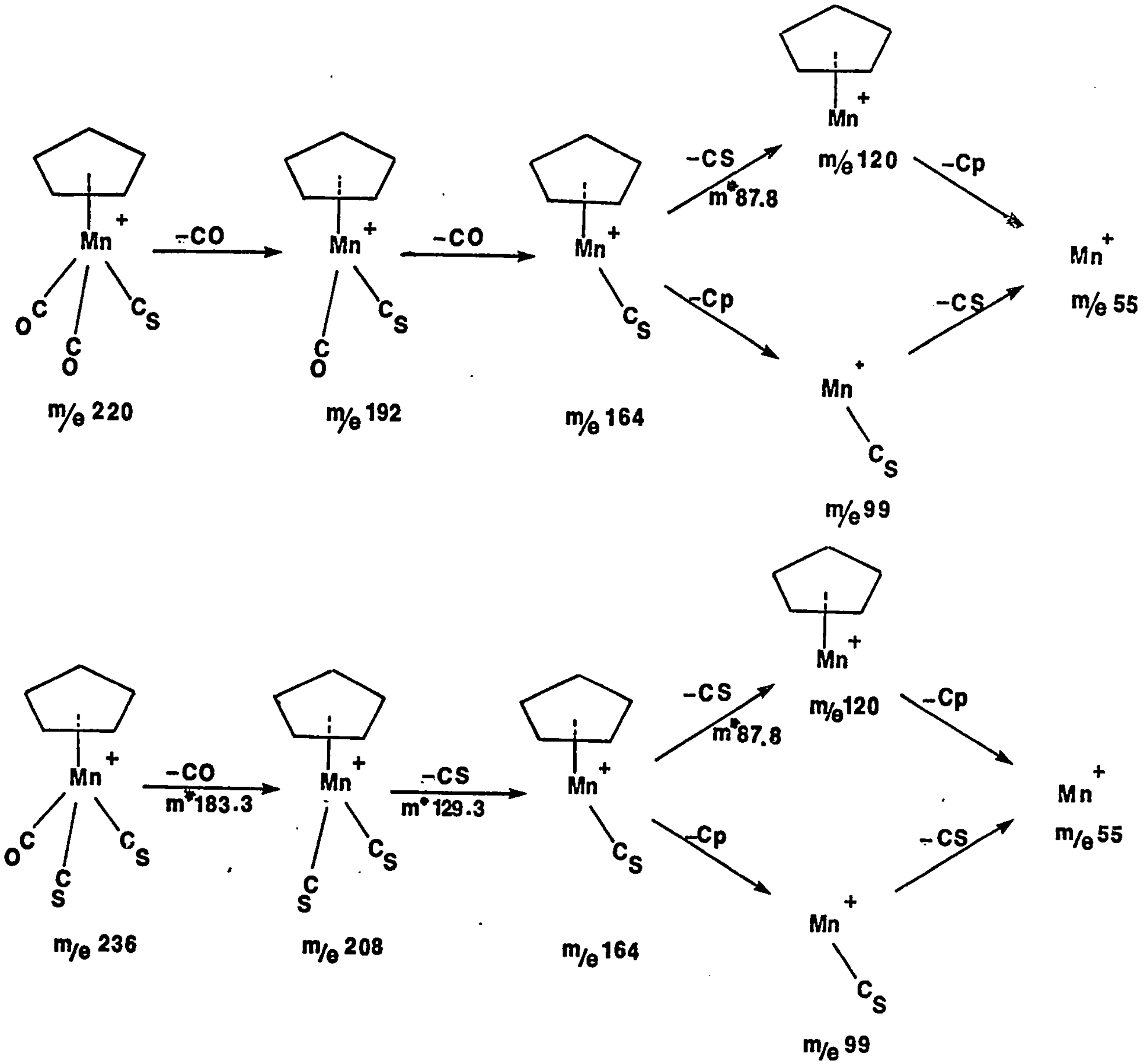

Fig. 20. Proposed fragmentation pathways for the degradation of $CpMn(CO)_2(CS)^+$ and $CpMn(CO)(CS)_2^+$.

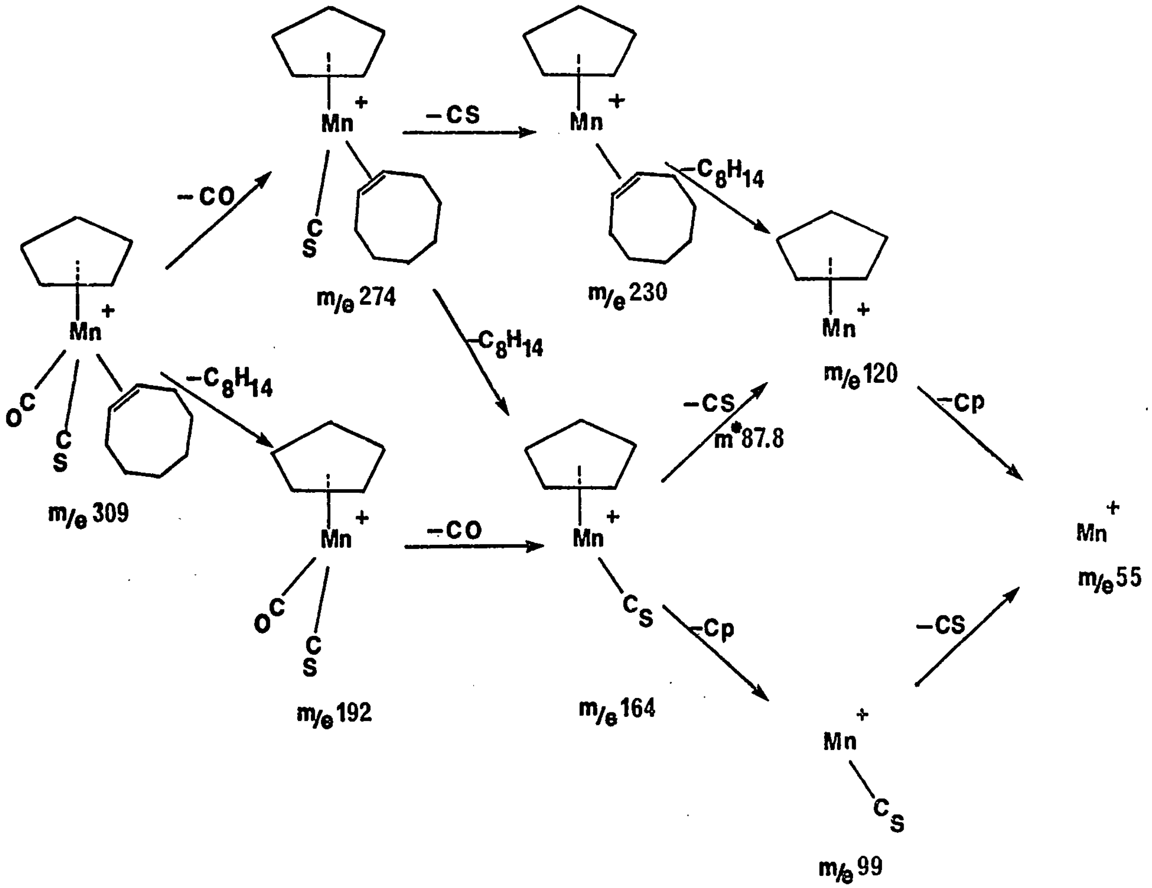

Fig. 21. Proposed fragmentation pathways for the degradation of CpMn(CO)(CS)$(C_8H_{14})^+$.

All three thiocarbonyl complexes exhibit a peak at m/e 99 which is assigned 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 manganese-CS bond. This contrasts the fragmentation of π-cyclopentadienylmetal carbonyl complexes where the CO groups are always lost before the ring[65].

d. Proton n.m.r. Spectra

Owing to the difficulty in obtaining appreciable yields of the new complexes, proton n.m.r. data were obtained only for $CpMn(CO)_2CS$ and $CpMn(CO)(CS)_2$. The spectra of these complexes in CS_2 both exhibit a single resonance at τ 5.18 which can be assigned to the π-cyclopentadienyl ring.

King[83] has suggested that the following relationship exists between the π-cyclopentadienyl proton n.m.r. chemical shifts (τ_{Cp}) and the carbonyl force constants (k_{CO}) in π-cyclopentadienylmetal carbonyl complexes:

$$\tau_{Cp} = 13.203 - 0.499\ k_{CO}$$

On the basis of this relationship he proposed that proton n.m.r. chemical shifts as well as CO stretching force constants can be

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*Exact mass: calculated 98.91017, found 98.91417.

used as an indicator of the electron density on the metal in this type of complex. Thus, the observed decrease in the chemical shift and the increase in the calculated force constant for $CpMn(CO)_2CS$ (τ 5.18, k_{CO} 15.83 mdyn/Å), when compared to $CpMn(CO)_3$ (τ 5.35, k_{CO} 15.61 mdyn/Å), both indicate decreased negative charge on the metal. However, there is no appreciable additional decrease in chemical shift for $CpMn(CO)(CS)_2$ (τ 5.18) even though the force constant increases further (k_{CO} 16.00 mdyn/Å).

4. Kinetic Studies

It was mentioned earlier (*vide supra*, p. 60) that Angelici and Loewen have reported kinetic data for the following reaction in methylcyclohexane solution:

$$CpMn(CO)_2(C_8H_{14}) + PPh_3 \longrightarrow CpMn(CO)_2PPh_3 + C_8H_{14} \qquad (2)$$

They proposed that reaction 2 proceeds by an S_N1 dissociative mechanism involving the slow loss of *cis*-cyclooctene in the rate-determining step, followed by rapid entry of PPh_3. The thiocarbonyl complex, $CpMn(CO)(CS)(C_8H_{14})$, also undergoes *cis*-cyclooctene substitution with PPh_3 in methylcyclohexane solution (*vide supra*, p. 85):

$$CpMn(CO)(CS)(C_8H_{14}) + PPh_3 \longrightarrow CpMn(CO)(CS)PPh_3 + C_8H_{14} \qquad (4)$$

Owing to the similarity of this reaction to reaction 2 its kinetics and mechanism were investigated in an attempt to compare the bonding properties of CO and CS in related transition metal complexes. Prior to this study, no kinetic data for transition metal thiocarbonyl complexes had been reported in the literature.

Kinetic data were obtained by monitoring the rates of disappearance of the infrared-active CO stretching absorption of CpMn(CO)(CS)(C_8H_{14}) at 1958 cm^{-1}. This disappearance was accompanied by the growth of two CO absorptions at 1938 and 1928 cm^{-1} due to CpMn(CO)(CS)PPh_3. Linear first-order plots of $\ln(A-A_\infty)$ *vs.* time were obtained. A typical plot is given in Fig. 22. A series of spectra from a typical kinetic run are shown in Fig. 23.

The observed pseudo-first-order rate constants (k_{obsd}) for reaction 4 given in Table XII are independent of the concentration of PPh_3 over the temperature range investigated (50-70°). The associated activation entropy (19.7 ± 2.7 e.u.) is in the range expected for an S_N1 dissociative mechanism[84]. These data are in accord with the mechanism shown below involving the rupture of the manganese-olefin bond as the slow rate determining step i.e., a similar mechanism to that proposed by Angelici and Loewen for reaction 2.

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

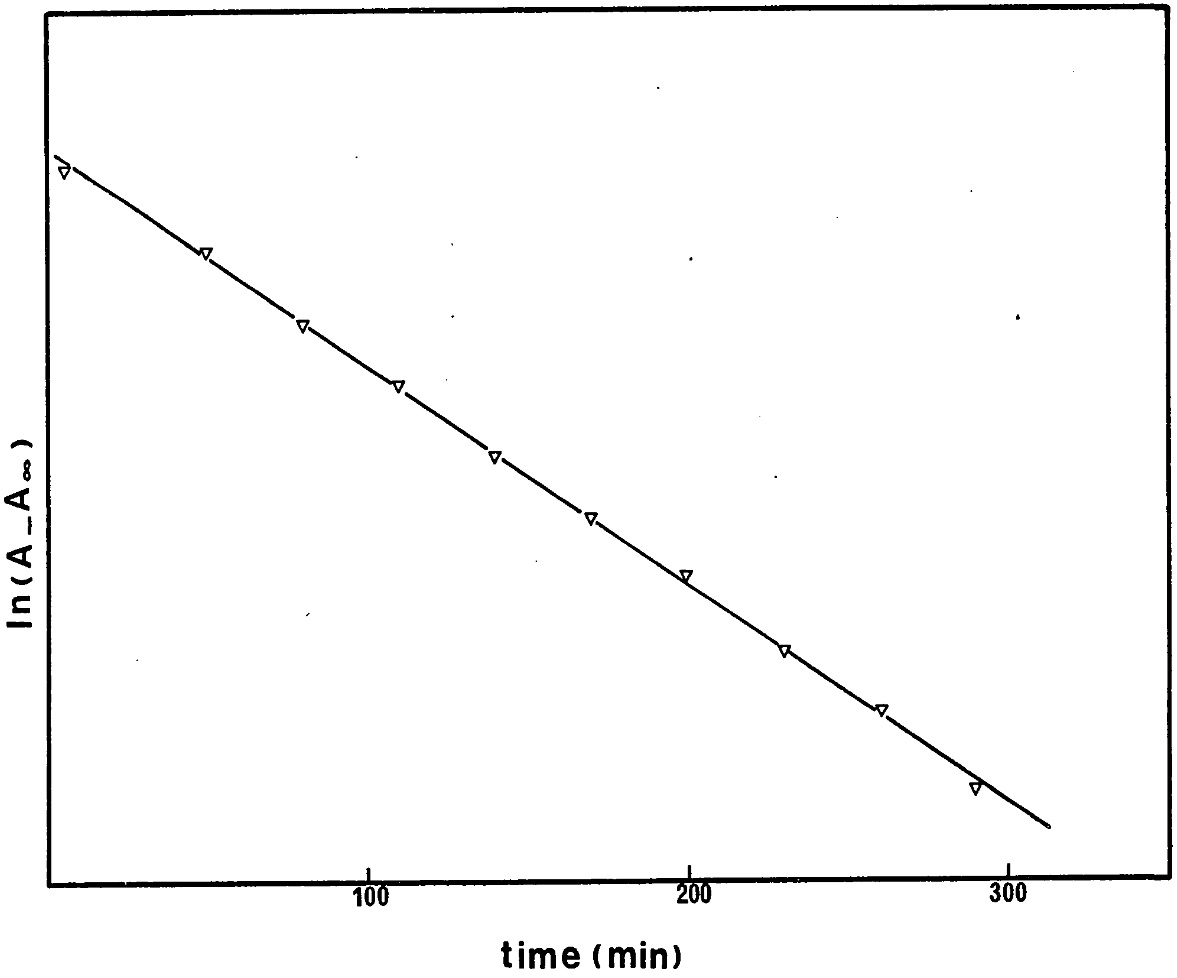


Fig. 22. First-order plot for the reaction of CpMn(CO)(CS)(C_8H_{14}) with PPh_3 in methylcyclohexane solution at 50°.

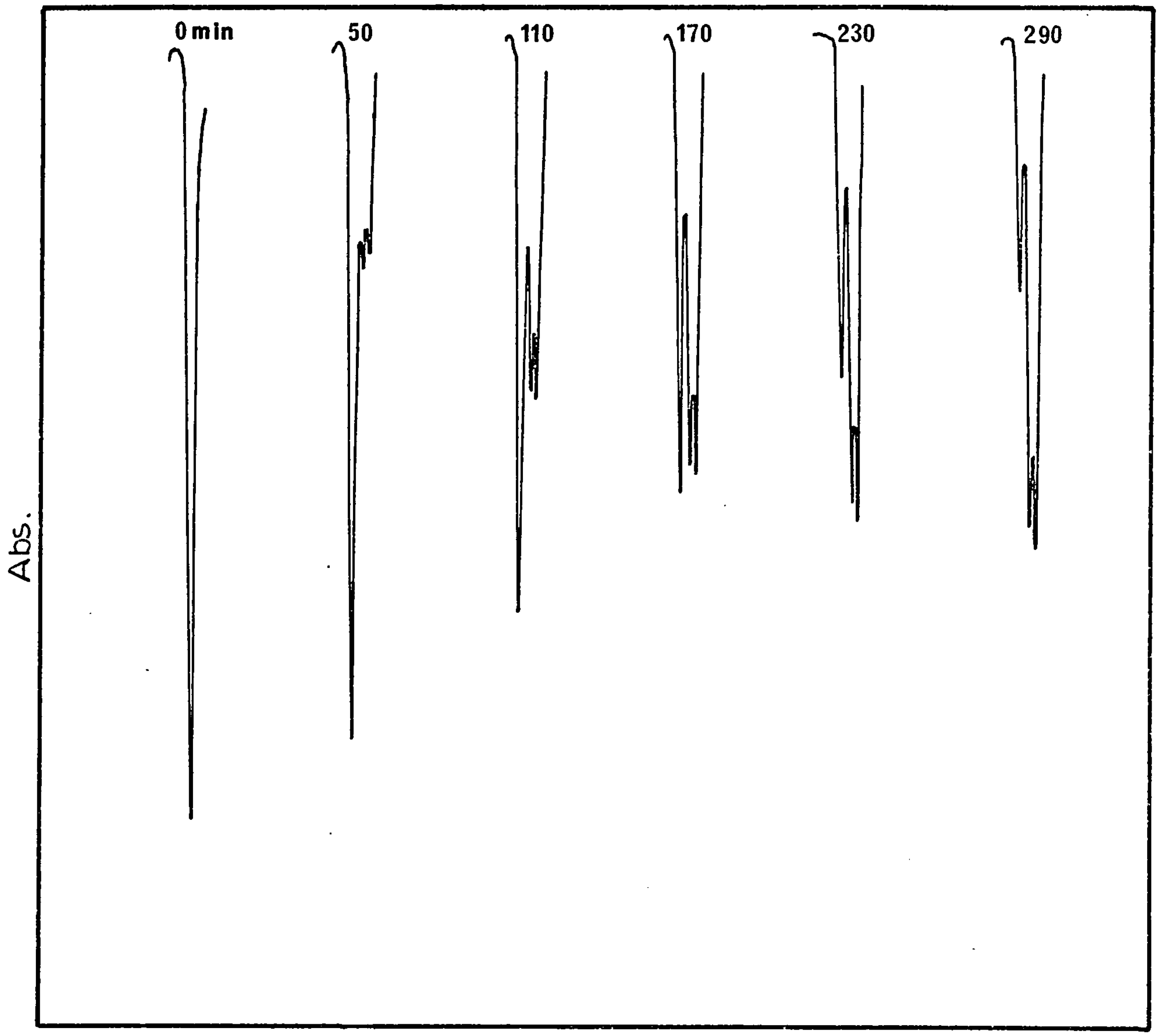


Fig. 23. Infrared spectra in the CO stretching region for the reaction of CpMn(CO)(CS)(C_8H_{14}) with PPh_3 in methylcyclohexane solution at 50° *vs.* time.

TABLE XII. PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF $CpMn(CO)(CS)(C_8H_{14})$ WITH PPh_3 IN METHYLCYCLOHEXANE SOLUTION

Temp. (°C)	$[PPh_3]^a$ (M)	$10^5 k_{obsd}$ (sec^{-1})
50.0	0.015	9.4
	0.025	9.8
	0.05	9.0
60.0	0.05	39
	0.1	39
	0.2	38
65.0	0.025	76
	0.05	80
70.0	0.025	170
	0.05	170

[a] $[CpMn(CO)(CS)(C_8H_{14})]$, 2×10^{-3}M

Some of the kinetic data for the replacement of *cis*-cyclooctene in CpMn(CO)(CS)(C_8H_{14}) and CpMn$(CO)_2$(C_8H_{14}) by PPh_3 in methylcyclohexane solution are compared in Table XIII. It is immediately evident that at 60.0 and 70.0° the reaction rates for the thiocarbonyl complex are about four times faster than those for the dicarbonyl complex. Furthermore, the activation parameters suggest that the increased reaction rate for the thiocarbonyl complex arises mainly because of a decrease in the enthalpy of activation. Thus, changing a CO to a CS group in CpMn$(CO)_2$(C_8H_{14}) has a marked effect on the kinetic behaviour of the resulting *cis*-cyclooctene complex.

The increased lability of the olefin in the thiocarbonyl complex can be readily explained if CS is a better π-acceptor than CO. When one CO group in CpMn$(CO)_2$(C_8H_{14}) is replaced by a CS group there will be a resultant lowering of electron density available on the manganese atom for back-bonding to the olefin. Consequently, the manganese-olefin bond in CpMn(CO)(CS)(C_8H_{14}) should be weaker than that in CpMn$(CO)_2$(C_8H_{14}) and thus be broken more easily, as is observed. This explanation receives some support from Mössbauer data for the iron cationic complexes $[CpFe(CO)_2CS]^+$ and $[CpFe(CO)_3]^+$ which also suggest that CS is a more effective π-acceptor than CO[85].

TABLE XIII. COMPARISON OF KINETIC DATA FOR THE REACTIONS OF $CpMn(CO)(CS)(C_8H_{14})$ AND $CpMn(CO)_2(C_8H_{14})$ WITH PPh_3 IN METHYLCYCLOHEXANE SOLUTION[a]

Complex	$10^5 k_{obsd}$ (sec^{-1})		ΔH* (kcal $mole^{-1}$)	ΔS* (e.u.)
	60.0°C	70.0°C		
$CpMn(CO)(CS)(C_8H_{14})$	38.7	165	30.6 ± 0.9	19.7 ± 2.7
$CpMn(CO)_2(C_8H_{14})$[b]	9.25	46.9	34.9 ± 0.7	27.5 ± 2.0

[a] The rate constants listed are averages of several kinetic runs at different concentrations of PPh_3. The limits of error on the activation parameters are 1 standard deviation.

[b] Data from ref. 50.

C. ATTEMPTED REACTIONS OF π-CYCLOPENTADIENYL COMPLEXES OF VANADIUM, COBALT, AND IRON WITH CARBON DISULPHIDE

The results of preliminary attempts to extend the work described earlier in this chapter to π-cyclopentadienyl derivatives of metals other than manganese were inconclusive.

1. Vanadium

Efforts to prepare the *cis*-cyclooctene derivative of vanadium, $CpV(CO)_3(C_8H_{14})$, from $CpV(CO)_4$ and C_8H_{14} failed. The photochemical reaction of $CpV(CO)_4$ with CS_2 resulted only in complete decomposition.

2. Cobalt

The 1,5-cyclooctadiene complex, $CpCo(C_8H_{12})$, does not react with CS_2 at reflux temperature. However, it should be noted that the displacement of the diene from the complex by other ligands appears to require drastic experimental conditions. For example, the reaction of $CpCo(C_8H_{12})$ with CO to give the parent compound, $CpCo(CO)_2$, proceeds only at 100° and 50 atmospheres[86].

The photochemical reaction of $CpCo(CO)_2$ with C_8H_{14} in *n*-hexane solution affords a mixture consisting of the starting materials and a complex exhibiting a strong i.r. band at 1960 cm^{-1}. It was not possible to isolate a pure sample of the complex but it appears likely that it is the monocarbonyl complex, $CpCo(CO)(C_8H_{14})$. When the above mixture is kept at reflux temperature in CS_2 solution in the presence of PPh_3 for 18 hr, the absorption at 1960 cm^{-1} is replaced by a new band at 1918 cm^{-1}. The CS stretching region of the spectrum was obscured by PPh_3 and C_8H_{14} absorptions. Attempts to isolate the complex were unsuccessful. Therefore, it could not be determined whether the 1918 cm^{-1} absorption is indicative of the formation of a thiocarbonyl (or a CS_2) complex.

Ultraviolet irradiation of $CpCo(CO)_2$ in CS_2 solution in the presence of PPh_3 results in extensive decomposition. However, monitoring the reaction by i.r. spectroscopy shows the appearance of new absorptions at 2039 and 1170 cm^{-1}. In addition to the above absorptions, there are also bands attributable to PPh_3S.

3. Iron

The reaction of $CpFe(CO)_2Me$ with CS_2 was also investigated to determine whether the complex would undergo CS_2 insertion to form a chelated species such as CpFe(CO)(SSCMe) in a similar manner to the synthesis of $Mn(CO)_4(SSCMe)$ from $Mn(CO)_5Me$ and CS_2 (*vide supra*, p. 21). The analogous trithiocarbonato- chelated complexes CpFe(CO)(SSCSR) (R = alkyl, aryl) are known but could not be prepared by direct CS_2 insertion into the mercaptides, $CpFe(CO)_2SR$[87].

The iron complex, $CpFe(CO)_2Me$, does react with CS_2. However, even at reflux temperature, the reaction appears extremely slow. An i.r. spectrum of the reaction mixture taken after one week shows only a slight decrease in the absorptions of $CpFe(CO)_2Me$ [ν(CO) 2008, 1952 cm^{-1}]. Nevertheless, there are two new weak peaks at 2033 and 1300 cm^{-1}. The latter band is in the frequency range expected for a CS_2-insertion product.

The above reaction was repeated in a Carius tube at 100° for 17 hr. An i.r. spectrum of the resulting brown solid in CS_2 solution exhibits, in addition to the bands mentioned above, new absorptions in the terminal CO stretching region (2019, 1995 cm^{-1}), the bridging CO stretching region (1712, 1693 cm^{-1}), and at 1253 and 1234 cm^{-1}. However, efforts to separate the different products from the mixture were unsuccessful.

CHAPTER IV EXPERIMENTAL

A. SOURCES OF MATERIALS

The π-cyclopentadienyl complexes, $CpMn(CO)_3$ and π-$MeC_5H_4Mn(CO)_3$ were generous gifts from Ethyl Corp., New York, N.Y. All other chemicals used were obtained from the sources listed below.

Chemical	Source
$CpV(CO)_4$	Strem Chemicals Inc.
$CpCo(CO)_2$	"
diphos	"
PPh_3	Aldrich Chemicals Co. Inc.
PPh_3S	"
$P(OMe)_3$	"
cis-cyclooctene	"
1,5-cyclooctadiene	"
norbornadiene	"
dimethyldisulphide	"
n-hexane	Fisher Scientific Co.
carbon disulphide	"
benzene	"
methylcyclohexane	B.D.H. Chemicals Ltd.
tetrahydrofuran	Aldrich Chemicals Co. Inc.

B. PHYSICAL MEASUREMENTS

Infrared spectra were recorded on a Perkin-Elmer model 337 spectrophotometer coupled to a Texas Instruments Servo/Riter model II expanded-scale recorder. The solution spectra were obtained using pairs of NaCl (0.1 and 1.0 mm) and KBr (1.0 mm) cells. Nujol mulls between NaCl plates were used for solid-state spectra. Calibrations were performed with a CO filled gas cell (2143.2 cm^{-1}) and a polystyrene film (1601.4 cm^{-1}). The frequencies presented in the Tables are precise to 1-2 cm^{-1}.

Raman spectra of the powdered solids in glass capillary tubes were recorded on a Jarell-Ash model 25-300 spectrophotometer using the 647.1 nm line of a krypton laser for excitation. Indene was used for calibration. The precision of frequencies obtained is considered to be better than 2 cm^{-1}.

Varian A-60 and AEI model MS902 instruments were used to record n.m.r. and mass spectra, respectively.

A Hewlett-Packard model 5720 chromatograph was used for the v.p.c. analyses. The stationary phase was 10% SE-30 on Chromosorb W.

Melting points were taken on a Gallenkamp Melting Points Apparatus and are uncorrected.

Elemental analyses and molecular weight determinations (by v.p. osmometry) were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York, N.Y.

C. PREPARATION OF COMPLEXES

All operations were carried out routinely under an atmosphere of nitrogen. Apparatus of the Schlenck type was used in nearly all cases[88].

The solvents, with the exception of methylcyclohexane and THF, were of spectrograde quality. Carbon disulphide, *n*-pentane, and *n*-hexane were dried over molecular sieves; benzene over sodium wire; THF over sodium wire and benzophenone; and methylcyclohexane over phosphorus pentoxide. The solvents were fractionally distilled under nitrogen immediately prior to use.

The tricarbonyl complex, $CpMn(CO)_3$, was purified by vacuum sublimation (0.01 mm Hg/25°). All the other commercial chemicals were used as received without further purification.

Large-scale photochemical reactions (200-400 ml) were carried out in a pyrex vessel fitted with a water-cooled quartz finger. The uv source (450 W Hanovia high-pressure mercury, No. 679A) was placed inside the finger. A quartz vessel placed in a Rayonet circular photochemical reactor (equipped with up to 16 low-pressure mercury lamps emitting at 2537 Å) was used for small-scale reactions (30-80 ml). In this case, cooling was provided by a fan mounted on the reactor.

The methods described in the literature were used to prepare the π-cyclopentadienyl derivatives, $CpMn(CO)_2(C_8H_{14})$[69],

π-$MeC_5H_4Mn(CO)_2(C_8H_{14})$ [50], $CpMn(CO)_2(C_7H_8)$ [69], $CpMn(CO)_2PPh_3$ [75], and $CpCo(C_8H_{12})$ [88].

A warning: Silicone lubricant dissolves readily in most organic solvents. Its i.r. spectrum[89] exhibits a strong sharp band (at 1256 cm^{-1} in CS_2 solution) which can easily be mistaken for a thiocarbonyl absorption.

Reactions of $CpMn(CO)_2(C_8H_{14})$ with CS_2

1. *In the Absence of PPh_3*

A solution of $CpMn(CO)_2(C_8H_{14})$ (2.5 g, 8.7 mmol) in CS_2 (500 ml) was kept at reflux temperature for 54 hr. Considerable decomposition was observed. The solution was then filtered and the volume of the dark-green filtrate was reduced to a minimum on the vaccum line. The solution remaining was chromatographed on a de-aerated alumina column using a 1:1 benzene:*n*-hexane mixture as eluent. The presence of four species – light-yellow, yellow, green, and purple – was noted on the column. The solvent was evaporated from the front-running light-yellow fraction and the resulting solid was redissolved in a minimum of *n*-hexane. Yellow crystals of $CpMn(CO)_2CS$ were obtained following the removal of the solvent under a slow stream of nitrogen. The complex is air-stable in the solid state but decomposes slowly in solution (yield: 45 mg, 6%; mp 52-53°). *Anal.* Calcd. for $C_8H_5O_2SMn$:

C, 43.6; H, 2.3; S, 14.6. Found: C, 43.1.; H, 2.6; S, 14.7. *Mol. wt.* Calcd.: 220. Found: 211 (osmometry), 220 (mass spectrum).

The product contained in the second yellow fraction was $CpMn(CO)_3$ (yield: *ca.* 5%). This complex was identified by comparison of its i.r. and mass spectra with the spectra of the known compound. The green species was too unstable to be isolated. The purple complex was obtained in too small a quantity to be analyzed.

The first step in the above reaction is the formation of $CpMn(CO)_2(\pi\text{-}CS_2)$. This complex was obtained alone when the reaction was carried out at 40° and for a $2 \times 10^{-3}M$ solution of $CpMn(CO)_2(C_8H_{14})$ in CS_2. The $\pi\text{-}CS_2$ complex, which could not be isolated in the solid state, was identified by its i.r. spectrum and from its reaction *in situ* with PPh_3 to give $CpMn(CO)_2CS$ and PPh_3S.

The related π-methylcyclopentadienyl derivatives, $\pi\text{-}MeC_5H_4Mn(CO)_2CS$ and $\pi\text{-}MeC_5H_4Mn(CO)_2(\pi\text{-}CS_2)$ were prepared as above but on spectroscopic scale from the reaction of $\pi\text{-}MeC_5H_4Mn(CO)_2(C_8H_{14})$ with CS_2.

2. *In the Presence of PPh_3*

One litre of a CS_2 solution containing $CpMn(CO)_2(C_8H_{14})$ (14.3 g, 50 mmol) and PPh_3 (13.1 g, 50 mmol) was refluxed for 27 hr. After removal of the solvent on the vacuum line, the crude reaction product was washed repeatedly with 50 ml portions of *n*-pentane until colourless washings were obtained. The white crystalline solid remaining was identified as PPh_3S by i.r. spectroscopy and v.p.c. analysis by comparison with data obtained for the known compound. Removal of *n*-pentane from the combined coloured washings afforded a yellow residue from which $CpMn(CO)_2CS$ was obtained in high yield (9.35 g, 85%) by vacuum sublimation (0.01 mm Hg/25°). The purity of the complex was established by the absence of any impurity peaks in its i.r., n.m.r., and mass spectra. Because the complex sublimes so readily at room temperature, some losses could not be avoided during the successive solvent removals on the vacuum line.

Preparation of $CpMn(CO)(CS)(C_8H_{14})$

A mixture of $CpMn(CO)_2CS$ (220 mg, 1 mmol) and C_8H_{14} (4 ml, *ca.* 30 mmol) in 200 ml *n*-hexane was irradiated with a 450 W Hanovia uv source for 20 min. Considerable decomposition was observed. The reaction mixture was filtered and then the solvent was evaporated from the filtrate under vacuum. A yellow, air-sensitive oil was obtained from which unreacted $CpMn(CO)_2CS$ was removed by sublimation. The remaining crude oily product was used as $CpMn(CO)(CS)(C_8H_{14})$ for further syntheses without additional purification (estimated yield: *ca.* 25%). For higher purity, the oil was first dried *in vacuo* for 24 hr when a black solid was obtained. Then, pure CpMn(CO)(CS)(C_8H_{14}) was sublimed (0.01 mm Hg/50°) from this black solid as small air-sensitive, yellow crystals (yield: 20 mg, 6%; decomp. ∿55°). *Anal.* Calcd. for $C_{15}H_{19}OSMn$: C, 59.6; H, 6.3; S, 10.6. Found: C, 57.7; H, 6.0; S, 10.3. *Mol. wt.* Calcd.: 302. Found: 302 (mass spectrum).

Efforts to prepare the complex on a larger scale by using more concentrated solutions of the starting materials resulted in even more extensive decomposition. Moreover, the black decomposition product coated the wall of the reaction vessel so thickly that transmission of uv light was impossible and the reaction was terminated at an early stage.

Thermal decomposition of CpMn(CO)(CS)(C_8H_{14}) in methylcyclohexane solution at 70° afforded, after 3 hr, CpMn$(CO)_3$, CpMn$(CO)_2$CS, and a brown precipitate. The carbonyl-containing products were identified by i.r. spectroscopy.

Preparation of CpMn(CO)(CS)PPh$_3$

A mixture of freshly prepared crude "oily" CpMn(CO)(CS)(C_8H_{14}) and excess PPh_3 (130 mg, 0.5 mmol) in 100 ml *n*-hexane was heated under reflux for 1 hr. The solvent was then removed on the vacuum line affording a dark-orange residue. The excess PPh_3 was sublimed off (0.001 mm Hg/50°)

and the remaining solid was dissolved in a minimum of CS_2. After filtration addition of *n*-hexane to the filtrate followed by removal of the solvent under a slow stream of nitrogen gave orange crystals of $CpMn(CO)(CS)PPh_3$ [yield: *ca.* 15% based on the amount of $CpMn(CO)_2CS$ used for the synthesis of $CpMn(CO)(CS)(C_8H_{14})$; decomp. ∿180°]. *Anal.* Calcd. for $C_{25}H_{20}OPSMn$: C, 66.1; H, 4.4; S, 7.0. Found: C, 66.0; H, 4.5; S, 6.3.

The related complex, $CpMn(CO)(CS)P(OMe)_3$, was prepared in a similar manner on a spectroscopic scale from crude $CpMn(CO)(CS)(C_8H_{14})$ and $P(OMe)_3$. The complex was identified by the similarity of its i.r. spectrum to that of $CpMn(CO)(CS)PPh_3$.

Preparations of $[CpMn(CO)(CS)]_2$(diphos) and CpMn(CS)(diphos)

A mixture of freshly prepared crude "oily" $CpMn(CO)(CS)(C_8H_{14})$ and diphos (200 mg, 0.5 mmol) in 100 ml *n*-hexane was heated at reflux temperature for 1 hr. The solution was filtered hot. The solvent was removed from the filtrate on the vacuum line. The orange residue was dissolved in a minimum of CS_2 and then chromatographed on a silica gel preparative t.l.c. plate using a 1:1 benzene:*n*-hexane mixture as eluent. The desired complexes corresponding to the yellow and the orange band on the plate, respectively, were extracted from silica gel with acetone. The solvent was removed and the materials were redissolved in CS_2. The resulting solutions were then filtered to remove the small amounts of silica gel remaining. After reducing the volume of CS_2 solutions to a minimum, *n*-hexane was added to them causing precipitation of the desired products:

(a) $[CpMn(CO)(CS)]_2$(diphos): (yield: *ca.* 5%; decomp. 212-214°). *Anal.* Calcd. for $C_{40}H_{34}O_2S_2P_2Mn_2$: C, 61.4; H, 4.3; S, 8.2; P, 7.9. Found: C, 62.0; H, 4.9; S, 7.9; P, 8.0. *Mol. wt.* Calcd.: 782. Found: 751.

(b) CpMn(CS)(diphos): (yield: *ca.* 5%, decomp. ∿140°). *Anal.* Calcd. for $C_{32}H_{29}SP_2Mn$: C, 68.3; H, 5.2; S, 5.7; P, 11.0. Found: C, 67.8; H, 5.8; S, 5.9; P, 11.2. *Mol. wt.* Calcd.: 562. Found: 634.

Preparation of $CpMn(CO)(CS)_2$

A mixture of freshly prepared crude "oily" $CpMn(CO)(CS)(C_8H_{14})$ and PPh_3 (130 mg, 0.5 mmol) was heated at reflux temperature for 12 hr. The desired dithiocarbonyl product (yield: *ca.* 20%, mp 71-72°) was isolated and purified by a procedure similar to that described for the analogous preparation of $CpMn(CO)_2CS$. *Anal.* Calcd. for $C_8H_5OS_2Mn$: C, 40.7; H, 2.1; S, 27.1. Found: C, 41.0; H, 2.5; S, 27.8. *Mol. wt.* Calcd.: 236. Found: 236 (mass spectrum).

Preparations of $CpMn(CS)_2(C_8H_{14})$ and $CpMn(CS)_3$

A mixture of $CpMn(CO)(CS)_2$ (20 mg, *ca.* 0.1 mmol) and C_8H_{14} (1.5 ml, *ca.* 10 mmol) in 40 ml *n*-hexane was irradiated (Rayonet reactor, 4/2437 Å lamps) for 1 hr. Considerable decomposition was observed. Filtration of the reaction mixture, followed by evaporation of the solvent, afforded a yellow oil containing $CpMn(CS)_2(C_8H_{14})$ and unreacted $CpMn(CO)(CS)_2$ and C_8H_{14}. The olefin complex is extremely air-sensitive and further purification could not be achieved. The yellow oil was dissolved in a CS_2 solution (10 ml) containing PPh_3 (20 mg). The resulting mixture was then heated at reflux temperature for 5 hr. After evaporation of the solvent, minute quantities of $CpMn(CS)_3$, together with unreacted $CpMn(CO)(CS)_2$ were removed from the reaction mixture by vacuum sublimation (0.01 mm Hg/ 25°).

D. KINETIC DATA

Kinetic data were obtained by monitoring the rate of decrease of the infrared-active CO stretching absorptions of $CpMn(CO)_2(C_8H_{14})$ and $CpMn(CO)(CS)(C_8H_{14})$ at ∿1900 and ∿1960 cm^{-1}, respectively. Pseudo-first-order conditions were employed in all cases; the substrate concentrations being kept at about $2 \times 10^{-3}M$. Carbon disulphide and methylcyclohexane solutions of the complexes and varying concentrations of PPh_3 were prepared in aluminium-foil-wrapped reaction vessels fitted with neoprene serum caps and thermostated in a constant temperature (±0.1°) oil bath. Samples were withdrawn with a syringe at appropriate intervals and their i.r. spectra scanned in the CO stretching region. Linear first-order plots of $\ln(A-A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs*. t were obtained. The reactions went to completion and the plots were linear to at least 85% completion. The rate constants for identical kinetic runs were reproducible to within ±6%. All the rate constants were calculated using a least-squares computer program.

PART II

REACTIONS OF π-CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES WITH ISOTOPICALLY ENRICHED CO

CHAPTER I INTRODUCTION

The infrared-active CO stretching modes of naturally-occurring ^{13}CO-substituted metal carbonyl complexes and the i.r. spectra obtained from the exchange reactions of these complexes with ^{13}CO and $C^{18}O$ have been used in numerous spectroscopic investigations over the past decade[90-94]. The chief uses to which these data have been put are summarized below[95].

(i) Determination of infrared-inactive CO stretching fundamentals associated with all-$^{12}C^{16}O$ species. The lowering of the symmetry of the molecule upon isotopic substitution may cause these fundamentals to become infrared-active.

(ii) Validation of band assignments and force constant calculations. This can be achieved by comparing the observed and calculated spectra of the all-$^{12}C^{16}O$ molecules and the various isotopically substituted species.

(iii) Force constant calculations. When the number of force constants to be calculated exceeds the number of CO stretching fundamentals available, the additional frequencies associated with the isotopically substituted species may provide the data necessary for the calculations to be made without any prior assumptions.

(iv) Assignment of fundamental frequencies. The number of isotopic bands and their shift from the parent modes may be useful in the assignment of the latter.

(v) Determination of reaction mechanisms. The observed changes in band intensitities in the 2000 cm^{-1} region may afford qualitative and sometimes quantitative data for systems involving CO as reactant.

(vi) Interpretation of absolute i.r. intensities. This may become possible from a study of the calculated force constants and the associated eigenvectors.

In most cases, the force constant calculations mentioned above have utilized simplified force fields based on the Cotton-Kraihanzel model[82]. In this model, only the CO stretching fundamentals are taken into account and the effect of anharmonicity is neglected. Furthermore, a number of approximations are made as to the signs and the relative magnitudes of the CO stretching and CO-CO interaction force constants. The question of the meaningfulness of the force constants obtained with these simplified methods has been amply debated[91]. Nevertheless, an important aspect of one of these models, *viz.*, the factored-off CO stretching model is that it can be used to calculate the spectra of ^{13}CO- or $C^{18}O$-substituted molecules with a high degree of accuracy[96]. This will be further exemplified by the work to be described here.

Spectroscopic studies of the CO exchange reactions of π-cyclopentadienylmetal carbonyl complexes with isotopically enriched CO have yet to be reported. In this part of the thesis the results of an i.r. spectroscopic investigation of the reactions of $CpMn(CO)_3$, $CpMn(CO)_2(C_8H_{14})$, $CpMn(CO)_2CS$, $CpMn(CO)(CS)(C_8H_{14})$, $CpV(CO)_4$, and $CpCo(CO)_2$ with ^{13}C- and/or ^{18}O-enriched CO are presented and discussed. Apart from the intrinsic value of the spectra of the isotopically enriched molecules themselves, it was felt of interest to study the above reactions to determine the relative lability of the CO groups and the other ligands in these π-cyclopentadienylmetal carbonyl complexes. In addition it was hoped to validate the method of "local symmetry"[97] for these complexes by comparing the number of observed and calculated CO stretching absorptions.

CHAPTER II EXPERIMENTAL

A. MATERIALS AND INFRARED SPECTRA

The sources of the materials used in this work, with the exception of 50% ^{13}C-enriched CO (Merck, Sharp, and Dohme of Canada Ltd.) and ∿90% ^{18}O-enriched CO (Miles Laboratories Inc.) are listed on p. 126. The literature method was used to prepare $CpMn(CO)_2(C_8H_{14})$[69]. The preparations of $CpMn(CO)_2CS$ and $CpMn(CO)(CS)(C_8H_{14})$ are given on p. 129 and 131, respectively. The purity of the π-cyclopentadienylmetal complexes was established by the absence of any impurity peaks in their i.r. spectra.

The i.r. spectra were recorded on a special slow-scanning Perkin-Elmer model 337 grating spectrophotometer equipped with a Texas Instruments Servo/Riter model II expanded scale recorder. The spectra were calibrated against the 2143.2 cm^{-1} band of CO and the 1601.4 and 1583.1 cm^{-1} bands of polystyrene. The frequencies presented in the Tables are in general the mean values obtained from the spectra of at least 5 samples taken from the reaction mixtures throughout the exchanges. The reproducibility of the frequencies is about ±0.5 cm^{-1}, while their absolute precision is 1-2 cm^{-1}. The intensities given in the Tables are relative to the most intense band in the spectral region being considered: w = weak, m = medium, s = strong, v = very, sh = shoulder.

B. ^{13}C- AND ^{18}O-ENRICHED π-CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES.

The CO groups in π-cyclopentadienylmetal carbonyls are relatively inert towards substitution under thermal conditions. Consequently, the ^{13}C- and ^{18}O-enriched species were prepared by uv light induced exchange of the carbonyl complexes with isotopically enriched CO at room temperature in freshly distilled *n*-hexane or CS_2 solutions. The uv source was a Rayonet reactor equipped with up to 16 low-pressure mercury lamps emitting at 2537 Å. Ultraviolet irradiation was unnecessary for the reactions of the *cis*-cyclooctene complexes — these reactions were carried out thermally. The general method used in all cases was similar to that described previously[91] except that for the uv light induced exchanges, the reaction vessel was constructed from quartz and was not blackened.

C. CALCULATIONS

The idealized geometries and definition of the "approximate" force constants for $CpMn(CO)_3$, $CpMn(CO)_2CS$, $CpV(CO)_4$, and $CpCo(CO)_2$ are shown in Fig. 24. The local symmetries and the internal CO bond stretching symmetry coordinates for the all-$^{12}C^{16}O$ and the various isotopically substituted carbonyl-containing moieties are given in Tables XIV-XVI and shown pictorially in Figs. 25 and 26. Optimum values of the force constants were calculated from the available data using an iterative computer program originally written by J.H. Schachtschneider and R.G. Snyder and modified for use on the IBM 360/75 computer of the McGill University Computing Centre[91]. Using these force constants and with appropriate changes in the G matrix elements, the computer was instructed to calculate the CO stretching frequencies of all the possible isotopically substituted molecules. In general, the observed CO stretching frequencies which were not used as input were predicted to within 4 cm^{-1} i.e., within the error range expected when using frequencies uncorrected for anharmonicity[98,99] and the CO-factored force field[100].

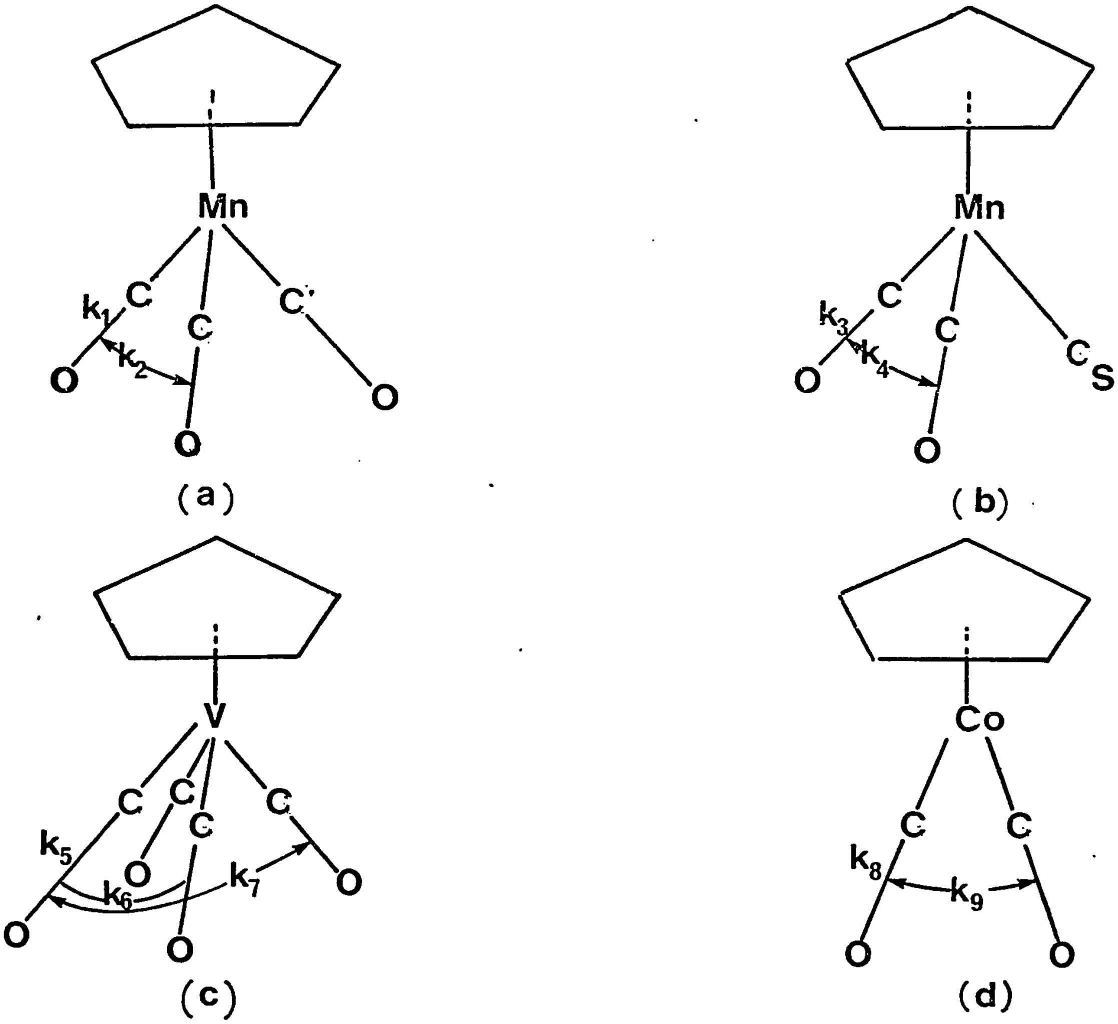


Fig. 24. Idealized geometries and definition of the "approximate" force constants for (a) $CpMn(CO)_3$, (b) $CpMn(CO)_2CS$, (c) $CpV(CO)_4$, and (d) $CpCo(CO)_2$.

TABLE XIV. SYMMETRY COORDINATES AND SECULAR EQUATIONS FOR THE ALL-$^{12}CO^{16}O$- AND THE ^{13}CO- AND $C^{18}O$-SUBSTITUTED CARBONYL-CONTAINING MOIETIES OF $CpMn(CO)_3$

Molecule and local symmetry	Symmetry species	Symmetry coordinate	Secular equation[a,b]
all-$^{12}C^{16}O$ C_{3v}	A_1	$S_1 = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$	$\lambda_1 = \mu(k_1 + 2k_2)$
	E	$S_{2a} = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$	$\lambda_2 = \mu(k_1 - k_2)$
		$S_{2b} = \frac{1}{\sqrt{2}}(r_1 - r_3)$	
mono-substitution C_s	A'	$S_3 = r_1$	$\lambda_3 = \mu^* k_1$
	A'	$S_4 = \frac{1}{\sqrt{2}}(r_2 + r_3)$	$\lambda_4 = \mu(k_1 + k_2)$
	A"	$S_5 = \frac{1}{\sqrt{2}}(r_2 - r_3)$	$\lambda_5 = \mu(k_1 - k_2)$
di-substitution C_s	A'	$S_6 = r_3$	$\lambda_6 = \mu k_1$
	A'	$S_7 = \frac{1}{\sqrt{2}}(r_1 + r_2)$	$\lambda_7 = \mu^*(k_1 + k_2)$
	A"	$S_8 = \frac{1}{\sqrt{2}}(r_1 - r_2)$	$\lambda_8 = \mu^*(k_1 - k_2)$
tri-substitution C_{3v}	A_1	$S_9 = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$	$\lambda_9 = \mu^*(k_1 + 2k_2)$
	E	$S_{10a} = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$	$\lambda_{10} = \mu^*(k_1 - k_2)$
		$S_{10b} = \frac{1}{\sqrt{2}}(r_1 - r_3)$	

[a] Diagonal elements. [b] $\mu = \mu_{^{12}C^{16}O}$, $\mu^* = \mu_{^{13}CO}$ or $\mu_{C^{18}O}$

TABLE XV. SYMMETRY COORDINATES AND SECULAR EQUATIONS FOR THE ALL-$C^{16}O$- AND THE $C^{18}O$-SUBSTITUTED CARBONYL-CONTAINING MOIETIES OF $CpMn(CO)_2CS$ AND $CpCo(CO)_2$

Molecule and local symmetry	Symmetry species	Symmetry coordinate	Secular equation[a,b,c]
all-$C^{16}O$ C_{2v}	A_1	$S_1 = \frac{1}{\sqrt{2}}(r_1 + r_2)$	$\lambda_1 = \mu(k_3 + k_4)$
	B_2	$S_2 = \frac{1}{\sqrt{2}}(r_1 - r_2)$	$\lambda_2 = \mu(k_3 - k_4)$
mono-$C^{18}O$ substitution C_1	A	$S_3 = r_1$	$\lambda_3 = \mu^* k_3$
	A	$S_4 = r_2$	$\lambda_4 = \mu k_3$
all-$C^{18}O$ C_{2v}	A_1	$S_5 = \frac{1}{\sqrt{2}}(r_1 + r_2)$	$\lambda_5 = \mu^*(k_3 + k_4)$
	B_2	$S_6 = \frac{1}{\sqrt{2}}(r_1 - r_2)$	$\lambda_6 = \mu^*(k_3 - k_4)$

[a] Diagonal elements.

[b] $\mu = \mu_{C^{16}O}$, $\mu^* = \mu_{C^{18}O}$.

[c] The equations shown refer to $CpMn(CO)_2CS$; the secular equations for $CpCo(CO)_2$ are identical except that k_3 and k_4 become k_8 and k_9, respectively.

TABLE XVI. SYMMETRY COORDINATES AND SECULAR EQUATIONS FOR THE ALL-$C^{16}O$- AND THE $C^{18}O$-SUBSTITUTED CARBONYL-CONTAINING MOIETIES OF $CpV(CO)_4$

Molecule and local symmetry	Symmetry species	Symmetry coordinate	Secular equation[a,b]
all-$C^{16}O$ C_{4v}	A_1	$S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4)$	$\lambda_1 = \mu(k_5 + 2k_6 + k_7)$
	B_1	$S_2 = \frac{1}{2}(r_1 - r_2 + r_3 - r_4)$	$\lambda_2 = \mu(k_5 - 2k_6 + k_7)$
	E	$S_{3a} = \frac{1}{\sqrt{2}}(r_1 - r_3)$	$\lambda_3 = \mu(k_5 - k_7)$
		$S_{3b} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	
mono-$C^{18}O$ substitution C_s	A'	$S_4 = r_1$	$\lambda_4 = \mu^* k_5$
	A'	$S_5 = r_3$	$\lambda_5 = \mu k_5$
	A'	$S_6 = \frac{1}{\sqrt{2}}(r_2 + r_4)$	$\lambda_6 = \mu(k_5 + k_7)$
	A"	$S_7 = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$\lambda_7 = \mu(k_5 - k_7)$
di-$C^{18}O$ *cis*-substitution C_s	A'	$S_8 = \frac{1}{\sqrt{2}}(r_1 + r_4)$	$\lambda_8 = \mu^*(k_5 + k_6)$
	A'	$S_9 = \frac{1}{\sqrt{2}}(r_2 + r_3)$	$\lambda_9 = \mu(k_5 + k_6)$
	A"	$S_{10} = \frac{1}{\sqrt{2}}(r_1 - r_4)$	$\lambda_{10} = \mu^*(k_5 - k_6)$
	A"	$S_{11} = \frac{1}{\sqrt{2}}(r_2 - r_3)$	$\lambda_{11} = \mu(k_5 - k_6)$

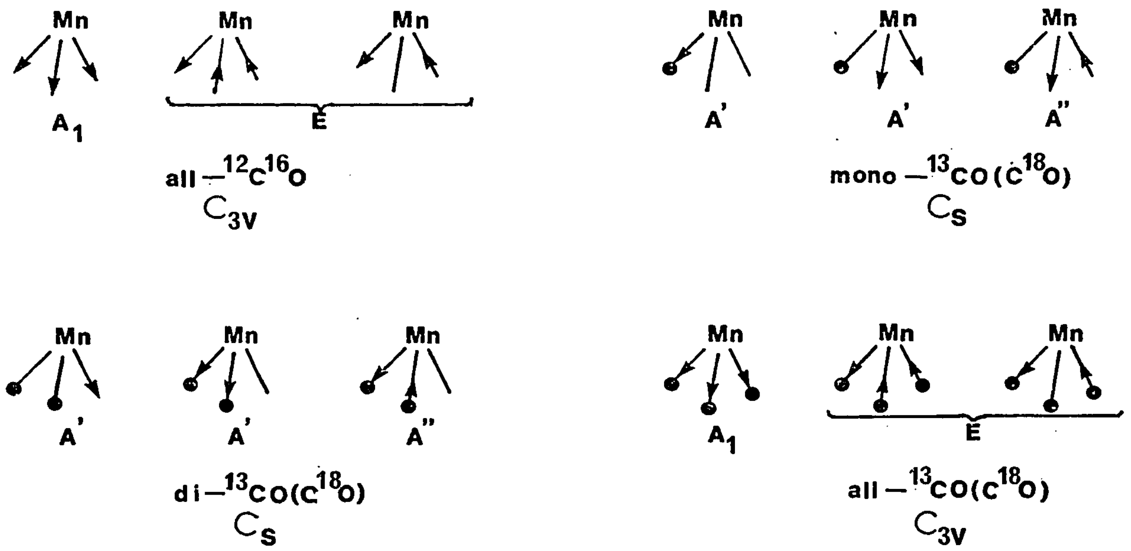
TABLE XVI (Cont'd)

di-$C^{18}O$ *trans*-substitution C_{2v}	A_1	$S_{12} = \frac{1}{\sqrt{2}}(r_1 + r_3)$	$\lambda_{12} = \mu^*(k_5 - k_7)$
	A_1	$S_{13} = \frac{1}{\sqrt{2}}(r_2 + r_4)$	$\lambda_{13} = \mu(k_5 + k_7)$
	B_1	$S_{14} = \frac{1}{\sqrt{2}}(r_1 - r_3)$	$\lambda_{14} = \mu^*(k_5 - k_7)$
	B_2	$S_{15} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$\lambda_{15} = \mu(k_5 - k_7)$
tri-$C^{18}O$ substitution C_s	A'	$S_{16} = r_1$	$\lambda_{16} = \mu^*k_5$
	A'	$S_{17} = r_3$	$\lambda_{17} = \mu k_5$
	A'	$S_{18} = \frac{1}{\sqrt{2}}(r_2 + r_4)$	$\lambda_{18} = \mu^*(k_5 + k_7)$
	A"	$S_{19} = \frac{1}{\sqrt{2}}(r_2 - r_4)$	$\lambda_{19} = \mu^*(k_5 - k_7)$
all-$C^{18}O$ C_{4v}	A_1	$S_{20} = \frac{1}{2}(r_1 + r_2 + r_3 + r_4)$	$\lambda_{20} = \mu^*(k_5 + 2k_6 + k_7)$
	B_1	$S_{21} = \frac{1}{2}(r_1 - r_2 + r_3 - r_4)$	$\lambda_{21} = \mu^*(k_5 - 2k_6 + k_7)$
	E	$S_{22a} = \frac{1}{2}(r_1 - r_3)$	$\lambda_{22} = \mu^*(k_5 - k_7)$
		$S_{22b} = \frac{1}{2}(r_2 - r_4)$	

[a] Diagonal elements

[b] $\mu = \mu_{^{12}C^{16}O}$, $\mu^* = \mu_{C^{18}O}$

(a) $CpMn(CO)_3$



(b) $CpMn(CO)_2CS$

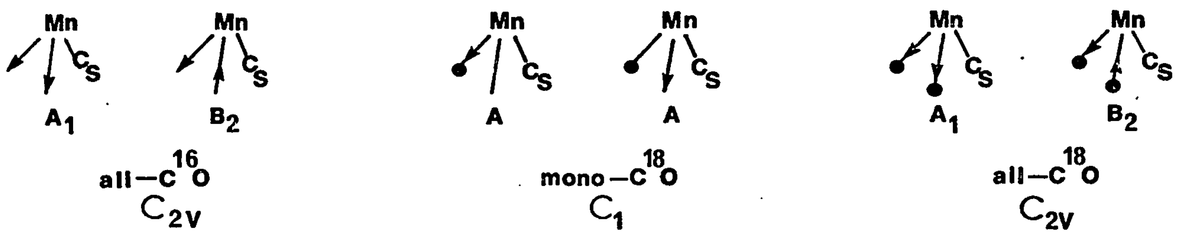
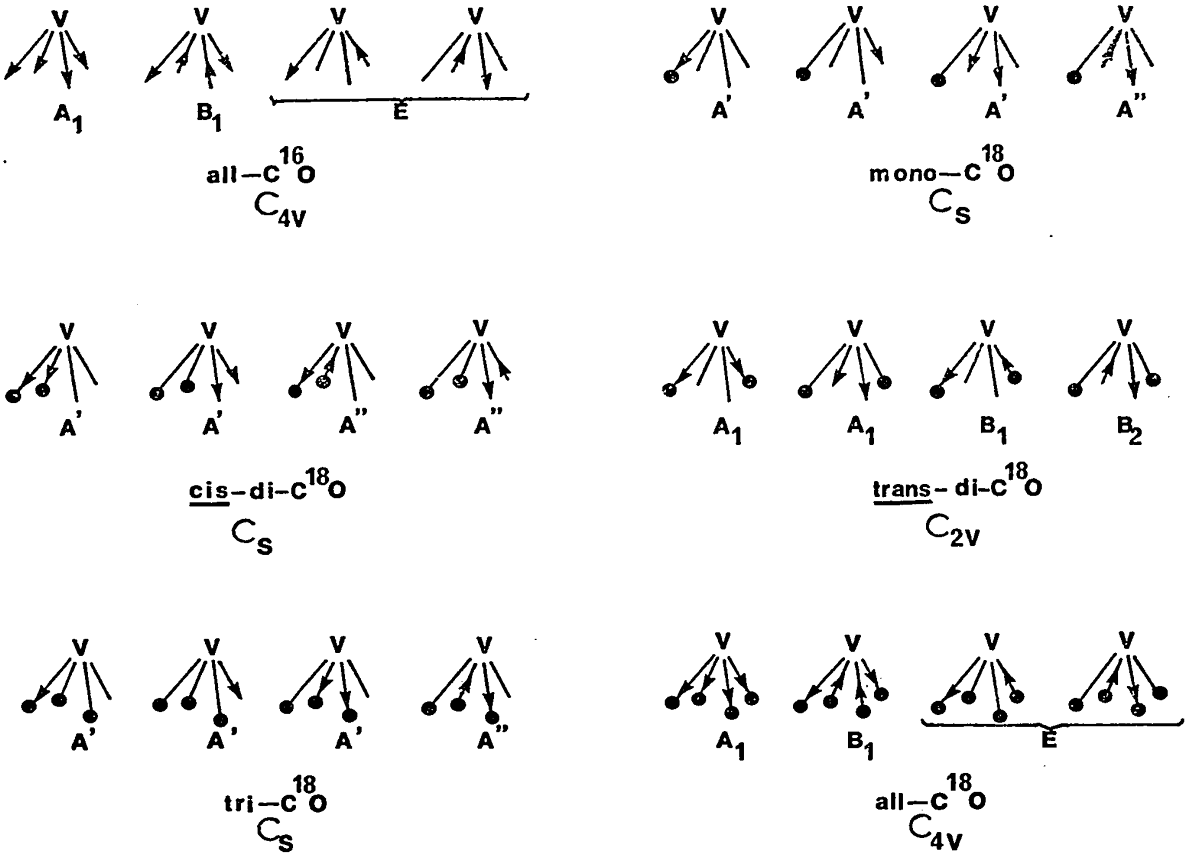


Fig. 25. Internal symmetry coordinates for the all-$^{12}C^{16}O$- and the ^{13}CO- and/or $C^{18}O$-substituted carbonyl-containing moieties of (a) $CpMn(CO)_3$ and (b) $CpMn(CO)_2CS$. The position of ^{13}CO or $C^{18}O$ is indicated by a heavy dot.

(a) CpV(CO)$_4$



(b) CpCo(CO)$_2$

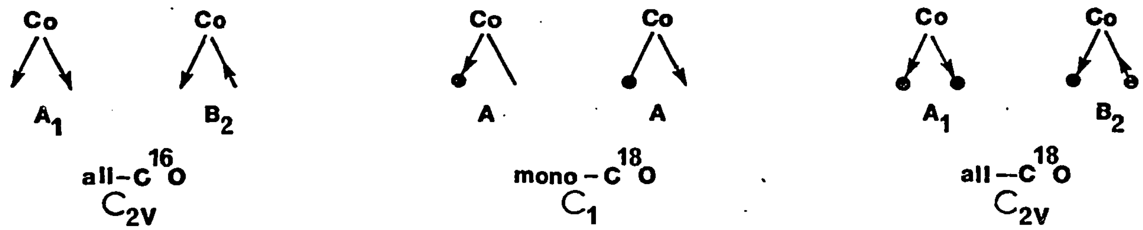


Fig. 26. Internal symmetry coordinates for the all-$^{12}C^{16}O$- and the $C^{18}O$-substituted carbonyl-containing moieties of (a) CpV(CO)$_4$ and (b) CpCo(CO)$_2$. The position of $C^{18}O$ is indicated by a heavy dot.

CHAPTER III RESULTS AND DISCUSSION

ASSIGNMENT OF THE CO STRETCHING FREQUENCIES OBSERVED DURING THE REACTIONS OF π-CYCLOPENTADIENYLMETAL CARBONYL COMPLEXES WITH ^{13}CO AND/OR C^{18}O

1. CpMn(CO)$_3$ and CpMn(CO)$_2$(*cis*-Cyclooctene)

The Mn(CO)$_3$ moiety in CpMn(CO)$_3$ possesses C_{3v} local symmetry for which two infrared-active CO stretching modes (A_1 and E) are expected. Substitution of one or two ^{13}CO (or C^{18}O) groups into the Mn(CO)$_3$ moiety lowers the symmetry to C_s for which three infrared-active CO stretching modes (2A' and A") should be observed in both cases. The trisubstituted species possesses the same local symmetry as the all-^{12}C^{16}O moiety and so two infrared-active CO stretching modes (A_1 and E) are expected for this species (see Table XIV and Fig. 25a).

The CO stretching absorptions of CpMn(CO)$_3$ in *n*-hexane solution before and after uv light induced exchange with 50% ^{13}C-enriched CO are shown in Figs. 27a and 27b, respectively. There is disagreement in the literature regarding the assignment of bands b and f. Haas and Sheline[101] have assigned them without any direct experimental proof to the two A' modes of the mono-^{13}CO substituted species present in natural abundance (3%) whereas Hyams *et al.*[102] prefer to assign them to overtone and/or combination vibrations. It is immediately

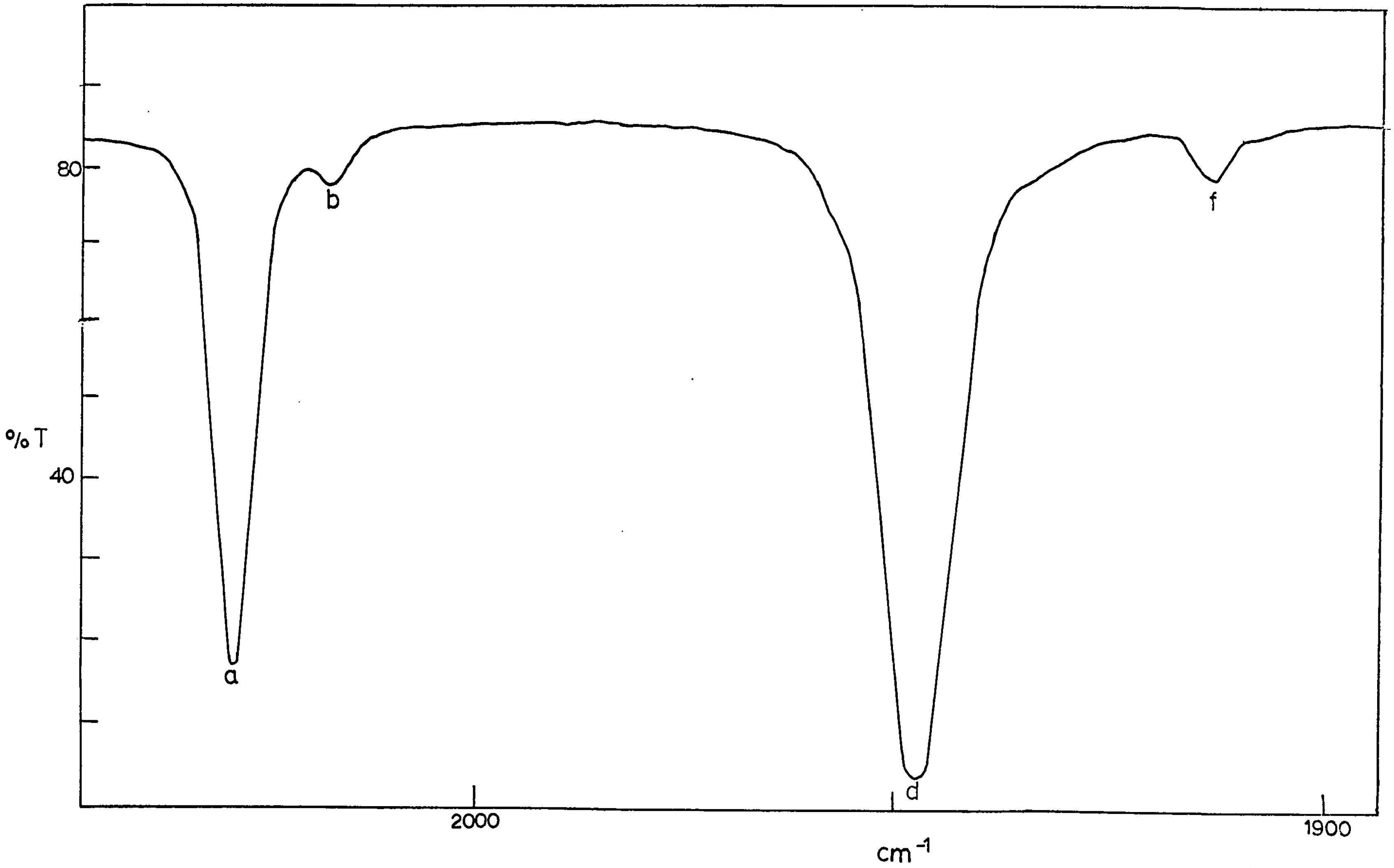


Fig. 27a. Infrared spectrum in the CO stretching region of CpMn(CO)$_3$ before uv light (16/2537 Å lamps) induced exchange with 50% ^{13}C-enriched CO (*n*-hexane solution).

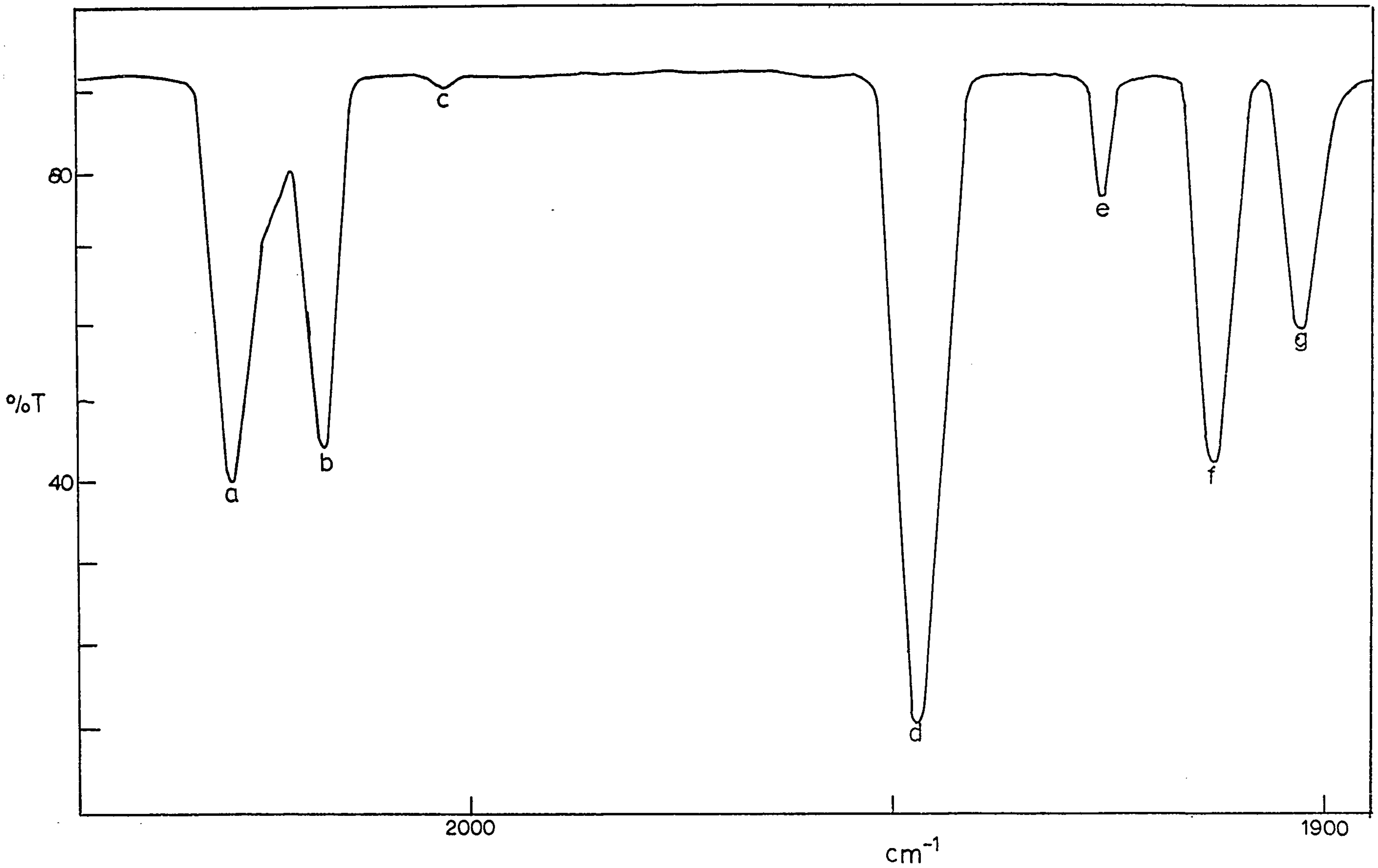


Fig. 27b. Infrared spectrum in the CO stretching region of CpMn$(CO)_3$ after 15 min uv light (16/2537 Å lamps) induced exchange with 50% ^{13}C-enriched CO (n-hexane solution).

evident from Fig. 27b that Haas and Sheline are correct in their assignment because bands b and f are greatly enhanced during the exchange with ^{13}CO. In addition, three new bands c, e, and g, attributable to the modes of the di-^{13}CO substituted species, have appeared. The actual frequencies and the proposed vibrational assignments are given in Table XVII. Since a band at *ca*. 1983 cm^{-1} is not observed, it appears that little or none of the all-^{13}CO species is formed during the reaction. This is not unexpected because of the relatively low enrichment of the ^{13}CO used and the photochemical instability of $CpMn(CO)_3$ itself. It may be mentioned in passing that the frequencies predicted for di-^{13}CO substituted species by Haas and Sheline are in excellent agreement (±1 cm^{-1}) with those observed in this work. This observation lends some credence to their method of calculating approximate force constants.

Angelici and Loewen[50] have shown that under kinetic conditions $CpMn(CO)_2(C_8H_{14})$ readily undergoes *cis*-cyclooctene substitution with triphenylphosphine in methylcyclohexane solution to form $CpMn(CO)_2PPh_3$. Consequently, it is reasonable to expect that CO might substitute into this olefin complex to give $CpMn(CO)_3$. To this end, the reactions of $CpMn(CO)_2(C_8H_{14})$ with ^{13}C- and ^{18}O-enriched CO in *n*-hexane solution at 40° were investigated. The CO stretching frequencies observed in these reactions and the proposed assignments are presented in Table XVII. The spectra before and after exchange for the

TABLE XVII. COMPARISON OF CALCULATED AND OBSERVED CO STRETCHING FREQUENCIES (cm^{-1}) FOR ^{13}CO- AND $C^{18}O$-SUBSTITUTED $CpMn(CO)_3$

			^{13}CO-Substituted				$C^{18}O$-Substituted		
				Observed from				Observed from	
Molecule and local symmetry	Vib. species	Input	Calcd.[a]	uv-induced exchange[b]		$CpMn(CO)_2(C_8H_{14})$[c]	Calcd.[a]	$CpMn(CO)_2(C_8H_{14})$	
all-$^{12}C^{16}O$ C_{3v}	A_1	2028.4	2028.4	$2028._4$s	(a)	$2028._4$s	2028.4	$2027._1$vvw	(h)
	E	1947.2	1947.2	$1947._2$vs	(d)	e	1947.2	e	
mono-substitution C_s	A'		2017.7	$2017._5$s	(b)	$2017._6$ms	2017.1	$2018._1$s	(i)
	A'		1914.0	$1912._4$s	(f)	$1912._8$ms	1910.9	$1913._6$s	(n)
	A"		1947.2	f		$1947._2$vs	1947.2	$1946._8$s	(l)
di-substitution C_s	A'		2004.4	$2003._3$w	(c)	$2003._3$vvw	2003.0	$2004._7$vvw	(j)
	A'		1926.7	$1925._6$m	(e)	$1925._6$vvw	1924.4	$1923._9$vw	(m)
	A"		1903.9	$1902._2$ms	(g)	g	1900.3	g	

TABLE XVII (Cont'd)

tri-sub-stitution C_{3v}	A_1	1983.3	1979.5
	E	1903.9	1900.3

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[a] Calculated force constants: $k_1 = 15.744$, $k_2 = 0.434$ mdyn/Å.

[b] After 15 min with 50% ^{13}C-enriched CO in *n*-hexane solution. Band designation in parentheses refer to Fig. 27b.

[c] After reaction for 1 week with 50% ^{13}C-enriched CO in *n*-hexane solution.

[d] After reaction for 9 days with 90% ^{18}O-enriched CO in *n*-hexane solution. Band designations in parentheses refer to Fig. 28b.

[e] Degenerate with A" mode of mono-substituted molecule.

[f] Degenerate with E mode of all-^{12}C^{16}O molecule.

[g] Hidden beneath the very weak band (o) due to the B_2 mode of the small amount of unreacted $CpMn(CO)_2(C_8H_{14})$ remaining. The A_1 and B_2 modes of $CpMn(CO)_2(C_8H_{14})$ are at $1964._3$ (k) and $1905._2$ cm^{-1} (o), respectively; the modes associated with the mono-^{13}CO species present in natural abundance are at $1949._4$ and $1876._8$ cm^{-1} (Fig. 28a).

reaction with 90% ^{18}O-enriched CO are shown in Figs. 28a and 28b, respectively. The data clearly indicate that CO under atmospheric pressure does indeed replace *cis*-cycloctene in $CpMn(CO)_2(C_8H_{14})$ to form $CpMn(CO)_3$.

The CO stretching frequencies for ^{13}C- and ^{18}O-enriched $CpMn(CO)_3$ are almost identical (to within 2 cm^{-1}). Similar results have been obtained previously for a number of other ^{13}C- and ^{18}O-enriched metal carbonyls e.g., *cis*-$Fe(CO)_4I_2$[103], $Mn(CO)_5Br$[104,105], and $CoCl_2(CO)(PEt_3)_2$[92]. This phenomenon is chiefly a consequence of the similarity of the reduced masses of ^{13}CO and $C^{18}O$ but it is also due in part to coupling of the CO modes with the low frequency metal-carbon stretching modes[92].

As expected, owing to the inertness of the CO groups in $CpMn(CO)_3$ towards exchange except under the influence of uv light, the product of the thermal reaction of $CpMn(CO)_2(C_8H_{14})$ with 90% ^{18}O-enriched CO is almost solely $CpMn(CO)_2(C^{18}O)$. There are also small amounts of $CpMn(CO)_3$, $CpMn(CO)(C^{18}O)_2$, and unreacted $CpMn(CO)_2(C_8H_{14})$ present. Some $CpMn(CO)_3$ is expected because the CO used was only 90% ^{18}O-enriched. It is also possible that $CpMn(CO)_3$ is formed by the thermal decomposition of $CpMn(CO)_2(C_8H_{14})$ (*vide supra*, p. 67). The di-$C^{18}O$ substituted species is formed probably because of some slight enrichment of $CpMn(CO)_2(C_8H_{14})$ prior to replacement of the olefin by $C^{18}O$.

It is of interest to note that in every $C^{18}O$ (or ^{13}CO) study on a metal carbonyl complex containing more than one CO

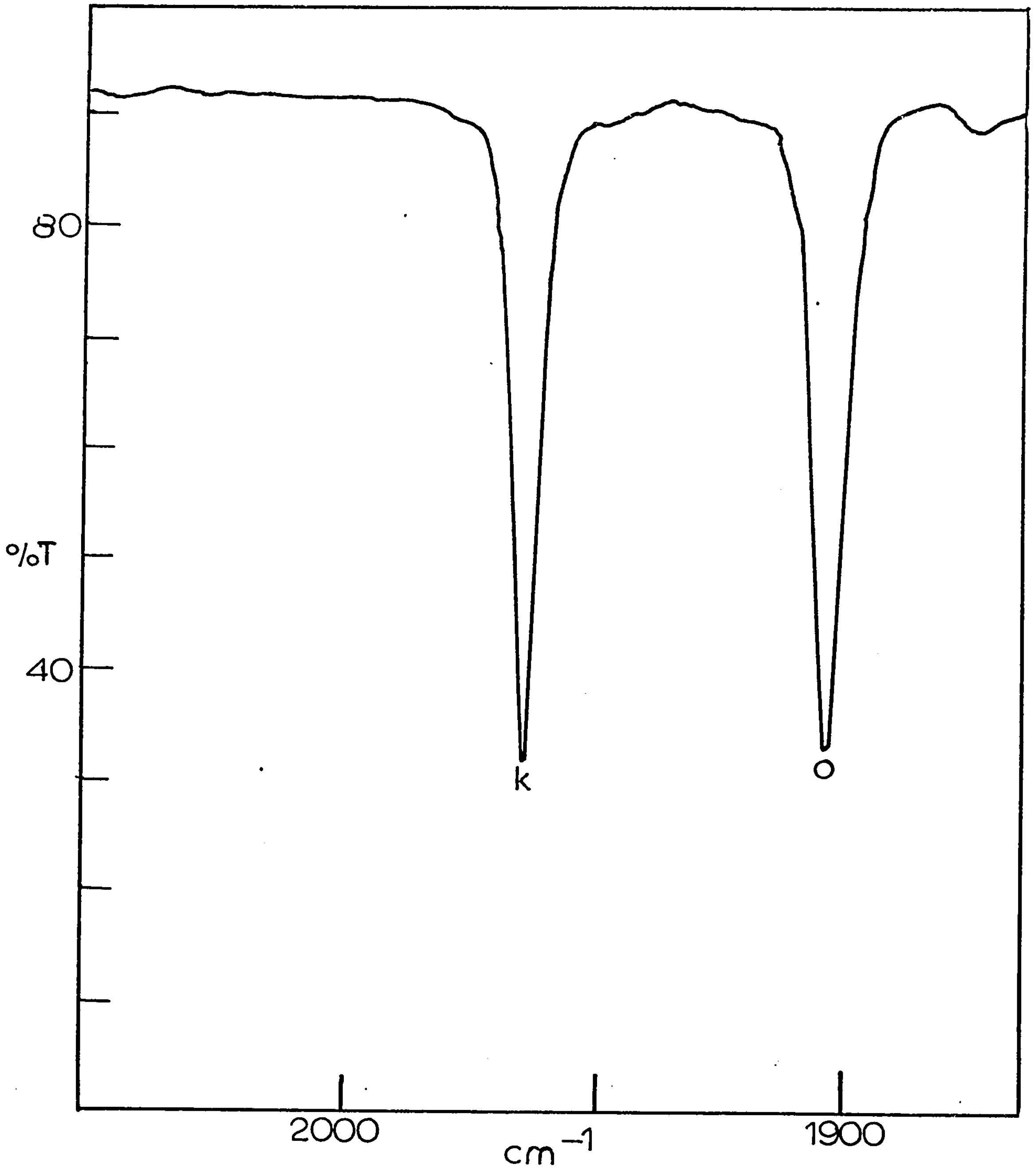

Fig. 28a. Infrared spectrum in the CO stretching region of $CpMn(CO)_2(C_8H_{14})$ before exchange with 90% ^{18}O-enriched CO at 40° (*n*-hexane solution).

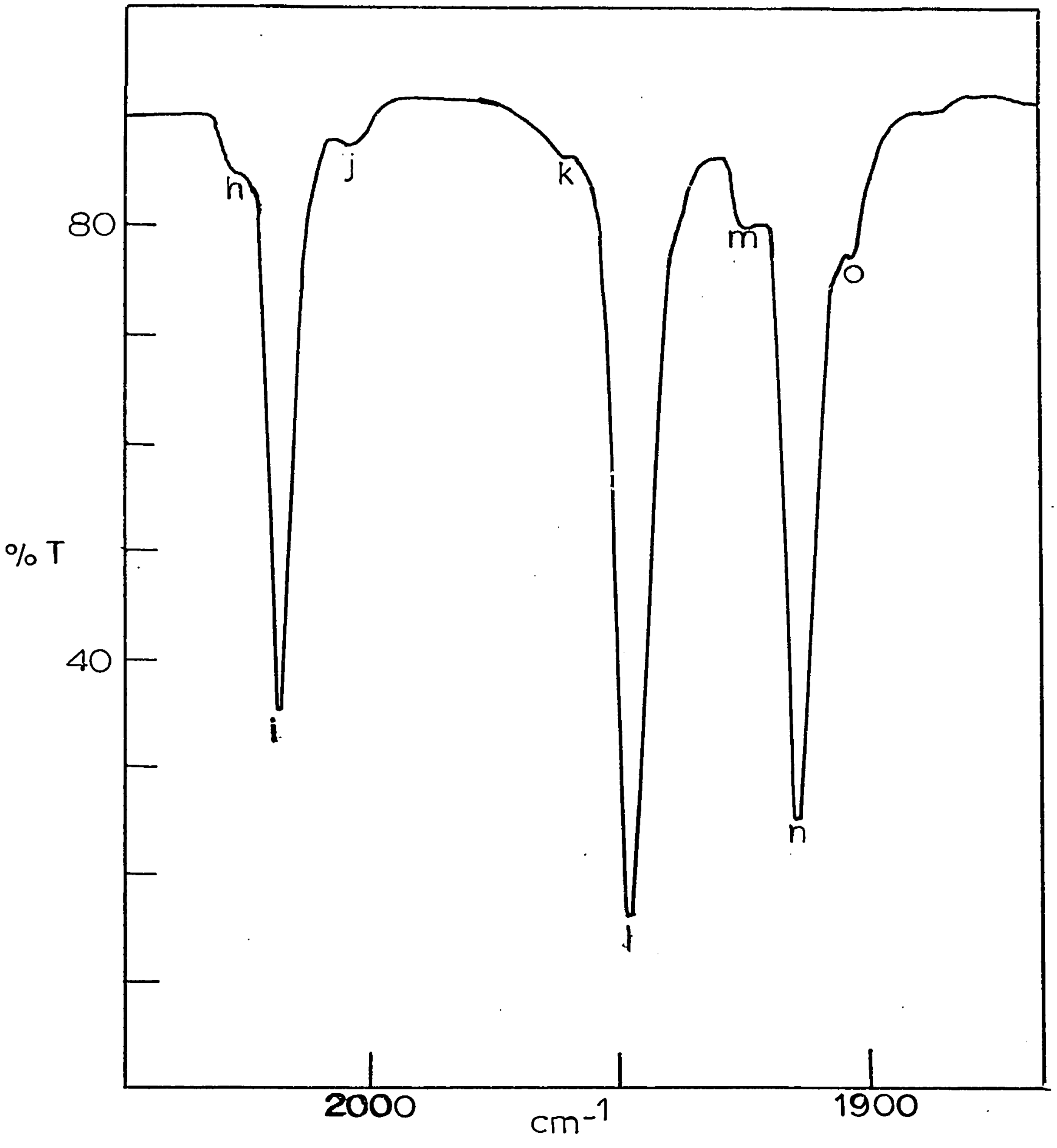

Fig. 28b. Infrared spectrum in the CO stretching region of $CpMn(CO)_2(C_8H_{14})$ after 9 days exchange with 90% ^{18}O-enriched CO at 40° (*n*-hexane solution).

group reported to date, it has not been possible to obtain the i.r. spectrum of a uniquely labelled species. For instance, in CO exchange reactions at least two CO groups are always replaced and the resulting i.r. spectra consist of the spectra of a variety of isotopically substituted species superimposed on the spectra of the parent molecules. In the present case, all three of the predicted CO stretching frequencies for CpMn$(CO)_2(C^{18}O)$ are observable directly (Fig. 28b). Moreover, bearing in mind that the intensity of the A" mode at 1947 cm^{-1} is enhanced slightly because of degeneracy with the E mode of the small amount of CpMn$(CO)_3$ present, the relative intensities of the three bands are approximately in the ratio 1:1:1, as predicted theoretically by Haas and Sheline[101]*. This is the first time that it has been possible to verify, even qualitatively, all the calculated intensities of the CO stretching modes of an isotopically substituted metal carbonyl species by direct experiment.

2. CpMn$(CO)_2$CS and CpMn(CO)(CS)(*cis*-Cyclooctene)

Following the synthesis of CpMn$(CO)_2$CS it was felt it would be of interest to study the photochemical reaction of the thiocarbonyl complex with $C^{18}O$ to determine whether or not

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*Strictly, their calculation was for the mono-^{13}CO substituted species. However, because the reduced masses of ^{13}CO and $C^{18}O$ are virtually identical and because the same force constants apply, the results of this calculation are also valid for the mono-$C^{18}O$ substituted species.

CO was replaced preferentially to CS. As with other π-cyclopentadienylmetal carbonyls, $CpMn(CO)_2CS$ is inert towards thermal substitution.

The $Mn(CO)_2$ moiety possesses C_{2v} symmetry for which two infrared-active CO stretching modes (A_1 and B_2) are expected. Substitution of one $C^{18}O$ group into the moiety lowers the symmetry to C_1 for which two modes (A) should be observed in the i.r. spectrum. Total substitution returns the symmetry to C_{2v} and two modes, A_1 and B_2, are expected (see Table XV and Fig. 25b).

The CO stretching absorptions present before and after uv induced reaction of $CpMn(CO)_2CS$ with 90% ^{18}O-enriched CO are shown in Figs. 29a and 29b, respectively. Continuation of the reaction for more than 5 min results in complete decomposition of the complexes present in the reaction mixture. This, despite the fact that four lamps, instead of 16 as for the uv exchange reaction with $CpMn(CO)_3$, were used. The measured CO stretching frequencies and the proposed assignments are given in Table XVIII.

Bands c and f are attributable to $CpMn(CO)(C^{18}O)CS$. These observed frequencies are in perfect agreement (±1 cm^{-1}) with those for bands h and i which are assigned to the corresponding ^{13}CO modes in the spectrum of $CpMn(CO)_2CS$ with natural abundance of ^{13}C (Fig.29a). The formation of $CpMn(CO)_3$ (bands a and e) is caused by the photochemical decomposition of $CpMn(CO)_2CS$ rather than replacement of CS by $C^{16}O$ present in the 90% ^{18}O-enriched CO. This was shown by irradiating

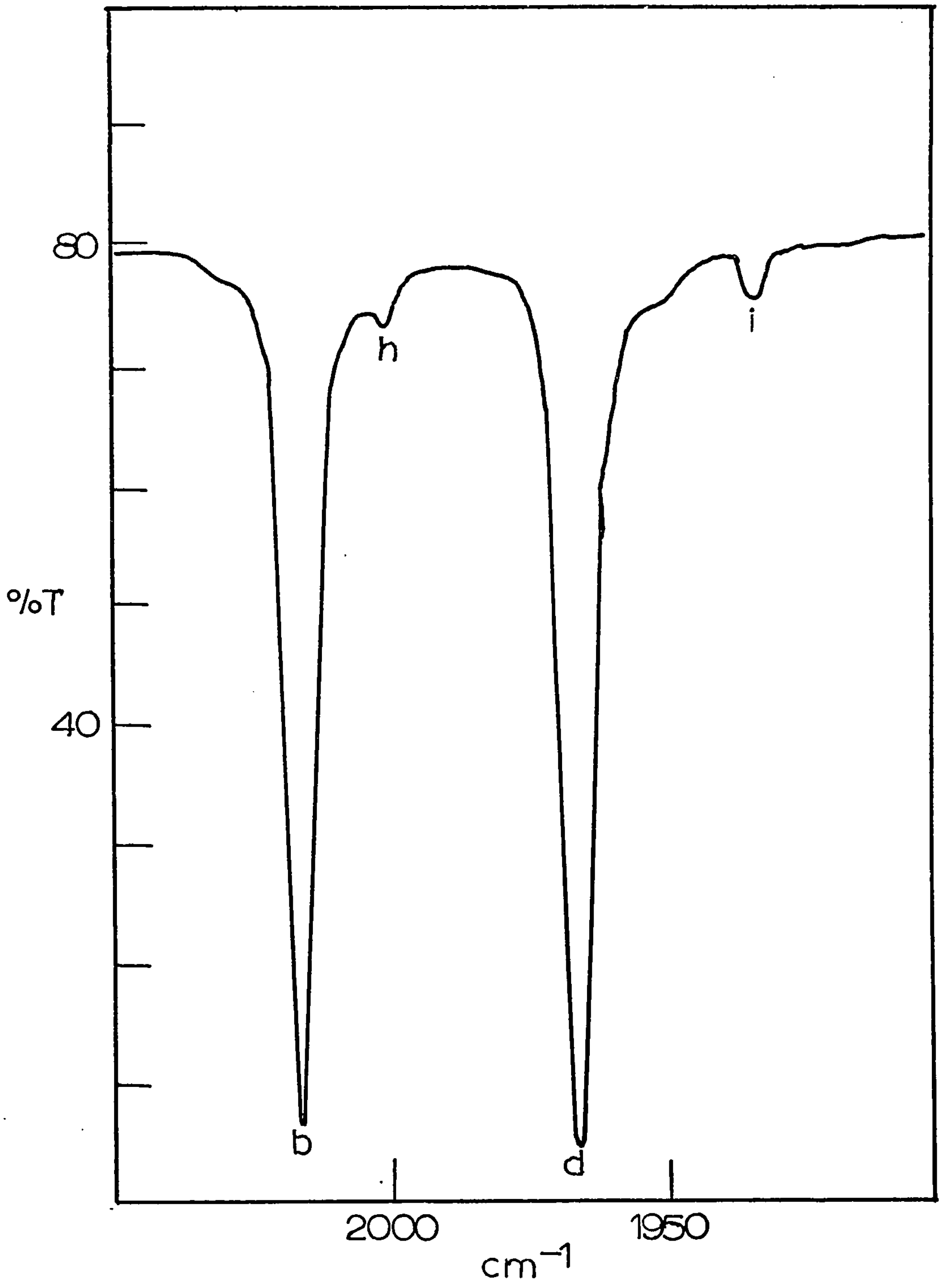

Fig. 29a. Infrared spectrum in the CO stretching region of $CpMn(CO)_2CS$ before uv light (4/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

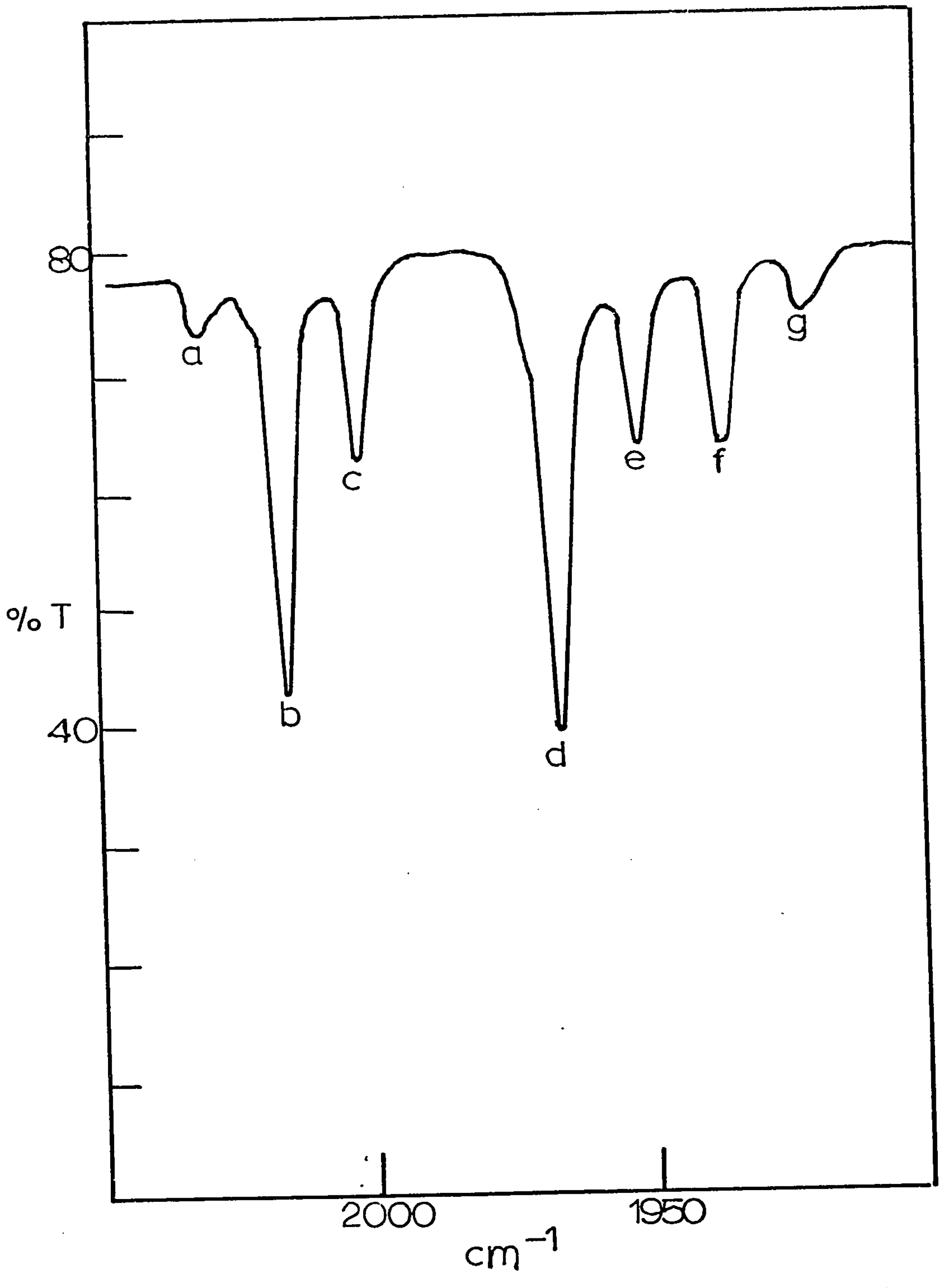

Fig. 29b. Infrared spectrum in the CO stretching region of $CpMn(CO)_2CS$ after 5 min uv light (4/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

TABLE XVIII. ASSIGNMENT OF THE CO STRETCHING FREQUENCIES OBSERVED AFTER REACTION OF CpMn(CO)$_2$CS WITH 90% ^{18}O-ENRICHED CO IN *n*-HEXANE SOLUTION

ν(CO) (cm^{-1})			Assignment	
Obsd.[a]	Band designation (Fig. 29b)	Calcd.[b]	Molecule	Vib. species and local symmetry
2027.$_7$w	(a)	2028.$_4$[c]	CpMn(CO)$_3$	$A_1(C_{3v})$
2012.$_5$s	(b)	2012.5	CpMn(CO)$_2$CS	$A_1(C_{2v})$
1998.$_5$m[d]	(c)	1997.9	CpMn(CO)(C^{18}O)CS	$A\ (C_1)$
1962.$_3$s	(d)	1962.3	CpMn(CO)$_2$CS	$B_2(C_{2v})$
		1964.0	CpMn(C^{18}O)$_2$CS	$A_1(C_{2v})$
1946.$_7$m	(e)	1947.$_2$[c]	CpMn(CO)$_3$	$E\ (C_{3v})$
1931.$_1$m[d]	(f)	1929.0	CpMn(CO)(C^{18}O)CS	$A\ (C_1)$
1917.$_8$w	(g)	1915.0	CpMn(C^{18}O)$_2$CS	$B_2(C_{2v})$

[a] After 5 min uv light induced reaction.

[b] The frequencies for the C^{18}O derivatives of CpMn(CO)$_2$CS were calculated using the frequencies of the parent complex at 2012.5 and 1962.3 cm^{-1} as input; the calculated force constants are: $k_3 = 15.951$, $k_4 = 0.403$ mdyn/Å.

[c] Observed frequencies (see Table XVII).

[d] The corresponding ^{13}CO modes (bands h and i in Fig. 29a) are at 1997.$_9$ and 1930.$_5$cm^{-1}, respectively.

$CpMn(CO)_2CS$ by itself in *n*-hexane solution; the amount of $CpMn(CO)_3$ formed was approximately the same as that for the exchange reaction.

At first sight, it seems impossible to say whether or not $CpMn(CO)_2(C^{18}O)$ and $CpMn(C^{18}O)_2CS$ are present. The former should exhibit absorptions at 2018, 1947, and 1914 cm^{-1} (Table XVII) – these could be associated with bands b, e, and g, respectively. The thiocarbonyl complex, $CpMn(C^{18}O)_2CS$, is expected to absorb at 1964 and 1915 cm^{-1} – these vibrations could possibly be associated with bands *d* and *g*. The solution to the problem hinges on whether or not it should be possible under the experimental conditions employed to differentiate between the A' mode of $CpMn(CO)_2(C^{18}O)$ at 2018 cm^{-1} and the A_1 mode of $CpMn(CO)_2CS$ at 2013 cm^{-1}. Fortunately, as it will be shown shortly, the absorptions due to these modes can be resolved in the reaction of $CpMn(CO)(CS)(C_8H_{14})$. This means that $CpMn(CO)_2(C^{18}O)$ is not formed in the reaction of $CpMn(CO)_2CS$ with ^{18}O-enriched CO. Moreover, the presence of band g indicates that the di-$C^{18}O$ substituted species, $CpMn(C^{18}O)_2CS$, is formed. The observed shift in the B_2 modes of $CpMn(CO)_2CS$ and $CpMn(C^{18}O)_2CS$ is $44._5$ cm^{-1} which is very close to the expected value of 47.2 cm^{-1}. That the exact shift expected is not observed for vibrations of totally ^{13}CO- or $C^{18}O$-substituted species has been explained by coupling of the CO stretching modes with the low-frequency metal-carbon stretching modes[92].

The fact that both CpMn(CO)($C^{18}O$)CS and CpMn($C^{18}O$)$_2$CS are formed whereas CpMn(CO)$_2$($C^{18}O$) is not indicates that, under the conditions employed, rupture of the Mn-CO bonds in CpMn(CO)$_2$CS is favoured over the rupture of the Mn-CS bond.

As mentioned above, the reaction of CpMn(CO)(CS)(C_8H_{14}) with ^{18}O-enriched CO has also been investigated. The CO stretching frequencies observed in *n*-hexane solution before and after exchange are shown in Figs. 30a and 30b, respectively; the actual frequencies and the proposed assignments are given in Table XIX. This reaction is much more complex than the analogous reaction of CpMn(CO)$_2$(C_8H_{14}) with ^{18}O-enriched CO discussed earlier.

Since CpMn(CO)(CS)(C_8H_{14}) is known to react with PPh$_3$ in methylcyclohexane solution to form CpMn(CO)(CS)PPh$_3$ (*vide supra*, p. 85), the chief product expected from the reaction with ^{18}O-enriched CO is CpMn(CO)($C^{18}O$)CS. A little CpMn(CO)$_2$CS should also be formed. However, in addition to these products it is possible to identify the following complexes from their infrared-active CO stretching absorptions: CpMn(CO)$_3$ (bands a and f), CpMn(CO)$_2$($C^{18}O$) (bands b, f, and h), and a little CpMn(CO)$_2$(C_8H_{14}) (band i, the other absorption expected is hidden beneath band e). Extensive decomposition occurs during the reaction, as evidenced by the formation of a large amount of a brown precipitate. These results emphasize that CpMn(CO)(CS)(C_8H_{14}) is much more thermally unstable than

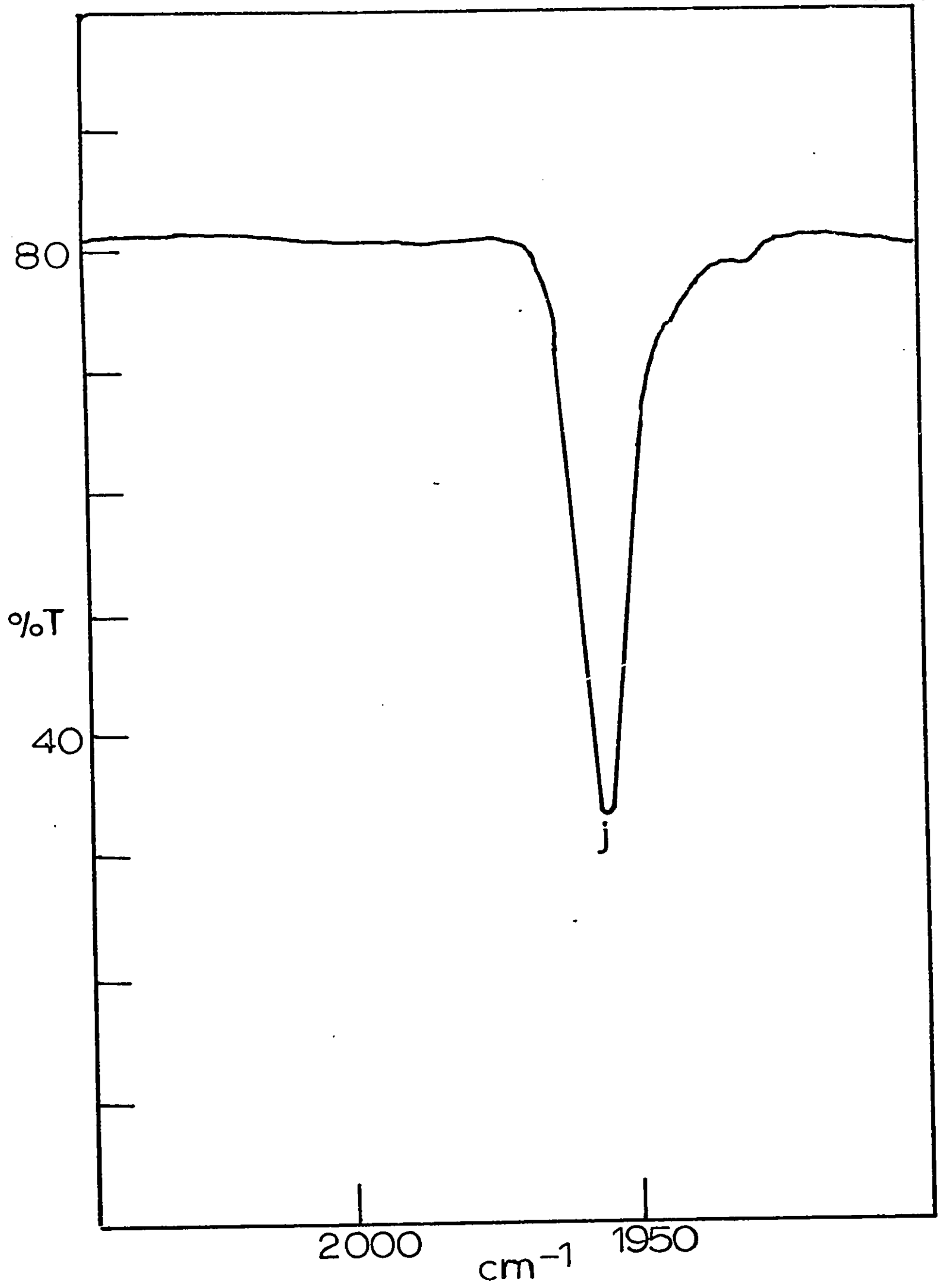

Fig. 30a. Infrared spectrum in the CO stretching region of $CpMn(CO)(CS)(C_8H_{14})$ before exchange with 90% ^{18}O-enriched CO at 45° (*n*-hexane solution).

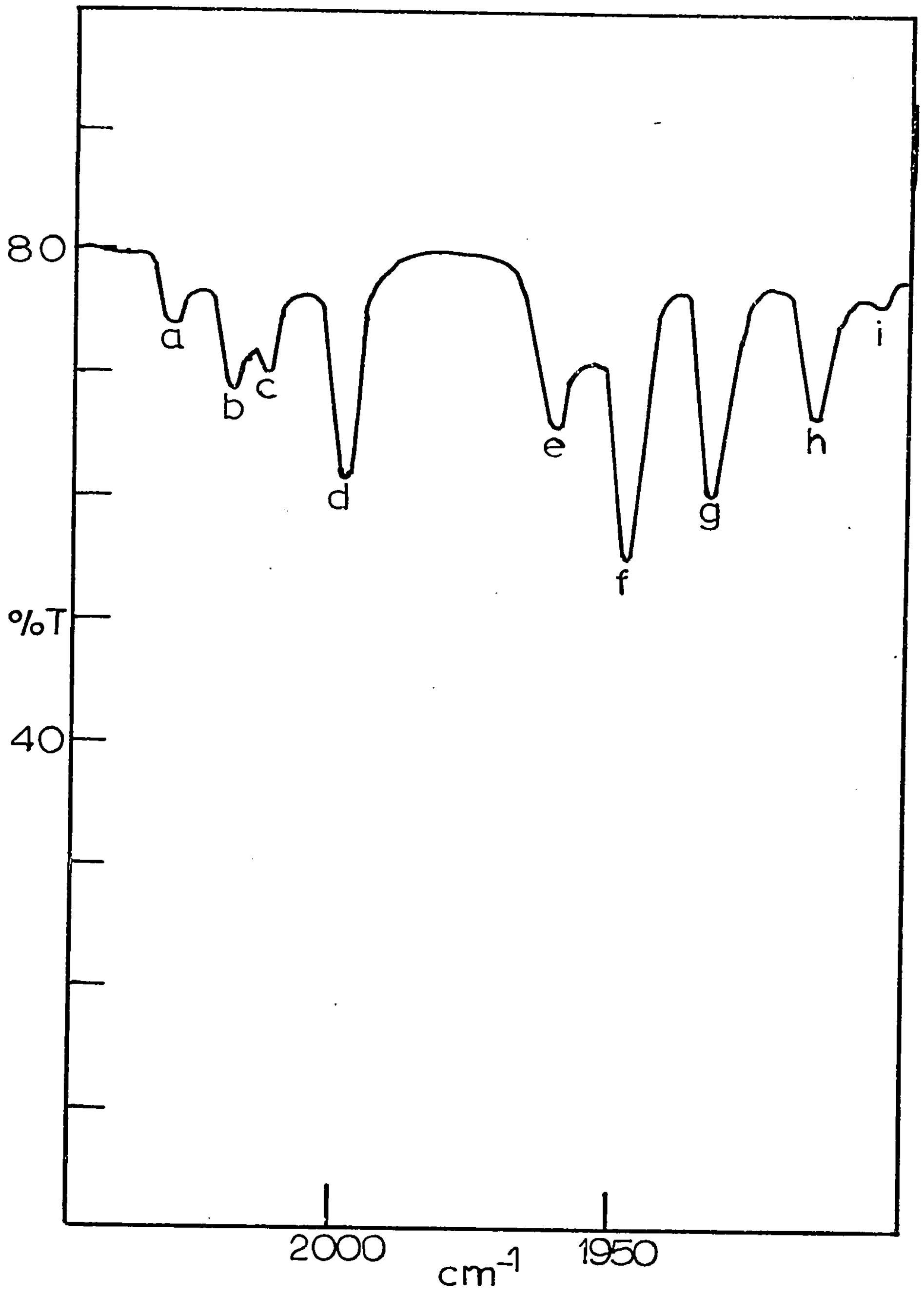

Fig. 30b. Infrared spectrum in the CO stretching region of CpMn(CO)(CS)(C_8H_{14}) after 19 hr exchange with 90% ^{18}O-enriched CO at 45° (*n*-hexane solution).

TABLE XIX. ASSIGNMENT OF THE CO STRETCHING FREQUENCIES OBSERVED AFTER REACTION OF CpMn(CO)(CS)(C_8H_{14}) WITH 90% ^{18}O-ENRICHED CO IN *n*-HEXANE SOLUTION

ν(CO) (cm^{-1})		Assignment		
Obsd.[a]	Band designation (Fig. 30b)	Molecule	Vib. species and local symmetry	Previously obsd. freq. (cm^{-1})[b,c]
$2027._8$w	(a)	CpMn(CO)$_3$	$A_1(C_{3v})$	$2028._4$
$2017._5$ms	(b)	CpMn(CO)$_2$($C^{18}O$)	$A'(C_s)$	$2018._1$
$2011._9$m	(c)	CpMn(CO)$_2$CS	$A_1(C_{2v})$	$2012._5$
$1997._9$s	(d)	CpMn(CO)($C^{18}O$)CS	$A\ (C_1)$	$1998._5$
$1961._3$ms	(e)	CpMn(CO)$_2$CS	$B_2(C_{2v})$	$1962._3$
		CpMn(CO)$_2$(C_8H_{14})	$A_1(C_{2v})$	$1964._3$
$1946._3$vs	(f)	CpMn(CO)$_3$	$E\ (C_{3v})$	$1947._2$
		CpMn(CO)$_2$($C^{18}O$)	$A''(C_s)$	$1946._8$
$1932._3$s	(g)	CpMn(CO)($C^{18}O$)CS	$A\ (C_1)$	$1931._1$
$1913._8$ms	(h)	CpMn(CO)$_2$($C^{18}O$)	$A'(C_s)$	$1913._6$
$1904._0$vw	(i)	CpMn(CO)$_2$(C_8H_{14})	$B_2(C_{2v})$	$1905._2$

[a] After reaction for 19 hr at 45°.

[b] See Tables XVII and XVIII.

[c] The single mode (A) associated with CpMn(CO)(CS)(C_8H_{14}) occurs at $1957._9$ cm^{-1} (band j in Fig. 30a).

$CpMn(CO)_2(C_8H_{14})$*. Presumably, the amount of $C^{18}O$ present in solution is insufficient to stabilize all of the highly reactive intermediate, CpMn(CO)CS, which is formed by the slow dissociation of C_8H_{14} from $CpMn(CO)(CS)(C_8H_{14})$ (*vide supra*, p. 116). Similar results are obtained for the reaction of $CpMn(CO)(CS)(C_8H_{14})$ with PPh_3 when the ligand is not present in excess; decomposition occurs and $CpMn(CO)_2CS$, $CpMn(CO)_3$, and $CpMn(CO)_2PPh_3$ are formed in addition to the expected product, $CpMn(CO)(CS)PPh_3$.

3. $CpV(CO)_4$

Recently, Durig *et al.*[106] successfully assigned the complete i.r. and Raman spectra of $CpV(CO)_4$ on the basis of the concept of local symmetry. Of particular interest to the work being discussed in this part of the thesis is the fact that these workers were able to assign unequivocally the two infrared-active (A_1 and E) and the solitary Raman-active (B_1) CO stretching modes of the C_{4v} $V(CO)_4$ moiety. Substitution of one of the four equivalent CO groups in the $V(CO)_4$ moiety by $C^{18}O$ will lower the symmetry to C_s for which four infrared-active CO stretching modes (3A' and A") are expected. The next $C^{18}O$ molecule can substitute either *cis* or *trans* to the first one. The symmetry of the *cis* species

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*In methylcyclohexane solution at 70°, the rate for the thermal decomposition of $CpMn(CO)(CS)(C_8H_{14})$ [to form $CpMn(CO)_3$, $CpMn(CO)_2CS$, and a brown precipitate] is approximately four times faster than that for $CpMn(CO)_2(C_8H_{14})$ [to form $CpMn(CO)_3$ and a brown precipitate].

is C_s for which four infrared-active CO stretching modes (2A' and 2A") should be observed. The *trans* species possesses C_{2v} symmetry and should also have four infrared-active CO stretching modes ($2A_1$, B_1, and B_2). Trisubstitution by $C^{18}O$ gives a species of symmetry C_s for which four infrared-active CO stretching modes (3A' and A") are expected. Finally, complete substitution returns the symmetry to the original C_{4v} for which one Raman-active (B_1) and two infrared-active (A_1 and E) CO are expected (see Table XVI and Fig. 26a).

The infrared spectral changes occurring in the CO stretching region during the uv light induced exchange of $CpV(CO)_4$ in *n*-hexane solution with 90% ^{18}O-enriched CO are shown in Figs. 31a-31d. It is evident from Fig. 31b that the four CO groups in $CpV(CO)_4$ are exchanged extremely rapidly; the half-life for the reaction is less than 1 min. The reaction reaches an equilibrium after 30 min. However, the A_1 and E modes of $CpV(C^{18}O)_4$ are easily identified as the absorptions at $1985._2$ (band n) and $1886._4$ cm^{-1} (band o), respectively, from their observed shifts (*ca.* 45 cm^{-1}) from the modes of the same symmetry for $CpV(CO)_4$. The frequency associated with the E mode of $CpV(C^{18}O)_4$ was used as the third input frequency necessary to calculate the three force constants associated with the $V(CO)_4$ moiety. The frequencies observed during the exchange and the proposed assignments are presented in Table XX. The data indicate that all the possible $C^{18}O$-substituted species are formed during the reaction.

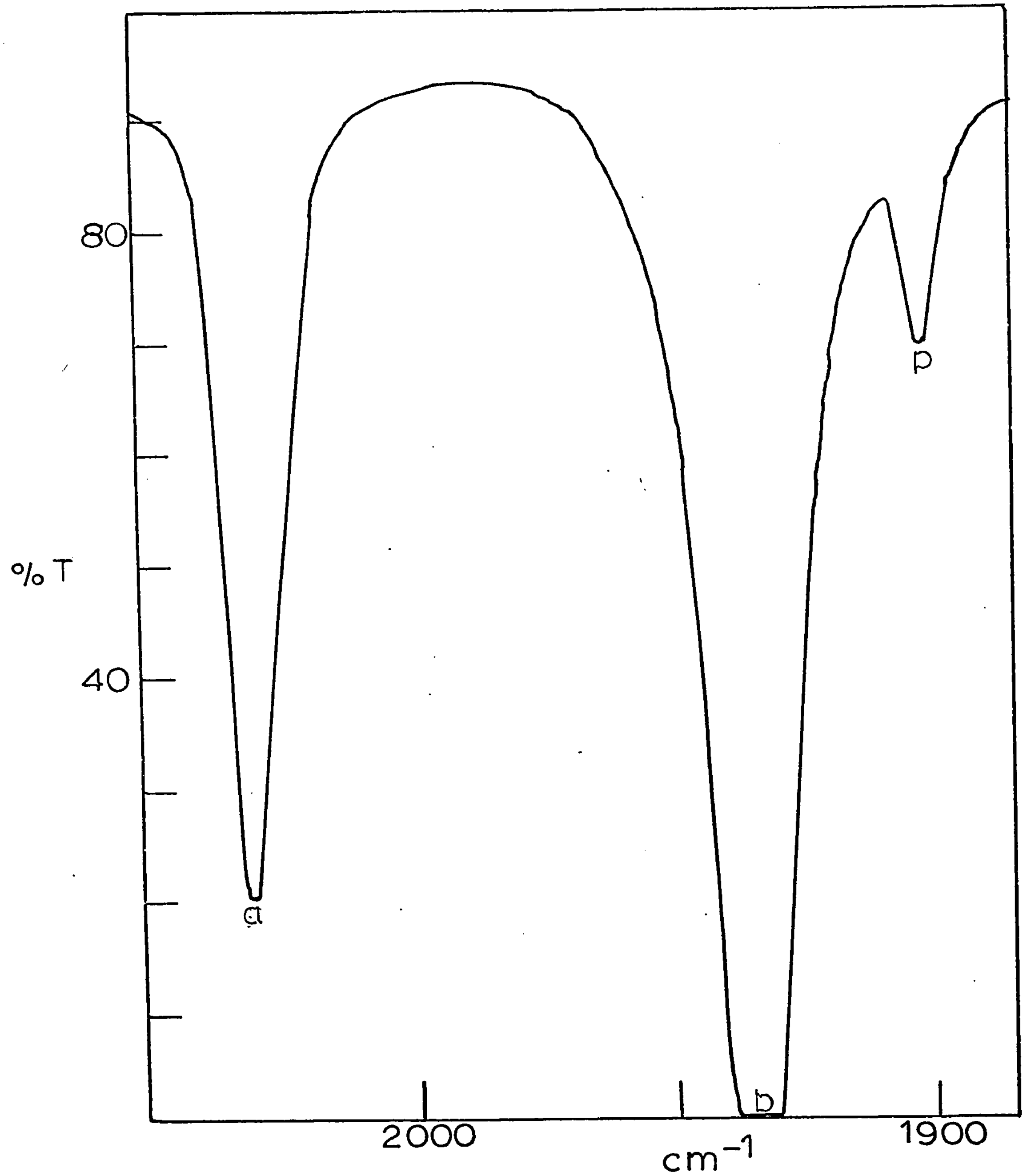

Fig. 31a. Infrared spectrum in the CO stretching region of $CpV(CO)_4$ before uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

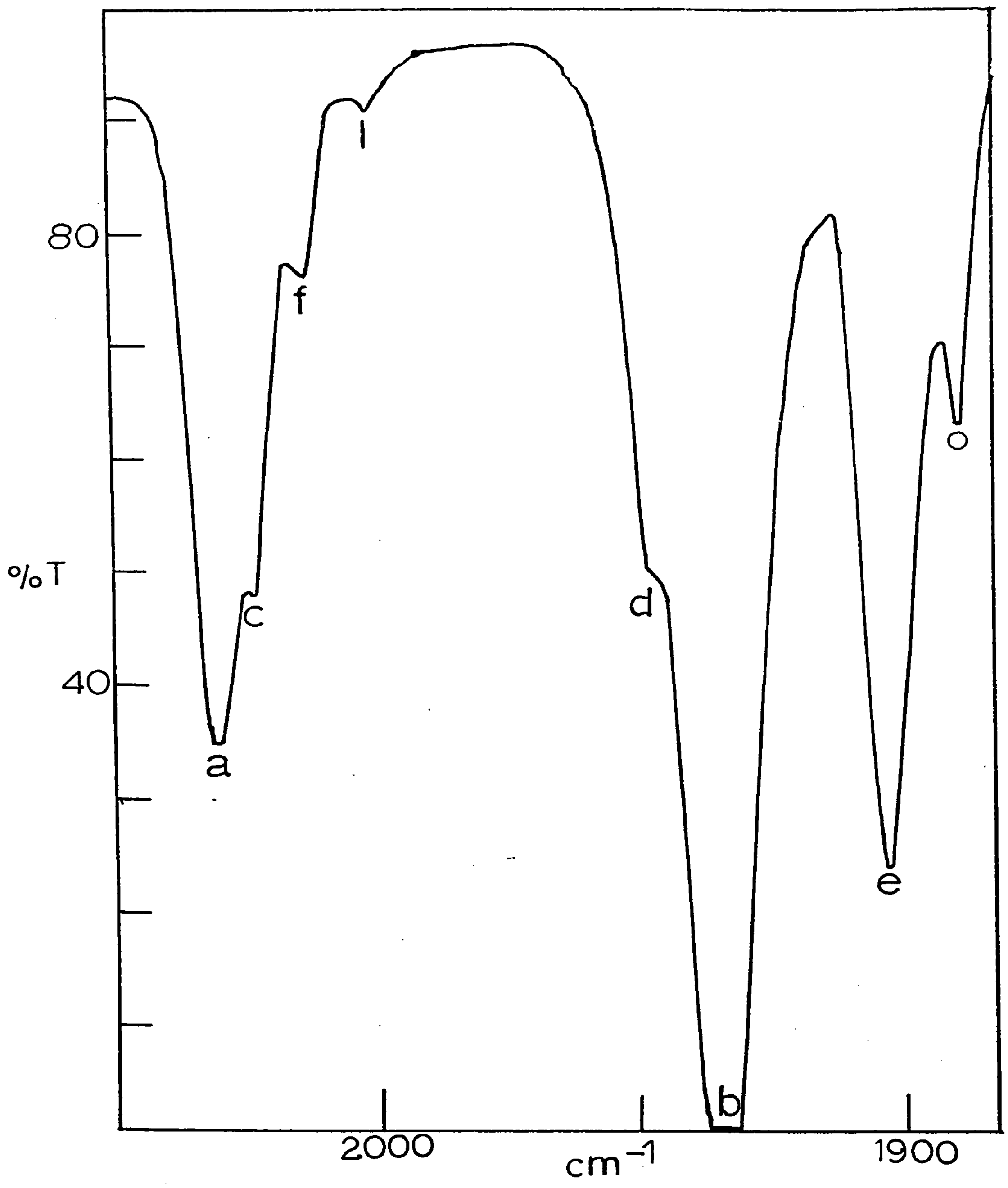

Fig. 31b. Infrared spectrum in the CO stretching region of $CpV(CO)_4$ after 1 min uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

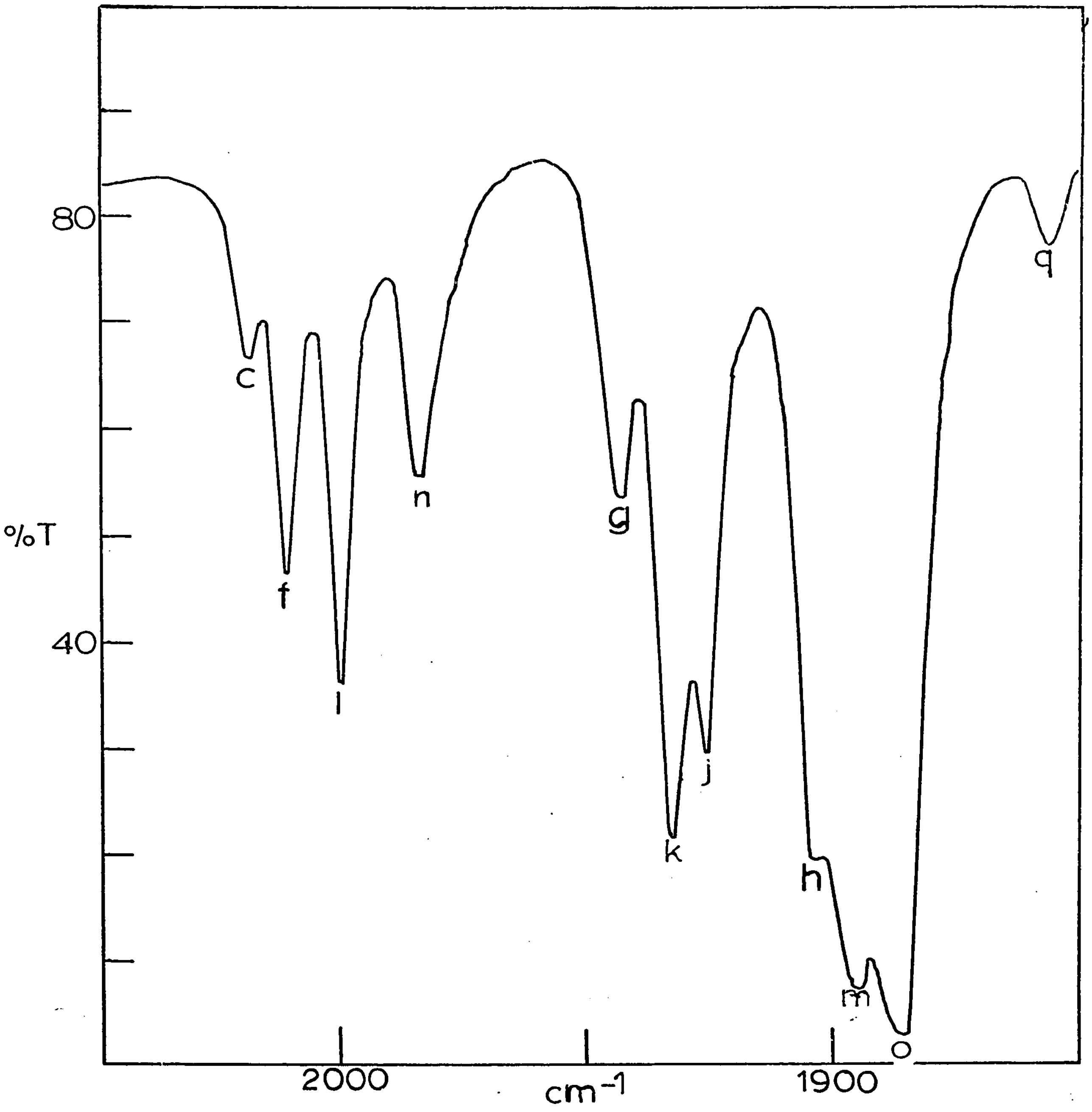

Fig. 31c. Infrared spectrum in the CO stretching region of $CpV(CO)_4$ after 10 min uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

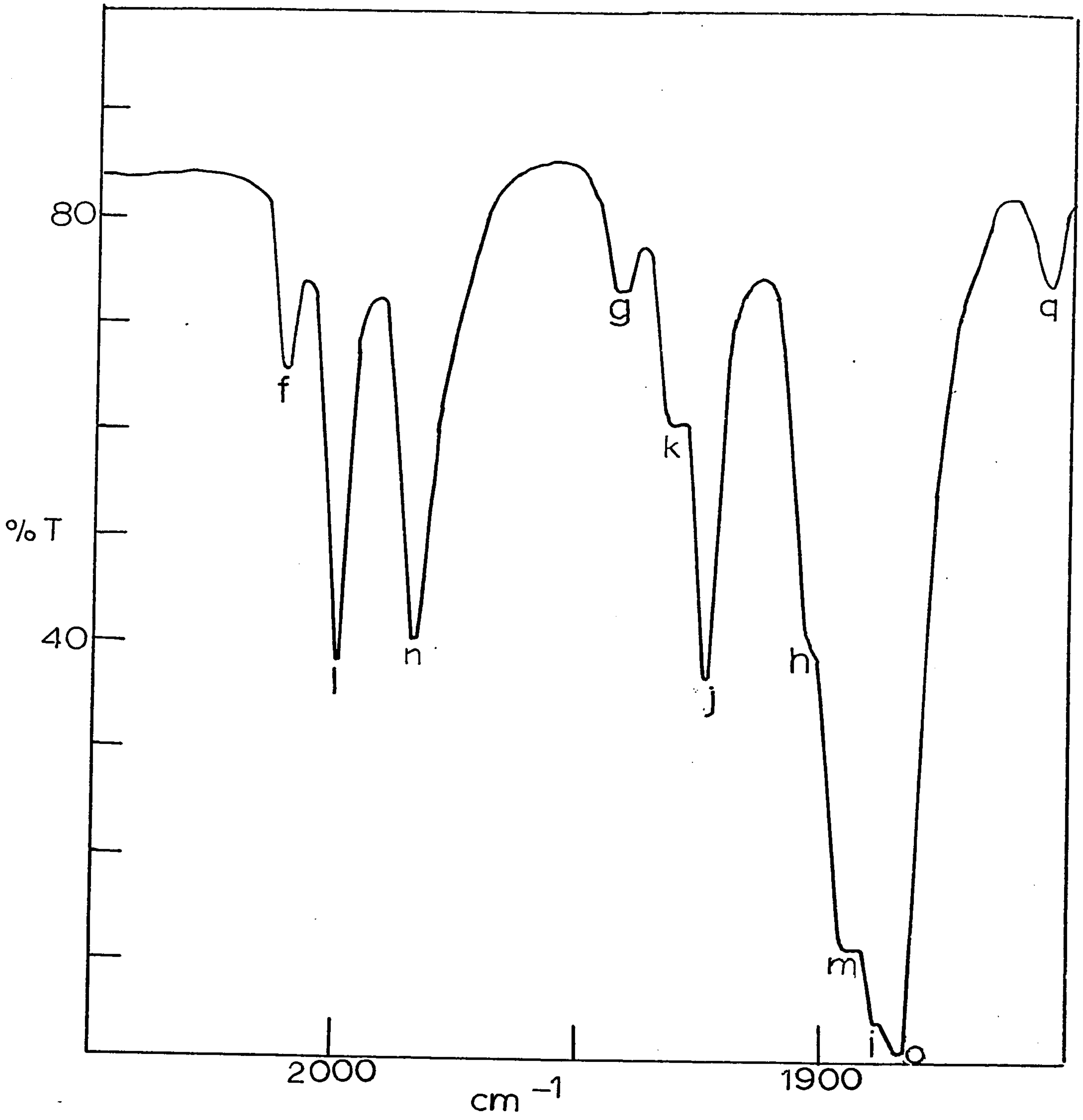

Fig. 31d. Infrared spectrum in the CO stretching region of $CpV(CO)_4$ after 30 min uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

TABLE XX. COMPARISON OF OBSERVED AND CALCULATED CO STRETCHING FREQUENCIES FOR $C^{18}O$-SUBSTITUTED $CpV(CO)_4$

Molecule and local symmetry	Vib. species	ν(CO) (cm^{-1}) Obsd.[a]	Band designation (Figs. 31a-31d)	Input	Calcd.[b]
all-$C^{16}O$ C_{4v}	A_1	2028.$_4$	(a)	2028.4	2028.4
	B_1	c,d			1959.2
	E	1932.$_2$	(b)	1932.2	1932.6
mono-$C^{18}O$ substitution C_s	A'	2021.9	(c)		2020.0
	A'	∿1946sh	(d)		1953.2
	A'	1900.$_9$[e]	(e)		1899.6
	A"	f			1932.6
di-$C^{18}O$ *cis*-substitution C_s	A'	2012.$_6$	(f)		2009.6
	A'	1944.$_0$	(g)		1949.3
	A"	1904.$_9$	(h)		1903.6
	A"	∿1891sh	(i)		1895.6
di-$C^{18}O$ *trans*-substitution C_{2v}	A_1	g			2011.7
	A_1	1926.$_5$	(j)		1928.0
	B_1	h			1886.0
	B_2	1933.$_4$	(k)		1932.7

TABLE XX (Cont'd)

tri-$C^{18}O$ substitution C_s	A'	$2001._3$	(l)		1998.2
	A'	i			1928.9
	A'	$1895._7$	(m)		1897.8
	A"	h			1886.0
all-$C^{18}O$ C_{4v}	A_1	$1985._2$	(n)		1979.5
	B_1	c			1912.0
	E	$1886._4$	(o)	1886.4	1886.0

[a] From spectra taken over a 30 min period after uv light initiation of the reaction in *n*-hexane solution.

[b] Calculated force constants: $k_5 = 15.569$, $k_6 = 0.279$, $k_7 = 0.488$ mdyn/Å.

[c] Raman-active only.

[d] Observed at 1954 cm^{-1} in cyclohexane solution[106].

[e] The corresponding ^{13}CO mode (band p in Fig.31a) occurs at $1899._5$ cm^{-1}.

[f] Degenerate with the E mode of the all-$C^{16}O$ molecule.

[g] Coincident with the highest frequency A' mode of the *cis*-di-$C^{18}O$ molecule.

[h] Degenerate with the E mode of the all-$C^{18}O$ molecule.

[i] Coincident with the lower frequency A_1 mode of the *trans*-di-$C^{18}O$ molecule.

In their study of $CpV(CO)_4$, Durig *et al.*[106] assigned a weak absorption in the solid-state Raman spectrum at 1960 cm^{-1} to the A_1 CO stretching mode of $CpV(^{13}CO)_4$. However, this assignment must be incorrect because only the mono-^{13}CO-substituted species will be present in any significant amount (4% natural abundance). It is possible that the 1960 cm^{-1} band is due to the A' mode of the mono-^{13}CO-substituted species expected at ∿1950 cm^{-1}. Alternatively, it could be a combination band of the A_1 ring breathing mode at 1117 cm^{-1} with the A_1 out-of-plane C-H deformation at 838 cm^{-1}.

The calculated frequency for the B_1 CO stretching mode of $CpV(CO)_4$ is 1959.2 cm^{-1} (Table XX), in good agreement with that observed[106] at 1954 cm^{-1} in the Raman spectrum in cyclohexane solution. This illustrates the utility of force constant calculations employing i.r. data from ^{13}CO and $C^{18}O$ exchange reactions in predicting the frequencies of infrared-inactive fundamentals of a parent molecule.

A new band (q) appears at 1857 cm^{-1} after the exchange reaction has proceeded for 10 min (Fig. 31c). This band is still present when the exchange reaction has reached equilibrium (Fig. 31d). It cannot be due to a $C^{18}O$-substituted $CpV(CO)_4$ molecule because the lowest frequency expected (and observed) is *ca.* 1886 cm^{-1}. Most probably, the 1857 cm^{-1} band is due to a combination vibration that was previously hidden in the case of the all-$C^{16}O$ molecule but, because of the isotopic shift associated with $C^{18}O$, has now become observable.

4. $CpCo(CO)_2$

The local symmetry of the $Co(CO)_2$ moiety in $CpCo(CO)_2$ is C_{2v}, the same as the $Mn(CO)_2$ moiety in $CpMn(CO)_2CS$. Consequently, the expected spectra for these two molecules in the CO stretching regions for the all-$C^{16}O$- and the $C^{18}O$-substituted species are similar (see Table XV and Fig. 26b). The CO stretching absorptions of $CpCo(CO)_2$ in *n*-hexane solution before and after 10 min exchange (when equilibrium is reached) with 90% O-enriched CO are shown in Figs. 32a and 32b, respectively. The measured frequencies and the proposed assignments are given in Table XXI. It is of interest that the extent of the exchange is affected by the nature of the solvent. In *n*-hexane solution, the reaction has reached equilibrium after 10 min and the CO absorption due to $CpCo(CO)_2$ have vanished completely; there are two pairs of CO absorptions present, one pair (bands c and d) belonging to $CpCo(CO)(C^{18}O)$, the other pair (bands e and f) to $CpCo(C^{18}O)_2$. However, in CS_2 solution after 30 min irradiation the exchange reaction has not reached equilibrium and the absorptions due to each of the three possible species are clearly discernible (Fig. 33). The reason for carrying out the exchange reaction in CS_2 as well as in *n*-hexane solution was to see whether any changes occur in the low i.r. frequency region during the exchange reaction. However, no significant changes could be detected. This is not unreasonable in view of the small shifts (<5 cm^{-1}) associated with the low frequency modes of $Ni(C^{16}O)_4$ and $Ni(C^{18}O)_4$[107].

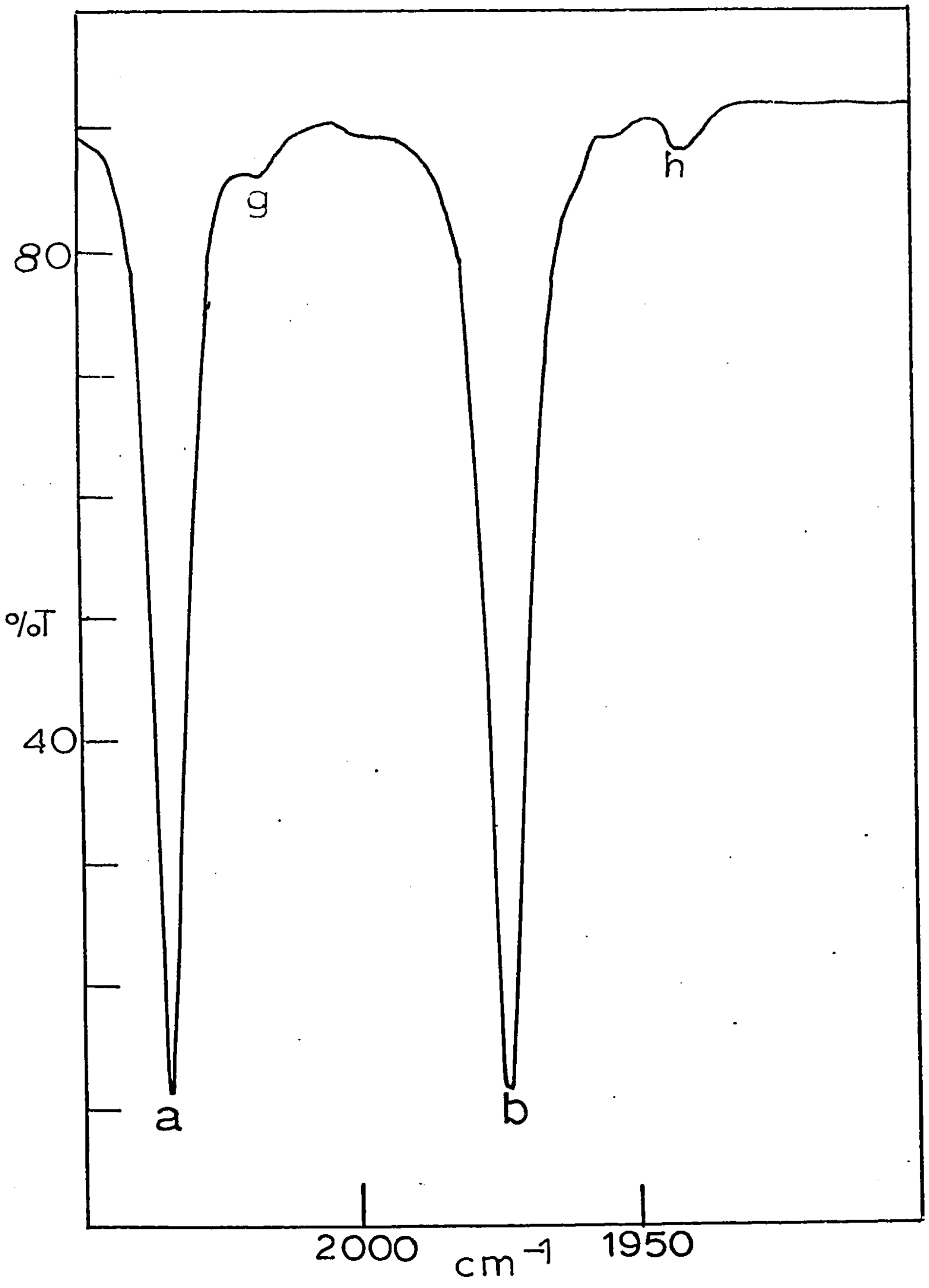

Fig. 32a. Infrared spectrum in the CO stretching region of $CpCo(CO)_2$ before uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

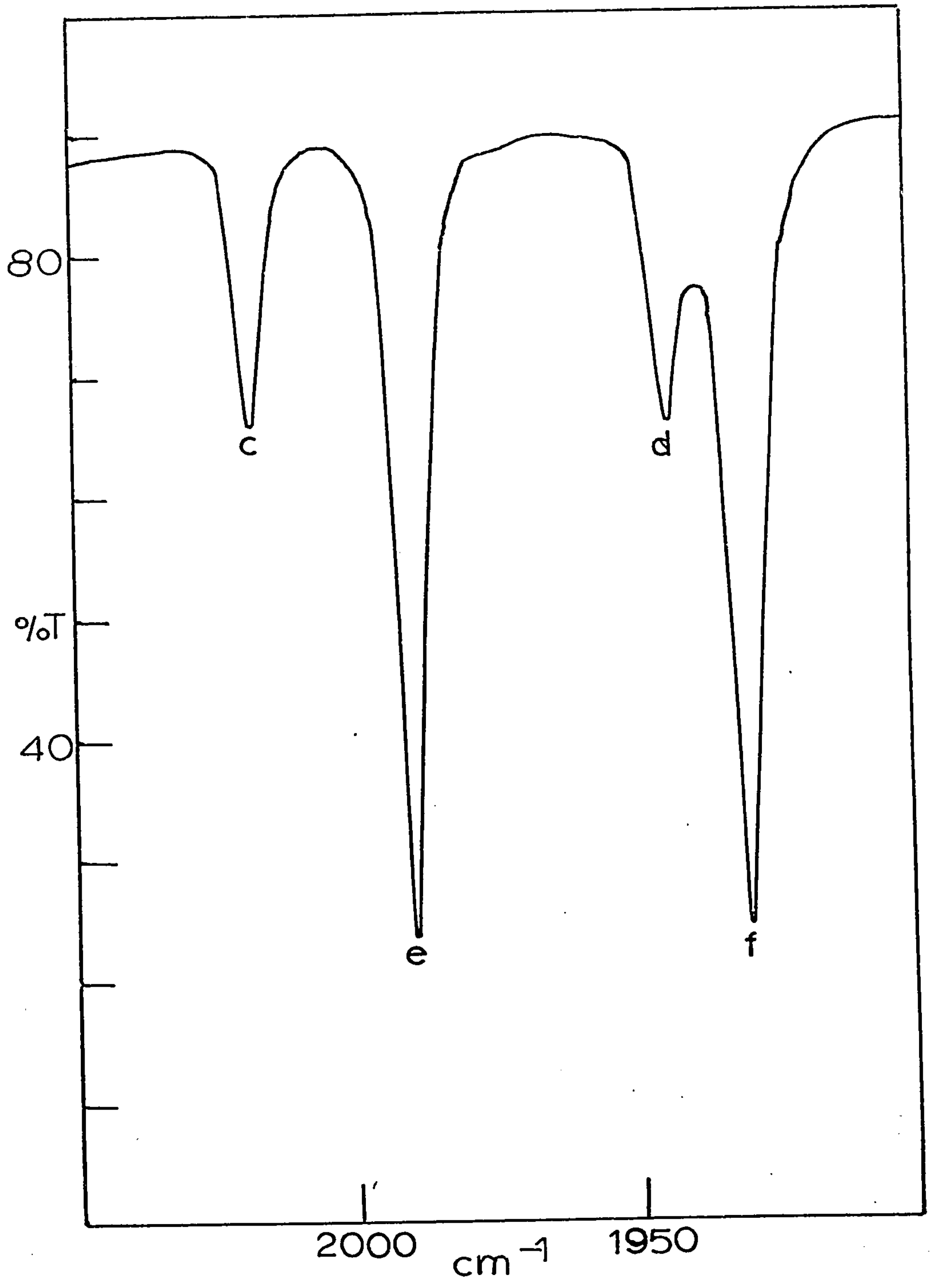

Fig. 32b. Infrared spectrum in the CO stretching region of $CpCo(CO)_2$ after 10 min uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (*n*-hexane solution).

TABLE XXI. COMPARISON OF OBSERVED AND CALCULATED CO STRETCHING FREQUENCIES FOR $C^{18}O$-SUBSTITUTED $CpCo(CO)_2$

Molecule and local symmetry	Vib. species	$\nu(CO)$ (cm^{-1})			
		Obsd.[a,b]	Band designation (Figs. 32a-32b)	Input	Calcd.[c]
all-$C^{16}O$ C_{2v}	A_1	$2029._8$	(a)	2029.8	2029.8
	B_2	$1970._4$	(b)	1970.4	1970.4
mono-$C^{18}O$ substitution[d] C_1	A	$2015._7$m	(c)		2014.0
	A	$1941._2$m	(d)		1938.0
all-$C^{18}O$ C_{2v}	A_1	$1987._0$s	(e)		1980.9
	B_2	$1927._7$s	(f)		1922.9

[a] After 10 min uv light induced reaction with 90% ^{18}O-enriched CO in *n*-hexane solution; bands a and b no longer present.

[b] The corresponding modes after 30 min uv light induced reaction with 90% ^{18}O-enriched CO in CS_2 solution are at: $2024._5$ (a), $1963._2$ (b), $2009._5$ (c), $1934._8$ (d), $1981._2$ (e), and $1919._9$ (f) cm^{-1}, respectively (Fig. 33).

[c] Calculated force constants: $k_8 = 16.157$, $k_9 = 0.480$ mdyn/Å.

[d] The corresponding ^{13}CO modes are at $2014._7$ (g) and $1938._9$ (h) cm^{-1}, respectively (Fig. 32a).

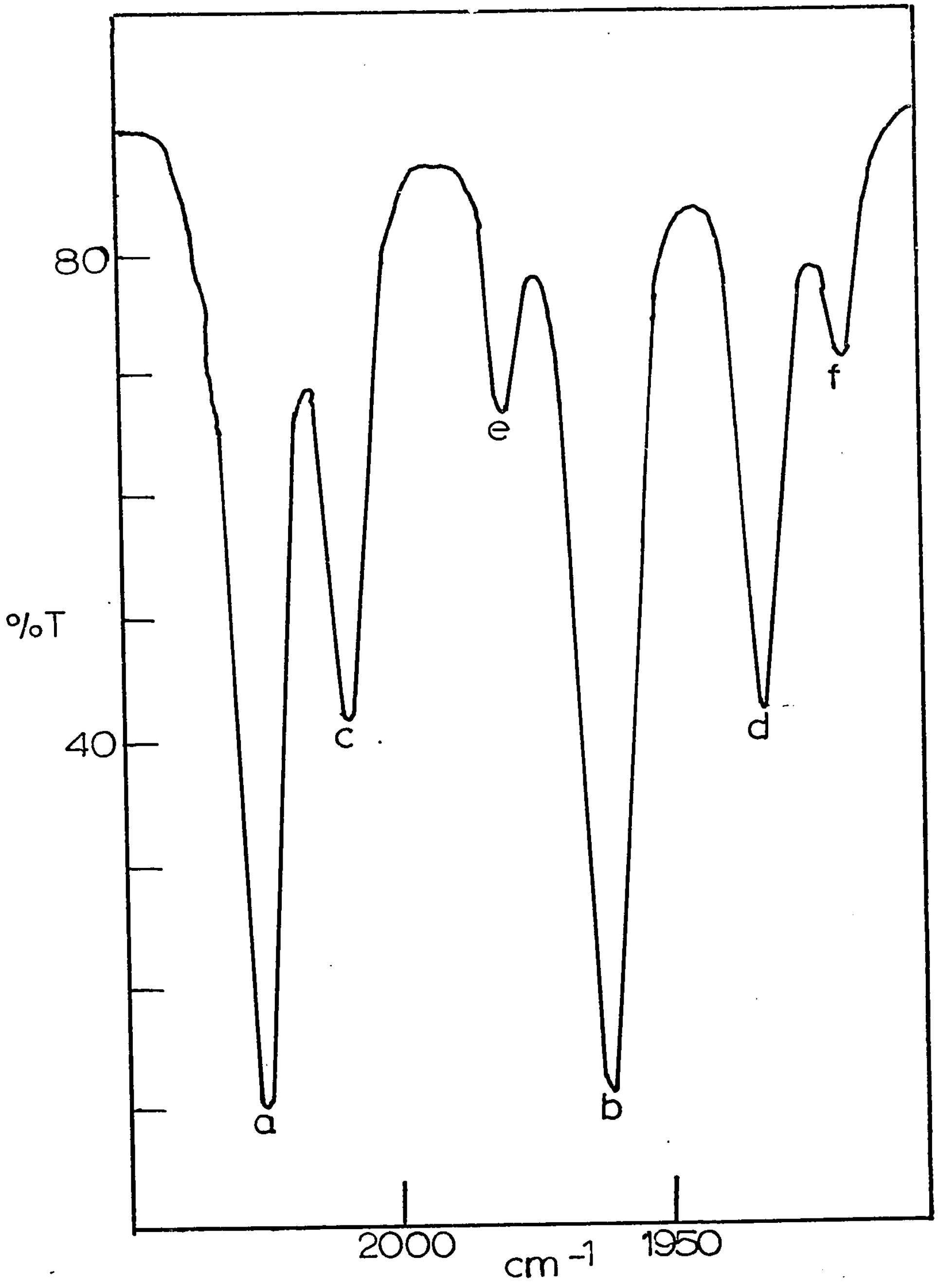

Fig. 33. Infrared spectrum in the CO stretching region of $CpCo(CO)_2$ after 30 min uv light (16/2537 Å lamps) induced exchange with 90% ^{18}O-enriched CO (CS_2 solution).

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SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

PART I

1. The literature on the activation of CS_2 by transition metal complexes has been reviewed for the first time.
2. The first thiocarbonyl complex, $CpMn(CO)_2CS$, has been synthesized in low yield from the reaction of the *cis*-cyclooctene complex, $CpMn(CO)_2(C_8H_{14})$, with CS_2. Addition of PPh_3 to this reaction mixture results in a high yield synthesis of the thiocarbonyl complex. Evidence has been obtained for the formation of the first π-CS_2 complex of manganese, $CpMn(CO)_2(\pi\text{-}CS_2)$, during the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2.
3. Kinetic data have been obtained for the reactions of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the absence and in the presence of PPh_3. A general mechanism for the synthesis of $CpMn(CO)_2CS$ from $CpMn(CO)_2$(olefin), CS_2, and PPh_3 has been proposed.
4. A preliminary spectroscopic investigation of the reaction of $CpMn(CO)_2(C_8H_{14})$ with Me_2S_2 has been conducted. On the basis of the data obtained it is suggested that the complex $CpMn(CO)_2(SMe)_2$ may be formed in the reaction.
5. The reactions of $CpMn(CO)_2CS$ with various ligands have been investigated. The complex, $CpMn(CO)(CS)(C_8H_{14})$, has been prepared from the photochemical reaction of $CpMn(CO)_2CS$ with C_8H_{14}. The complexes, $CpMn(CO)(CS)PPh_3$, $CpMn(CO)(CS)P(OMe)_3$, $[CpMn(CO)(CS)]_2$(diphos), and $CpMn(CS)$(diphos), have been

synthesized from the thermal reactions of CpMn(CO)(CS)(C_8H_{14}) with the appropriate ligand in *n*-hexane solution.

6. The dithiocarbonyl CpMn(CO)$(CS)_2$ has been obtained from the reaction of CpMn(CO)(CS)(C_8H_{14}) with CS_2 in the presence of PPh_3. The photochemical reaction of the dithiocarbonyl with C_8H_{14} affords the olefin derivative, CpMn$(CS)_2$(C_8H_{14}). This complex reacts with CS_2 and PPh_3 to give the trithiocarbonyl, CpMn$(CS)_3$, in low yield. The dithiocarbonyl and trithiocarbonyl complexes are the first examples of multiple CS groups attached to a single central metal. The olefin dithiocarbonyl and the trithiocarbonyl complexes are the first derivatives of CpMn$(CO)_3$ containing three non-carbonyl ligands to be prepared.
7. The i.r. spectra of the new complexes have been recorded in the CO and the CS stretching regions. A model has been proposed for the formation of M-CS bonds taking into account the observed shifts in the stretching frequency of the CS ligand upon coordination.
8. Laser Raman and proton n.m.r. data have been obtained for some of the new thiocarbonyl complexes. The mass spectra of CpMn$(CO)_2$CS, CpMn(CO)$(CS)_2$, and CpMn(CO)(CS)(C_8H_{14}) were obtained and fragmentation pathways from the respective molecular ions have been proposed. Prior to this work no Raman, proton n.m.r, or mass spectroscopic data on thiocarbonyls had been reported in the literature.

9. The kinetics and mechanism of the reaction in methylcyclohexane solution of CpMn(CO)(CS)(C_8H_{14}) with PPh_3 to form CpMn(CO)(CS)PPh_3 and C_8H_{14} have been investigated.

PART II

1. The reactions of the π-cyclopentadienyl carbonyl complexes, CpMn$(CO)_3$, CpMn$(CO)_2$(C_8H_{14}), CpMn$(CO)_2$CS, CpMn(CO)(CS)(C_8H_{14}), CpV$(CO)_4$, and CpCo$(CO)_2$ with isotopically enriched CO have been investigated by i.r. spectroscopy.
2. The observed frequencies associated with the different isotopically CO-substituted species formed have been assigned with the aid of approximate force constant calculations.