Thiocarbonyl complexes of chromium and tungsten

Bernard Duane Dombek

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Thiocarbonyl complexes of chromium and tungsten

by

Bernard Duane Dombek

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

1975
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**LIST OF SYMBOLS AND ABBREVIATIONS**

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<tr>
<th>Symbol</th>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>B</td>
<td>a base</td>
<td></td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridine</td>
<td></td>
</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
<td></td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
<td></td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl</td>
<td></td>
</tr>
<tr>
<td>DABCO</td>
<td>1,4-diazabicyclo [2.2.2] octane</td>
<td></td>
</tr>
<tr>
<td>decalin</td>
<td>decahydronaphthalene</td>
<td></td>
</tr>
<tr>
<td>diars</td>
<td>o-phenylenebis(dimethylarsine)</td>
<td></td>
</tr>
<tr>
<td>diphos</td>
<td>ethylenebis(diphenylphosphine)</td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
<td></td>
</tr>
<tr>
<td>HA</td>
<td>a protonic acid</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>a donor ligand</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
<td></td>
</tr>
<tr>
<td>Py</td>
<td>pyridine</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>an organic substituent group</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>a coordinating solvent molecule</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
<td></td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
<td></td>
</tr>
<tr>
<td>triphos</td>
<td>bis(2-diphenylphosphinoethyl)phenylphosphate</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>a halogen</td>
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I. INTRODUCTION

The thiocarbonyl ligand has recently attracted research of both theoretical and experimental nature because of its similarity to the familiar carbonyl ligand. The CS ligand is one of the simplest possible variations of the CO ligand, and can thus be considered as a "perturbation" of the carbonyl. The study of its complexes may therefore enhance the understanding of bonding and reactions of transition metal carbonyls in general.

The main barrier to the extensive study of transition metal thiocarbonyl complexes is the difficulty of initial formation of the metal-CS bond. Carbon monosulfide, unlike carbon monoxide, is unstable under normal levels of temperature and pressure. Therefore, few metal thiocarbonyl complexes were known when this work began, and surprisingly little was known about the chemical properties and reactions of the complexes or the coordinated ligand. The available evidence, however, indicated that the CS ligand was a stronger pi-acceptor than CO and thus was more strongly bound to the metal atom. The thiocarbonyl ligand also appeared to be more reactive than its oxygen analog. The field of transition metal thiocarbonyl chemistry was thus regarded as a potentially fruitful area of research. It was with the hope of preparing thiocarbonyl complexes suitable for spectroscopic and chemical study that this work was undertaken.
II. REVIEW OF THE LITERATURE

A. Carbon Monosulfide

1. Preparation and properties of carbon monosulfide

For many years carbon monoxide was the only formally divalent carbon compound known. Since it was expected that a sulfur analog should also be preparable, chemists made many attempts to form carbon monosulfide, which was anticipated to be a gas at room temperature. Several reactions were reported to give a polymeric form of CS; in one, CS$_2$ was exposed to sunlight for several months, and a similar polymeric product was obtained from the reaction between Ni(CO)$_4$ and Cl$_2$CS. Dewar and Jones, in 1910, were the first to observe monomeric CS, prepared from gaseous CS$_2$ by a high-frequency discharge. They were able to condense a liquid at the temperature of liquid air which exploded on warming to give a brown polymeric solid. Shortly thereafter, J. J. Thompson reported that the mass spectrum of CS$_2$ showed a strong peak at m/z 44 when an electric discharge was passed through the CS$_2$ vapor. Soon the electronic spectrum of carbon monosulfide was investigated. This provided a certain method for detection of the CS molecule.

Carbon monosulfide has been shown to be a product in the following reactions:

a. Photolysis of CS$_2$ in the vapor phase

b. Photolysis of CS$_2$ in a matrix

c. Thermal CS$_2$ dissociation
d. Dissociation of $\text{CS}_2$ in a high-frequency discharge$^{3,12,27-34}$
e. Reaction of $\text{CS}_2$ with $\text{O}$ atoms$^{8,35-37}$
f. Reaction of $\text{CS}_2$ with $\text{S}$ atoms$^{38}$
g. Dissociation of $\text{COS}$ in a high-frequency discharge$^{39}$
h. Reaction of MnS and C at elevated temperature$^{40}$
i. Ar and Xe metastable atom energy transfer to $\text{CS}_2$, $\text{COS}$, and $\text{Cl}_2\text{CS}^{41}$

Carbon monosulfide has also been observed in the upper atmosphere$^{42}$ and in interstellar space.$^{43}$ The best synthetic method for preparing useful quantities of CS is by the use of a high-frequency discharge.$^{32,34}$

The stability of CS in the gas phase is determined by many factors, including the temperature, partial pressure, dimensions of the container, and the condition of the surface of the container.$^{8,16,29,44}$ In a clean vessel the lifetime of CS at 40-80 torr is on the order of minutes, but it is reduced to seconds once a surface deposit is formed. The loss of CS from the gas phase is a wall reaction, and the data are not consistent with the simple polymerization of the molecule. A carbon-rich solid and $\text{CS}_2$ are reported$^{44}$ to be the products of the surface decomposition.

The decomposition of CS in the condensed phase is also apparently not a simple polymerization. Steudel$^{32}$ has concluded that the condensed ($-190^\circ$) product resulting from passing $\text{CS}_2$ through a discharge is a mixture of $\text{CS}_2$, $\text{CS}$, and $\text{C}_3\text{S}_2$. As the mixture is slowly warmed, the amount of CS decreases as more $\text{C}_3\text{S}_2$ is produced, perhaps by disproportionation of the CS. The polymer that results often contains free sulfur
which is extracted with CS₂. The composition of the product thus obtained corresponds to a polymerized mixture of CS and C₃S₂ in a ratio of about 3:1. Different methods of preparation give polymers of different properties,²¹²,²⁹ and it appears that there is no simple "CS polymer".

These polymerization reactions point out the high reactivity of CS even at low temperatures. Steudel concluded that this property makes its isolation in a pure state impossible.³²

Recent spectroscopic studies of CS include the vacuum ultraviolet absorption spectrum,⁴⁵ an emission study in the vacuum and near ultraviolet regions,⁴⁶ and spectroscopic studies of excited electronic states.⁴⁷,⁴⁸ Several microwave studies have been performed.²⁷,³¹,⁴⁹-⁵¹

By this method, the internuclear distance²⁷ has been determined to be 1.53 ± 0.0002 Å and the dipole moment⁴⁹-⁵¹ reported to be 1.958 ± 0.005 D, in the direction -CS+. It was determined from the quadrupole moment⁵⁰ that, unlike CO which has considerable electron density present at the ends of the molecule, the electrons in CS are shifted toward the center of the molecule.

Vacuum ultraviolet photoelectron spectroscopy has also been applied to carbon monosulfide.⁵²-⁵⁴ Four ionization potentials are reported,⁵⁴ the first occurring at 11.34 eV. The vibrational structure of this band indicates ionization of an antibonding σ M0. The second ionization is the removal of a strongly bonding π electron and the third and fourth ionizations result from the removal of σ bonding electrons.
All of the ionizations occur at lower energy than the corresponding bands for CO.

From the CS stretching frequency of 1274 cm\(^{-1}\) a force constant of 8.4 mdyn/\(\AA\) is calculated. By comparing this with the CS stretching force constant in CS\(_2\), a bond order of 2.2 is estimated for the CS molecule.\(^{32}\)

The thermodynamic properties of CS have been determined by several methods, and there is a wide variation in the reported values.\(^{41}\) Values reported for the enthalpy of formation range from 50 to 70 kcal/mole; some recent studies give \(\Delta H^\circ_{f,0}(\text{CS}) = 64.96 \pm 0.4\) kcal/mole\(^{56}\) and \(\Delta H^\circ_{f,298}(\text{CS}) = 70.0 \pm 2\) kcal/mole.\(^{38}\) A recent value for the bond dissociation energy is \(D^\circ_o = 166.1 \pm 2\) kcal/mole.\(^{38,57}\) Some molecular properties of CS and the corresponding values of CO are listed in Table 1.

Table 1. Selected molecular properties of CS and CO

<table>
<thead>
<tr>
<th>Property (units)</th>
<th>CS</th>
<th>Reference</th>
<th>CO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole moment, (\mu) (D)</td>
<td>1.958 (-CS+)</td>
<td>(50)</td>
<td>0.112 (-CO+)</td>
<td>(58)</td>
</tr>
<tr>
<td>Force constant, (k) (mdyne/(\AA))</td>
<td>8.4</td>
<td>(55)</td>
<td>19.0</td>
<td>(59)</td>
</tr>
<tr>
<td>Internuclear distance, (r_e) ((\text{\AA}))</td>
<td>1.535</td>
<td>(27)</td>
<td>1.128</td>
<td>(59)</td>
</tr>
<tr>
<td>Dissociation energy, (D) (kcal/mole)</td>
<td>166</td>
<td>(38)</td>
<td>256</td>
<td>(60)</td>
</tr>
<tr>
<td>Ionization potential, I.P. (eV)</td>
<td>11.34</td>
<td>(54)</td>
<td>14.01</td>
<td>(59)</td>
</tr>
</tbody>
</table>
An ab initio SCF LCAO molecular orbital calculation has been performed on the carbon monosulfide molecule. The results, when compared to those of similar calculations on CO, showed that the \( \pi^* \) orbital of CS which back-bonds with a metal has much lower energy than the corresponding \( \pi^* \) orbital in CO; therefore CS should form stronger \( \pi \) bonds with metals than does CO. A similar comparison of the \( \sigma \) lone pairs on C showed that CS should also form slightly stronger \( \sigma \) bonds with metals. It was also concluded that d orbitals on C or S will not be involved in bonding to a metal atom.

2. Reactions of carbon monosulfide

Most of the early work on carbon monosulfide was connected with its preparation, decomposition, or spectroscopic properties. Therefore, the chemistry of CS was almost totally un researched until 1967, when Steudel\(^{32,62}\) reported that the gas-phase reaction of CS with \( \text{Cl}_2 \), \( \text{Br}_2 \), or \( \text{I}_2 \) gave \( \text{Cl}_2\text{CS} \), \( \text{Br}_2\text{CS} \), and \( \text{I}_2\text{CS} \), respectively. In the chlorine reaction excess halogen produced \( \text{Cl}_3\text{CSCl} \).\(^{32}\) It was also reported\(^{32}\) that CSSe and CSTe could be prepared by the reaction of gas-phase CS with the solid chalcogen. An earlier report\(^{63}\) noted that the reaction between CS and \( \text{O}_2 \) was very slow at temperatures between 20 and 100°. Recently the reaction between CS and atomic oxygen has been studied.\(^{64,65}\) This reaction produces vibrationally excited carbon monoxide and is the basis of a CO chemical laser.\(^{65}\)

Klabunde and co-workers\(^{34}\) have recently investigated some reactions of CS. They were able to prepare \( \text{Cl}_3\text{CSCl} \), \( \text{Br}_3\text{CSBr} \), and \( \text{Cl}_2\text{BrCSCl} \) by reacting
CS with halogens and mixed halogens. Similar reactions with HCl and HBr gave HClCS and HBrCS; no products resulting from a second addition were observed. These thioformyl halides trimerized readily upon warming.

Although Steudel concluded from its reactions with halogens and chalcogens that CS behaves as an electrophilic carbene, the work of Klabunde et al. suggests that it is better described as a weak Lewis base. Carbon monosulfide will not react at low temperatures with olefins, alcohols, or other electron-rich compounds, but will react with Lewis acids, such as hydrogen halides and boron halides. However, carbon monosulfide will not displace CO or PPh$_3$ from Ni(CO)$_4$, Fe(CO)$_5$, or Rh(PPh$_3$)$_3$Cl at low temperatures.

Carbon monoselenide has been observed, but it is much less stable than CS and could not be trapped at low temperatures. It is reported to have a lifetime in the gas phase of less than one second. Presently CTe and CPo are unknown.

B. Metal Thiocarbonyl Complexes

1. Formation of the metal-thiocarbonyl bond

The first preparations of transition metal thiocarbonyl complexes followed by more than 50 years the first observation of CS, largely because of the instability of the free carbon monosulfide molecule. Even up to the present there is only one report in the literature of the preparation of a metal thiocarbonyl complex from free CS, and the product could not
be isolated. Carbon monosulfide generated from \( \text{CS}_2 \) in a microwave discharge was condensed with Ni atoms, and spectroscopic evidence indicates the formation of \( \text{Ni(\text{CS})}_4 \). Thus, indirect methods have been used to prepare all other known thiocarbonyl complexes. These may be grouped into two major categories.

a. Addition of \( \text{CS}_2 \) to a metal complex followed by cleavage of a C-S bond. This method was used in the first preparation of a transition metal thiocarbonyl by Baird and Wilkinson in 1966. It was found that added triphenylphosphine acted as a sulfur acceptor, according to Eq. 1.

\[
\text{CH}_3\text{OH} \quad \text{RhCl(PPh}_3\text{)}_3 + \text{CS}_2 + \text{PPh}_3 \rightarrow \text{trans} - \text{RhCl(PPh}_3\text{)}_2(\text{CS}) + \text{Ph}_3\text{PS} \quad (1)
\]

A similar reaction was performed with \( \text{IrCl(PPh}_3\text{)}_3 \), but only low yields of \( \text{IrCl(PPh}_3\text{)}_2(\text{CS}) \) were obtained. Better yields resulted when \( \text{trans} - \text{IrCl(PPh}_3\text{)}_2(\text{N}_2) \) was reacted with \( \text{CS}_2 \) in the presence of \( \text{PPh}_3 \) and methanol. Another complex, \( \text{IrCl(\text{CS})_2(PPh}_3\text{)}_2 \), could also be isolated from this reaction and was thought to be an intermediate.

The reaction of \( \text{RuCl}_2(\text{PPh}_3)_3 \) or \( \text{RuCl}_2(\text{PPh}_3)_4 \) with \( \text{CS}_2 \) in the absence of added \( \text{PPh}_3 \) leads to the formation of a \( \pi - \text{CS}_2 \) complex and some of the dimer \( \text{[RuCl}_2(\text{CS})(\text{PPh}_3)_2]_2 \). Other workers found that the same reaction also produces another related binuclear thiocarbonyl complex, \( \text{[PPh}_3\text{]}_2\text{ClRuCl}_3\text{Ru(PPh}_3\text{)}_2(\text{CS}) \). It was also found that by extending the reaction time a dithiocarbonyl complex, \( \text{RuCl}_2(\text{PPh}_3)_2(\text{CS})_2 \) could be prepared. The analogous triphenylarsine complex was also prepared.
The ruthenium (III) complexes, RuBr$_3$L$_2$(CS), (L = PPh$_3$, AsPh$_3$), were obtained$^{78}$ by refluxing RuBr$_3$L$_2$(CH$_3$OH) in CS$_2$. Shorter reaction times yield the RuBr$_3$L$_2$(CS$_2$) complexes also, which suggests that they are intermediates in thiocarbonyl formation.

The reaction of Co$_2$(CO)$_8$ with CS$_2$ yields many products, one of which has the formula Co$_3$(CO)$_6$CS$_2$ and has been suggested to contain a triply bridging CS ligand.$^{79}$ The evidence, however, appears to be inconclusive.

The CpFe(CO)$_2$ ion reacts$^{80}$ with CS$_2$ in a process which can be viewed as either a nucleophilic attack at the CS$_2$ carbon or the oxidative addition of CS$_2$ to iron (Eq. 2).

\[
\text{CpFe(CO)$_2$}^{-} + \text{CS}_2 \rightarrow \text{CpFe(CO)$_2$CS}_2 \rightarrow \text{CpFe(CO)$_2$C-SCH}_3 \overset{S}{\rightarrow} [\text{CpFe(CO)$_2$(CS)}]Cl + \text{CH}_3\text{SH}
\]

(2)

The sulfur atom is eventually removed as CH$_3$SH.

The manganese (I) thiocarbonyl complex CpMn(CO)$_2$(CS)$^{81}$ has been prepared by refluxing CpMn(CO)$_2$(cis-cyclooctene) in CS$_2$ for one week; yields were greatly improved by the addition of PPh$_3$ which acts as a sulfur acceptor (Eq. 3).

\[
\text{CpMn(CO)$_2$} \rightarrow \text{CpMn(CO)$_2$(CS)} + \text{Ph}_3\text{PS}
\]

(3)

After the photochemical replacement of CO in the thiocarbonyl complex with cis-cyclooctene, CpMn(CO)(CS)$_2$ was prepared in an identical process.$^{81}$
Spectroscopic evidence also indicates the formation of CpMn(CS)_3 by
extending the process to replacement of the third CO. It was found that
CpMn(CO)_2(THF) also reacts with CS_2 and PPh_3 to yield the thiocarbonyl
complex. This method was used to prepare CpRe(CO)_2(CS). 82

Finally, a similar reaction sequence was used to obtain
(Ar)Cr(CO)_2(CS) (Ar = methyl benzoate) from (Ar)Cr(CO)_2(cis-cyclooctene),
CS_2 and PPh_3. 83

It should be noted that there are many known CS_2 complexes of metals
which do not decompose or react with sulfur acceptors to yield thiocarbonyl
complexes. 84

b. Oxidative addition of thiophosgene and its derivatives to metal
complexes The iron complex [CpFe(CO)_(2)(CS)]^+ (vide supra) was also
prepared by the oxidative addition of ClCOR (R = CH_3, C_2H_5) to
CpFe(CO)_2^-, followed by reaction with HCl (Eq. 4).

\[
\text{CpFe(CO)_2^- + ClCOR} \rightarrow \text{CpFe(CO)_(2-C-OR)^-} \rightarrow \text{[CpFe(CO)_(2)(CS)]^+ + ROH}
\]  (4)

The oxidative addition of ClCOCH_3 to Pt(PPh_3)_4 yields
PtCl(PPh_3)_2(C-OCH_3). When reacted with BF_3 a product resulted which was
identified as [trans-PtCl(PPh_3)_2(CS)]BF_4. 86 Kubota and Curtis 87 have
recently reported that the oxidative addition of thiophosgene to certain
Ir(I) and Rh(I) species (Eqs. 5-7) yields thiocarbonyl complexes.

\[
\text{Ir(PPh_3)_2(N_2)Cl + Cl_2CS} \rightarrow \text{Ir(PPh_3)_2(CS)Cl_3 + N_2}
\]  (5)
Aside from the work described in this dissertation, these are the only reactions known at the present in which a metal-thiocarbonyl bond is formed. It is evident that the chemistry of metal thiocarbonyl complexes has been severely limited by the difficulty of initially forming the M-CS linkage.

2. Reactions of metal thiocarbonyl complexes

The chemistry of thiocarbonyl complexes up to early 1973 has been reviewed, and aside from the studies discussed in this dissertation, the review includes nearly all known reactions of metal thiocarbonyl complexes. As expected, metal thiocarbonyls undergo normal substitution reactions in which other ligands are replaced. Thus both CO groups in the CpMn(CO)₂(CS) complex undergo photochemical substitution by another ligand; however, the CS ligand does not. The S_N_1 replacement of cis-cyclooctene from CpMn(CO)_2(C_8H_14) with PPh_3 is approximately four times faster than the same reaction of the dicarbonyl analog. This observation was presented as evidence of the greater pi-acceptor ability of CS relative to CO. Other ligand addition and substitution reactions

\[
[\text{Ir(PPh}_3\text{)}_2(\text{CO})(\text{NCCH}_3)]\text{PF}_6 + \text{Cl}_2\text{CS} \rightarrow [\text{Ir(PPh}_3\text{)}_2(\text{CO})(\text{CS})\text{Cl}_2]\text{PF}_6 + \text{NCCH}_3
\]  

(6)

\[
\text{Rh(PPh}_3\text{)}_3\text{Cl} + \text{Cl}_2\text{CS} \rightarrow \text{Rh(PPh}_3\text{)}_2(\text{CS})\text{Cl}_3 + \text{PPh}_3
\]  

(7)
of thiocarbonyl complexes include: the preparation of
\[ \text{RuCl}_2(\text{PPh}_3)_2(\text{CS})(\text{py}), \] \[ \text{RuCl}_3(\text{PPh}_3)_2(\text{CS})^- \] \[ \text{RuCl}_2(\text{PPh}_3)_2(\text{CO})(\text{CS}) \] from \[ \text{RuCl}_2(\text{PPh}_3)_2(\text{CS}) \]; the replacement of Cl⁻ in \text{trans-RhCl}(\text{CS})(\text{PPh}_3)_2\] and \text{trans-IrCl}(\text{CS})(\text{PPh}_3)_2\] by CS₂; the phosphine exchange reaction yielding \text{trans-IrCl}(\text{CS})(\text{PCy}_3)_2\] from \text{trans-IrCl}(\text{CS})(\text{PPh}_3)_2\] and the conversion of these two complexes to \[ \text{Ir}^+(\text{CO})_2(\text{CS})L_2 \] + \[ \text{Ir}^+(\text{CO})_2(\text{CS})\] \[ \text{PMePh}_2 \] and PMePh₂; the preparation of adducts of \text{trans-IrCl}(\text{CS})(\text{PPh}_3)_2\] with CO, SO₂ and NO₂; and the transformation of \text{trans-IrCl}(\text{CS})(\text{PPh}_3)_2\] into \[ \text{Ir}^+\text{(diphos)}_2(\text{CS}) \] +. It was noted that replacement of the CS ligand in \text{trans-RhCl}(\text{PPh}_3)_2(\text{CS})\] by CO at 1 atm and 25° was not possible; under these conditions the parent carbonyl complex exchanges instantaneously with labeled CO. In fact, there are no known simple reactions in which the thiocarbonyl group in a metal complex is displaced by another ligand.

The Rh(I) thiocarbonyl complexes, \text{trans-RhX}(CS)(PPh₃)_2\] (X = Cl, Br) undergo oxidative addition reactions with halogens and tetracyanoethylene but, unlike their carbonyl analogs, do not add HCl. The Ir(I) thiocarbonyl complexes, \text{trans-IrCl}(CS)(PPh₃)_2\] and \[ \text{Ir}^+(\text{CO})_2(\text{CS})L_2 \] + (L = PPh₃, PCy₃) also undergo numerous oxidative addition reactions. Likewise, it was observed in these reactions and in attempts to form adducts of these complexes with Lewis bases that the thiocarbonyl derivatives were considerably less reactive than the
carbonyl analogs. It was suggested that these results might indicate less nonbonding electron density on the metal atoms due to the stronger pi-acceptor character of CS.

Reactions with nucleophilic reagents have been reported for only three metal thiocarbonyl complexes, other than those described in this dissertation. Busetto et al. have investigated several reactions of \([\text{CpFe(CO)}_2(\text{CS})]^{+}\) (Eqs. 8-12) in which there is preferential attack at the thiocarbonyl carbon.\(^95\)

\[
\begin{align*}
\text{CpFe(CO)}_2(\text{CS})^{+} + \text{N}_3^- & \rightarrow \text{CpFe(CO)}_2\text{NCS} + \text{N}_2 \\
\text{CpFe(CO)}_2(\text{CS})^{+} + \text{H}_2\text{NNH}_2 & \rightarrow \text{CpFe(CO)}_2\text{NCS} + \text{NH}_3 \\
\text{CpFe(CO)}_2(\text{CS})^{+} + \text{RO}^- & \rightarrow \text{CpFe(CO)}_2\text{C}-\text{OR} \quad (R = \text{CH}_3, \text{C}_2\text{H}_5) \\
\text{CpFe(CO)}_2(\text{CS})^{+} + \text{NH}_2\text{R} & \rightarrow \text{CpFe(CO)}_2\text{C}-\text{NH} + \text{H}^+ \quad (R = \text{CH}_3, \text{C}_2\text{H}_5) \\
\text{CpFe(CO)}_2(\text{CS})^{+} + \text{NCX}^- & \rightarrow \text{CpFe(CO)}_2\text{CN} + \text{COX} \quad (X = 0, S)
\end{align*}
\]

In contrast, Mays and Stefanini\(^92\) observed that nucleophilic attack by \(\text{CH}_3\text{O}^-\) on \([\text{Ir(CO)}_2(\text{CS})(\text{PPh}_3)_2]^{+}\) occurred only at the carbonyl carbon. It should be noted, however, that nucleophilic addition of \(\text{CH}_3\text{O}^-\) to a carbonyl in \([\text{CpFe(CO)}_2(\text{CS})]^{+}\) is observed in the presence of small amounts of water.\(^95\) In a very recent report, \(\text{H}_2\text{O}\) was observed to react very
readily with $\text{trans-PtCl(CS)(PPh}_3)_2^+ \text{ to form } [\text{trans-PtCl(CO)(PPh}_3)_2]^+$. 86

No reactions, other than those discussed in this dissertation, 96,97 are known which give products resulting from electrophilic addition to the sulfur of a metal thiocarbonyl complex. However, it was suggested that the decomposition of $\text{trans-RhCl(PPh}_3)_2$(CS) on reaction with CH$_3$I and HgCl$_2$ might result from attack at the sulfur atom. 72

3. Spectroscopic and structural studies

Three X-ray crystallographic structure determinations have been performed on metal thiocarbonyl complexes up to the present time. The $\text{trans-RhCl(PPh}_3)_2$(CS) complex was found 98 to contain a nearly linear thiocarbonyl ligand with a C-S bond length of 1.536Å. The metal-carbon distance was determined to be 1.787Å, compared to a M-Co distance of 1.86Å in the carbonyl analog. The structure of $[\text{Ir(CO)}_2$(CS)(PPh$_3$)$_2$]PF$_6$ was determined to be trigonal bipyramidal with the phosphines in the axial positions. 99 The Ir-CS bond length of 1.867Å is significantly shorter than the Ir-CO bond distance (mean 1.938Å). The C-S bond length was found to be 1.511Å. The structure 100 of $[\text{CpFe(CO)}_2$(CS)]PF$_6$, however, was nearly identical to that of the carbonyl analog. The C-O distances (mean 1.150Å) and all of the Fe-C distances (mean 1.815Å) are unchanged from those in the tricarbonyl complex. A C-S bond length of 1.501Å was found.

Infrared spectroscopy has been an essential tool in the detection and characterization of thiocarbonyl complexes. The presently known metal thiocarbonyls exhibit a very strong, distinctive IR band arising
from the CS stretching mode in the range from 1161\(^{96}\) to 1409 cm\(^{-1}\).\(^{87}\) This absorption thus occurs at frequencies both higher and lower than the 1274 cm\(^{-1}\) band of the free CS molecule. By way of contrast, the CO stretch is always lowered on coordination to a metal. It has been suggested that coupling of the CS stretch with low-frequency modes in the thiocarbonyl complex could cause this difference.\(^{84}\) This explanation seems unlikely, particularly in view of a comparison of the CS bond lengths in the free molecule and in its complexes. In the three structures reported, the CS bond length has been shortened, in agreement with the higher CS stretching frequencies in these complexes. In contrast, CO bond lengths are decreased on coordination to a metal. The fact that the CS frequency may be either raised or lowered upon coordination may be due solely to electronic effects in view of the large electronic differences between CO and CS, both free and in metal complexes.

A comparison of the \(^{57}\)Fe Mössbauer spectrum of \([\text{CpFe(CO)}_2(\text{CS})]\)^\(^+\) with those of other \([\text{CpFe(CO)}_2\text{L}]^+\) complexes led to the conclusion that the CS ligand is a better pi-acceptor in these complexes than is CO.\(^{101}\)

The mass spectra of \(\text{CpMn(CO)}_2(\text{CS})\) and some of its derivatives have been recorded.\(^{88}\) Some of the Mn-CS\(^+\) fragment was observed in these spectra, contrasting with other cyclopentadienylmanganese carbonyl complexes, in which all other ligands are lost before the C\(_5\)H\(_5\) ring.

Bodner\(^{102}\) has recorded the \(^{13}\)C NMR spectra of \(\text{CpMn(CO)}_2(\text{CS})\) and \([\text{CpFe(CO)}_2(\text{CS})]\)PF\(_6^+\). The chemical shifts of the CS carbons (-442.9 and -307.9 ppm, downfield from TMS in acetone -d\(_6\)) are shifted far downfield
from the respective CO carbon resonances (-224.5 and -203.3 ppm). In fact, the manganese thiocarbonyl carbon has the largest chemical shift yet observed for carbon. Bodner interpreted these results in terms of a resonance structure (\( t^+ = s^- \)) which is stabilized by metal-to-thiocarbonyl back-donation.

Lichtenberger\(^{103} \) has used ultraviolet photoelectron spectroscopy to study the electronic structure of \( \text{CpMn(CO)}_2(\text{CS}) \), \( \text{W(CO)}_5(\text{CS}) \), and \( \text{Cr(CO)}_5(\text{CS}) \). (The preparation and chemistry of the latter two compounds are discussed in this dissertation.) In \( \text{Cr(CO)}_6 \) and \( \text{W(CO)}_6 \) the first ionization band is attributed to the removal of an electron from the \( t_{2g} \) metal d-orbitals. However, in \( \text{Cr(CO)}_5(\text{CS}) \) and \( \text{W(CO)}_5(\text{CS}) \) these highest occupied orbitals should be split into the \( e \) and \( b_2 \) representations because of the lower symmetry of the complexes. Surprisingly, no splitting was observed in the \( \text{Cr(CO)}_5(\text{CS}) \) spectrum and a very small splitting may be detected for \( \text{W(CO)}_5(\text{CS}) \). Thus, the degeneracy of the metal d-orbitals is barely disturbed. The only significant difference between these ionization bands of the thiocarbonyl complexes and those of the parent hexacarbonyl complexes is that the bands have shifted by about 0.25 eV to lower energy in the thiocarbonyl complexes. This shift was also observed in the manganese thiocarbonyl species. The direction of the shift seems to be in contradiction to the anticipated stronger \( \pi \)-acceptor character of the CS ligand.
4. **Molecular orbital calculations**

Molecular orbital calculations using the Fenske approximate method were performed to assist in the interpretation of the ionization results. The calculations on \( \text{Cr(CO)}_5(\text{CS}) \) predict that the \( \text{CS} \) pi-antibonding orbitals accept 0.60 electrons in comparison to 0.51 electrons accepted by the \( \text{CO} \) pi-antibonding orbitals. Moreover, the calculations suggest that the reduction of electron density in the metal d-orbitals which results from this back-bonding interaction is offset by the destabilizing interaction of the relatively high-energy \( \text{CS} \) pi-bonding orbitals with the metal orbitals. Both interactions produce a stronger M-CS bond and a weaker C-S bond, as well as slightly weaker M-CO bonds. The shift of the first ionization band to lower energy is explained by the destabilization of the metal orbitals because of an increase in electron density at the thiocarbonyl carbon. This higher carbon electron density is due to the lower electronegativity of sulfur as compared to oxygen and the greater pi-acceptance of \( \text{CS} \) relative to \( \text{CO} \). The calculations suggest that \( \text{CS} \) is only a slightly better \( \sigma \)-donor than \( \text{CO} \). Calculations on \( \text{CpMn(CO)}_2(\text{CS}) \) led to the same general results.

It is interesting to note that, although various descriptions of the \( \text{CS} \) ligand based on reactivity and spectroscopic studies place a high positive charge on the CS carbon, the calculations predict that this carbon has a smaller positive charge than an analogous carbonyl carbon.
III. EXPERIMENTAL

A. General

All reactions were performed under an atmosphere of dry nitrogen unless specified otherwise. Dioxane was distilled from calcium hydride and tetrahydrofuran was distilled from lithium aluminum hydride before use. Other reagent grade chemicals were used without further purification, except where noted otherwise. Gas chromatographic analyses were performed using a 0.25 in. X 5 ft. 2% SE-30 column at temperatures of 60 to 150° and a helium flow rate of 25 cc/min. The same column was used for preparative collections at temperatures of 55 to 65° and a helium flow rate of 100 cc/min. Approximately 45 μl of a saturated pentane or hexane solution was injected for each preparative collection. Conductivity measurements were performed on solutions of approximately 10⁻³ M in nitrobenzene. Elemental analyses were performed by Chemalytics, Inc. or Schwarzkopf Microanalytical Laboratory.

B. Spectra

Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer. Positions of the peaks were determined with an expanded scale recorder calibrated in the carbonyl region with gaseous CO and DCl and in the thiocarbonyl region with polystyrene. Proton NMR spectra were recorded with Varian A-60 and Perkin-Elmer Hitachi R-20B instruments, except when specified otherwise. The ¹³C NMR spectra were obtained with a Bruker HX-90 spectrometer operating in the Fourier transform mode.
at 22.64 MHz. Deuterochloroform was used as the solvent, lock material and internal standard, \((\delta = -77.029)\). The shiftless, paramagnetic relaxing agent \(^{104}\text{Cr(acetylacetonate)}_3\) was used to reduce the data collection time.

C. Kinetic Experiments

Decalin solvent was purified by stirring at 130° with Na for 12 hr and distilling at reduced pressure. Chlorobenzene was distilled from P_4O_10. Reagent grade hexane was used without further purification. Several experiments were performed with hexane purified by shaking with H_2SO_4-HNO_3, fractional distillation and passage through an alumina column; these experiments gave the same kinetic results as those done in reagent grade hexane. Triphenylphosphine was recrystallized twice from hexane and dried in a high vacuum. Tetrabutylammonium iodide was recrystallized twice from chlorobenzene, powdered and dried in a high vacuum. Amines were fractionally distilled before use; DABCO was sublimed. Kinetic experiments were performed in flasks capped with rubber serum stoppers under N_2. Samples were withdrawn periodically by syringe. Experiments at temperatures above 100° were carried out in 10-ml syringes immersed in the constant-temperature bath to prevent sublimation of the complex. Long hypodermic needles were bent up above the surface to allow withdrawal of samples. The reaction vessels were immersed in a constant-temperature oil or water bath (± 0.05°). Rates were determined by following the disappearance of the 2096 cm\(^{-1}\) band of W(CO)_5(CS) using a Perkin-Elmer 337 or Beckman IR-8 spectrometer.
Plots of $\ln(A - A_0)$ vs. $t$ were linear with slopes of $k_{obs}$, confirming first order or pseudo-first order kinetics.

D. Preparation and Reactions of Complexes

1. Preparation of $\text{CpFe(CO)}_2\text{CS}_2\text{CH}_3$

The cyclopentadienyliron dicarbonyl dimer (10.3 g, 28.3 mmol) was reduced to $\text{CpFe(CO)}_2^-$ by stirring under $\text{N}_2$ for one hr with sodium amalgam (2 g Na, 87 mmol in 35 ml Hg) in 125 ml THF. The amalgam was withdrawn from the flask through a stopcock on the bottom. Carbon disulfide (7 ml, 103 mmol) was then added to the solution, which was stirred for 10 seconds before the rapid addition of $\text{CH}_3I$ (7 ml, 110 mmol). After stirring for 10 min, the solution was evaporated to dryness under reduced pressure. The residue was extracted repeatedly with warm pentane and the combined extracts were filtered. After concentrating with warming, the solution was cooled slowly to $-20^\circ$. After having collected 0.1 g of brown crystals, the solution was concentrated and again cooled to give 1.0 g of a second crop, for a total yield of 58%.

$\text{IR (hexane)}$ 2035 vs, 1988 vs. $\text{NMR (CCl}_4)$ 7.08 ($\text{C}_5\text{H}_5$), 7.40 ($\text{-SCH}_2$).

MP 72$^\circ$. Anal. Calcd. for ($\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CS}_2\text{CH}_3$): C 40.3; H, 2.98; S, 23.8. Found: C, 40.4; H, 2.95; S, 22.7.

2. Preparation of $[\text{(C}_5\text{H}_5\text{Fe(CO)}_2\text{CS}_2\text{)]PF}_6$

The iron dimer (10.7 g, 30.3 mmol) was reduced with sodium amalgam and treated with $\text{CS}_2$ (5 ml, 73 mmol) and $\text{CH}_3I$ (5 ml, 79 mmol) as in the procedure for the preparation of ($\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CS}_2\text{CH}_3$). The reaction
mixture was evaporated to dryness, dissolved in 75 ml of benzene, and filtered through Celite filter-aid. Another 75 ml of benzene was used to wash the flask and filter. Hydrogen chloride gas was then bubbled into the combined benzene solutions for 25 min. The solution was concentrated to approximately 75 ml under reduced pressure. A solution of excess NH₄PF₆ (11g, 67 mmol) in 40 ml acetone was added to the solution with stirring. The solution was immediately filtered to remove the insoluble NH₄Cl, and some of the product crystallized after the filtration (4.0g). After cooling to -20° over night, 10.6g of crystals was collected (66%). Addition of ether and cooling gave more impure product.

IR(acetone) 2102vs, 2072vs, (hexachlorobutadiene) 1348vs. MP 190° (decomp. without melting). Anal. Calcd. for [(C₅H₅)Fe(CO)₂(CS)]PF₆: C, 26.2; H, 1.37; S, 8.75. Found: C, 26.6; H, 1.19; S, 8.77.

3. Reaction of Re(CO)₅⁻ with CS₂ and CH₃I

Rhenium decacarbonyl (1.5g, 4.6 mmol) was reduced to Re(CO)₅⁻ by stirring in 75 ml of THF with excess sodium amalgam for 20 min. The amalgam was removed through a stopcock at the bottom of the flask. Carbon disulfide (5 ml, 73 mmol) was added to the solution, and the mixture was stirred for 15 sec. Then CH₃I (5 ml, 79 mmol) was added with stirring. The infrared spectrum at this time showed one major product, tentatively identified as Re(CO)₅CS₂CH₃.

IR(hexane) 2072w, 2053vs, 2000s.
The solution was evaporated to dryness, dissolved in 40 ml benzene and reacted with gaseous HCl for 20 min. Addition of NH₄PF₆ (2g, 12 mmol) in 15 ml of acetone was followed by filtration and concentration under reduced pressure. One sample treated in this manner yielded a white powder tentatively identified as [Re(CO)₅(CS)]PF₆. However, several attempts to repeat this preparation did not succeed.

IR(acetone) 2173w, 2095m,sh, 2078vs, (KBr) ~ 1400s.

4. Reaction of (C₅H₅)W(CO)₃ with CS₂ and CH₃SO₂F

After reducing [(C₅H₅)W(CO)₃]₂ (2.0g, 6.1 mg) by stirring for 15 min in 50 ml THF with excess sodium amalgam (which was then removed), carbon disulfide (5 ml, 73 mmol) was added to the solution. The mixture was then added dropwise to a solution of CH₃SO₂F (3 ml, 38 mmol) in 20 ml THF. This solution was evaporated to an oil, which was dissolved in CH₂Cl₂ and placed on top of a 2 x 40 cm column of florisil. Elution with CH₂Cl₂ gave a dark red band which was collected and evaporated to dryness. The solid (0.6g) was dissolved in ether and crystallized by adding pentane and cooling to -20°C. The analytical and spectroscopic data show the compound to be (C₅H₅)W(CO)₃SO₂F. The infrared analysis of a similar reaction done without CS₂ shows that the same product is formed.

5. Reaction of \( \text{(C}_5\text{H}_5\text{)Ru(CO)}_2^- \) with \( \text{CS}_2 \) and \( \text{CH}_3\text{I} \)

The method of Cleare and Griffith \(^{105}\) was used to prepare \([\text{Ru(CO)}_3\text{Cl}_2]_2\) from "RuCl\(_3\cdot\text{H}_2\text{O}" (Englehard Industries). The crude \([\text{Ru(CO)}_3\text{Cl}_2]_2\) (1.81g, 7.1 mmol) was dissolved in 20 ml THF, and thallium cyclopentadienide (2.4g, 7.9 mmol) was added. After refluxing for 20 hr, the IR spectrum showed the presence of \([\text{(C}_5\text{H}_5\text{)Ru(CO)}_2^-]_2\) \(^{106}\) and some \((\text{C}_5\text{H}_5\text{)Ru(CO)}_2\text{Cl}\). The orange THF solution was cooled, filtered and stirred with excess sodium amalgam for 20 min. Reaction of a small sample of this solution with \( \text{CH}_3\text{I} \) gave only one product, based on the infrared spectrum; presumably this is \((\text{C}_5\text{H}_5\text{)Ru(CO)}_2\text{CH}_3\). The \((\text{C}_5\text{H}_5\text{)Ru(CO)}_2^-\) solution was then stirred for about 20 sec with \( \text{CS}_2 \) (3 ml, 43 mmol). Methyl iodide (4 ml, 63 mmol) was added to the mixture, stirring was continued for 10 min, and the solution was evaporated to dryness. The product is identified as \((\text{C}_5\text{H}_5\text{)Ru(CO)}_2\text{CS}_2\text{CH}_3\), since its infrared spectrum was very similar to the IR of \((\text{C}_5\text{H}_5\text{)Fe(CO)}_2\text{CS}_2\text{CH}_3\).

\[ \text{IR(hexane) 2043vs, 1990vs.} \]

After dissolving the solid in benzene and filtering through Celite filter-aid, HCl gas was bubbled into the solution for 20 min. Addition of excess (2.09, 12 mmol) \( \text{NH}_4\text{PF}_6 \) in 20 ml acetone followed by the addition of ether gave a brown precipitate. The infrared spectrum of the remaining solution indicated that much of the \((\text{C}_5\text{H}_5\text{)Ru(CO)}_2\text{CS}_2\text{CH}_3\) had not reacted. The infrared spectrum of the precipitate suggested, however, that some \([\text{(C}_5\text{H}_5\text{)Ru(CO)}_2\text{(CS)}]_\text{PF}_6\) had been produced.

\[ \text{IR(acetone) 2107s, 2070s.} \]
6. **Preparation of Cr(CO)$_5$(CS)**

A THF solution of Cr(CO)$_6$ (20.0g, 9.1 mmol) was refluxed and stirred 12 hr with excess sodium amalgam (4g Na, 17.3 mmol and ~1.5 lb. Hg). This solution was removed from the amalgam and added with rapid stirring over a 5 min period to Cl$_2$CS (9 ml, 11.7 mmol) in 72 ml THF. The mixture was stirred until it had cooled to room temperature, and was then evaporated to dryness at reduced pressure. Sublimation at 55$^\circ$ under high vacuum onto a water-cooled probe yielded 6.5g of a mixture of Cr(CO)$_5$(CS) and Cr(CO)$_6$. Gas chromatographic analysis of the mixture showed that 0.9g of Cr(CO)$_5$(CS) had been produced (8.4%).

7. **Purification of Cr(CO)$_5$(CS)**

The mixture of Cr(CO)$_5$(CS) (3.0g) and Cr(CO)$_6$ (17g) obtained from several preparative reactions was dissolved in refluxing pentane (700 ml). The flask containing the solution was placed in warm water in a covered dewar flask which was then put in the refrigerator and allowed to cool for two days. The solution was decanted off the crystals, concentrated and warmed, and cooled very slowly as before. After four crystallizations the solution was run through a florisil column (2 x 30 cm), evaporated to dryness and sublimed. Gas chromatographic analysis indicated that less than 1% Cr(CO)$_6$ remained.

IR(hexane) 2091w, 2023m, 1997vs, (CS$_2$) 1253vs. Mass spectrum parent ion m/e 236. **Anal. Calcd. for Cr(CO)$_5$(CS): C, 30.51; H, 0.00; S, 13.56. Found: C, 30.14; H, <0.01; S, 13.59.**
8. **Preparation of Mo(CO)$_5$(CS)**

Molybdenum hexacarbonyl (20.0 g, 7.6 mmol) was stirred with excess sodium amalgam in 350 ml of refluxing THF for 12 hr. Twenty-milliliter quantities of the THF solution (0.22 meq) were withdrawn and added to a solution of 0.35 ml Cl$_2$CS in 3 ml THF with stirring. Each small reaction mixture was evaporated and sublimed individually. The infrared spectrum of the product indicated a yield of Mo(CO)$_5$(CS) of approximately 2-4%. The use of larger quantities of the reduced molybdenum species greatly reduced the yield; increasing the quantities by a factor of four gave no Mo(CO)$_5$(CS).

The combined sublimates of many small reactions were dissolved in warm pentane and allowed to cool to 0° in several hours. The solution was then concentrated, warmed, and crystallized in this manner two more times. Evaporation of the solution gave a small quantity of a mixture containing approximately 75% Mo(CO)$_5$(CS).

IR(hexane) 2096w, 2020m, 1995vs, (CS$_2$) 1247vs. Mass spectrum parent ion m/e 280.

9. **Preparation of W(CO)$_5$(CS)**

Tungsten hexacarbonyl (50 g, 142 mmol) in a solution of 400 ml THF was mechanically stirred with excess sodium amalgam (7 g Na, 304 mmol, ~4 lb. Hg) and refluxed for 12 hr. The mixture was allowed to cool to room temperature and the solution was decanted from the amalgam into an addition funnel under N$_2$. It was then added over a five min period, with stirring, to Cl$_2$CS (14 ml, 183 mmol) in 100 ml of THF in a 1000 ml
round-bottom flask. After having cooled to room temperature, the mixture was evaporated to dryness on a rotary evaporator and sublimed under reduced pressure onto a water-cooled probe. The crystals collected (14g) were found by gas chromatography to contain approximately 45% W(CO)$_5$(CS) (25% yield). The complex was purified by repeated crystallization (5 steps) of a hexane solution of the mixture, as outlined for Cr(CO)$_5$(CS), to yield 1.5g of 99% W(CO)$_5$(CS).

IR(hexane) 2096w, 2007m, 1989vs. Mass spectrum parent ion m/e 368.

Anal. Calcd. for W(CO)$_5$(CS): C, 19.55; H, 0.00; S, 8.70. Found: C, 18.93; H, <0.01; S, 8.36.

10. **Preparation of W(CO)$_4$(CS)(PPh$_3$)**

A xylene solution (15 ml) of W(CO)$_5$(CS) (0.20g, 0.54 mmol) and PPh$_3$ (0.14g, 0.54 mmol) was heated near reflux for 20 min. At this time the IR showed nearly complete consumption of the W(CO)$_5$(CS), so the reaction mixture was immediately cooled and placed on top of a 1.5 x 40 cm florisil/pentane column. After washing well with pentane, elution with 2:1 pentane-benzene was begun until the yellow band had begun to move. The top 5 cm of the column was mechanically removed, and development was accomplished with CH$_2$Cl$_2$. The yellow W(CO)$_4$(CS)(PPh$_3$) band was concentrated, hexane was added, and the concentration was continued until crystals began to form. Cooling to -20° gave 0.14g of yellow crystals (42%). The complex was recrystallized from hexane.

IR(hexane) 2061vw, 2052w, 1981w, 1956vs, (CS$_2$) 1247vs. NMR(DCCl$_3$) $\tau$2.75m. Mass spectrum parent ion m/e 602. Anal. Calcd. for
W(CO)$_4$(CS)(PPh$_3$): C, 45.8; H, 2.49; S, 5.32. Found: C, 46.15; H, 2.50; S, 5.11.

11. **Preparation of Cr(CO)$_4$(CS)(PPh$_3$)**

A toluene solution (5 ml) of Cr(CO)$_5$(CS) (0.32 g, 1.45 mmol) and PPh$_3$ (0.40 g, 1.52 mmol) was refluxed (110°) for 15 min, and the progress of the reaction was followed by IR spectroscopy. The mixture was cooled and placed on the top of a florisil/hexane column (1.5 x 40 cm). After washing with hexane, the column was developed with 1:1 hexane-CH$_2$Cl$_2$ and the yellow Cr(CO)$_4$(CS)(PPh$_3$) band was collected. Concentration and cooling of the solution to -20° gave 0.20 g of yellow crystals (34%). The product was recrystallized from 1:1 CH$_2$Cl$_2$-hexane.

IR(hexane) 2063 vvw, 2044 w, 1992 vw, 1960 vs, (CS$_2$) 1230 s. NMR(DCCl$_3$) $\tau$ 2.77 m. Mass spectrum parent ion m/e 470. **Anal. Calcd. for Cr(CO)$_4$(CS)(PPh$_3$):** C, 58.7; H, 3.19; S, 6.80. **Found:** C, 59.11; H, 3.24; S, 6.01.

12. **Preparation of trans-W(CO)$_5$(CS)(NC$_5$H$_5$)**

A mixture of W(CO)$_5$(CS) and W(CO)$_6$ containing 1.5 g of W(CO)$_5$(CS) (4.1 mmol) was refluxed in 10 ml of xylene with pyridine (2.5 ml, 31 mmol) for 5 min. At this time, the amount of remaining W(CO)$_5$(CS) was still quite large, but W(CO)$_5$(py) began to appear, so the reaction was stopped. The mixture was poured onto a 1.5 x 35 cm florisil/hexane column and washed with hexane. Development with benzene brought down a broad yellow band, the front of which was W(CO)$_5$(py). The latter portion of the band
was quite pure $\text{trans-W(CO)}_4(\text{CS})(\text{py})$, which was collected and evaporated to dryness. Crystallization from pentane gave 0.17g of the product (10%).

IR(hexane) 2062vw, 1950vs, (CS$_2$) 1224vs. NMR(DCCl$_3$) $\tau$1.5 (2H)m, 2.3 (1H)m, 2.7 (2H)m. Mass spectrum parent ion m/e 419. Anal. Calcd. for $\text{W(CO)}_4(\text{CS})(\text{NC}_5\text{H}_5)$: C, 28.6; H, 1.19; S, 7.64. Found: C, 28.83; H, 1.18; S, 7.38.

13. **Preparation of $\text{W(CO)}_3(\text{CS})(\text{diphos})$**

A mixture of $\text{W(CO)}_5(\text{CS})$ and $\text{W(CO)}_6$ containing 1.5g $\text{W(CO)}_5(\text{CS})$ (4.1 mmol) was dissolved in 50 ml of xylene along with diphos (2.0g, 5.0 mmol). The solution was heated to 132° for one hr then cooled and evaporated to dryness under vacuum. The residue was dissolved in 100 ml CH$_2$Cl$_2$ and filtered. Approximately 80 ml of pentane was added with warming, and crystallization was accomplished by cooling to $-20^\circ$. Yellow flakes of the product were collected and washed with pentane (2.55g, 88%).

IR(CH$_2$Cl$_2$) 2013w, 1925vs, (CS$_2$) 1215s. NMR(DCCl$_3$) $\tau$2.6m, 7.42m. Mass spectrum parent ion m/e 710. Anal. Calcd. for $\text{W(CO)}_3(\text{CS})(\text{diphos})$: C, 50.7; H, 3.38. Found: C, 49.0; H, 3.48.

14. **Preparation of $\text{Cr(CO)}_3(\text{CS})(\text{diphos})$**

A xylene solution (10 ml) of 0.17g $\text{Cr(CO)}_5(\text{CS})$ (0.77 mmol) and 0.32g diphos (0.80 mmol) was heated to 110° for approximately one hr and the reaction was followed by IR spectroscopy. Substantial amounts of $\text{Cr(CO)}_4(\text{CS})(\text{diphos})$ formed in the initial stages of the reaction, and
continued heating was necessary to cause the second phosphorus atom to coordinate. After evaporation of the solvent, the residue was dissolved in 15 ml CH$_2$Cl$_2$, filtered, and crystallized by the addition of pentane and cooling to -20°. Yellow-orange crystals of the product were collected and washed with pentane (0.31g, 75%).

IR(CS$_2$) 2006w, 1924vs, 1249vs. Mass spectrum parent ion m/e 578.

Anal. Calcd. for Cr(CO)$_3$(diaphos): C, 62.2; H, 4.15; S, 5.53.
Found: C, 61.1; H, 4.29; S, 5.05.

15. Preparation of W(CO)$_3$(CS)(diars)

A solution of W(CO)$_5$(CS) (1.0g, 2.7 mmol) and o-phenylenebis(dimethylarsine) (diars) (0.84g, 2.9 mmol) in 5 ml xylene was heated to 140° under a stream of N$_2$ for 2.5 hr. In the early stages of the reaction only a monosubstituted complex was seen in the IR spectrum (2070w, 1940vs in hexane). However, after this time mainly W(CO)$_3$(CS)(diars) had formed. The solution was cooled and put on a 2 x 35 cm florisil/hexane column under N$_2$. The yellow band was eluted with CH$_2$Cl$_2$, collected, concentrated, and crystallized by the addition of pentane with cooling to -20° (1.2g, 78%).

IR(hexane) 2010w, 1928m, 1919vs, (CS$_2$) 1213s. Mass spectrum parent ion m/e 568. Anal. Calcd. for W(CO)$_3$(CS)(diars): C, 28.09; H, 2.68.
Found: C, 27.26; H, 2.55.

16. Preparation of W(CO)$_2$(CS)(triphos)

A xylene solution (15 ml) of W(CO)$_5$(CS) (0.15g, 0.41 mmol) and triphos (0.22g, 0.41 mmol) was heated at 135° for 3.5 hr. The solvent was
 evaporated under reduced pressure, and the residue was dissolved in CH₂Cl₂ and filtered. Addition of hexane and cooling to -20° gave 0.22g of yellow crystals (66%). The product was recrystallized from CH₂Cl₂-hexane.

IR(CS₂) 1933s, 1874s, 1197s, 1185m. Anal. Calcd. for W(CO)₂(CS)(triphos): C, 54.28; H, 4.03. Found: C, 53.01; H, 4.23.

17. Preparation of W(CO)(CS)(diphos)₂

A flask containing a mixture of W(CO)₃(CS)(diphos) (4.70g, 6.6 mmol) and diphos (2.70g, 6.8 mmol) was evacuated on a vacuum line and filled with N₂ at atmospheric pressure. After connecting to a nitrogen bubbler, the flask was heated to 195°. After approximately 30 min the molten mixture solidified, but heating was continued for a total of one hr. The solid was cooled to room temperature and slurried in 15 ml of CH₂Cl₂. The mixture was then filtered, leaving a bright yellow powder on the filter. This was washed with 15 ml of CH₂Cl₂ and dried to yield 6.92g of quite pure W(CO)(CS)(diphos)₂ (99%). A small sample of the product was re-crystallized by repeatedly extracting with hot CS₂, filtering, and cooling the solution to -20°.


18. Preparation of Bu₄N[trans-iW(CO)₄(CS)]

A solution of W(CO)₅(CS) (0.15g, 0.41 mmol) and Bu₄Nl (0.15g, 0.41 mmol) in 15 ml THF was stirred at 35° for 1.5 hr. The THF solution was then concentrated to about 10 ml and 20 ml of a mixture of hexane and ethyl ether was added. Cooling to -20° gave 0.23g of yellow crystals.
A second crop of 0.03g was also collected, for a total yield of 90%.
The product was recrystallized from CH$_2$Cl$_2$-ethyl ether.

$\text{IR(}CH_2Cl_2)\ 2062\text{w},\ 1947\text{vs,}\ 1195\text{vs}$. Molar conductivity $\Lambda = 25.6$ ohm$^{-1}$cm$^2$mol$^{-1}$. Anal. Calcd. for Bu$_4$N[W(CO)$_4$(CS)]: C, 35.54; H, 5.08; S, 4.52. Found: C, 35.05; H, 5.09; S, 4.67.

This preparation was also commonly performed on a large scale using a mixture of W(CO)$_6$ and W(CO)$_5$(CS). For example, a THF solution (125 ml) of such a mixture containing 3.3g W(CO)$_5$(CS) (9.0 mmol) and Bu$_4$NI (3.3g, 9.0 mmol) was stirred at 55° for 2 hr. The solution was then concentrated to about 20 ml and crystallized by the addition of 30 ml of ethyl ether. The solid was washed well with ether and dried at 50° under high vacuum overnight to remove any traces of W(CO)$_6$. A yield of 6.4g (99%) was collected.

**Preparation of Bu$_4$N[trans-BrW(CO)$_4$(CS)]**

A THF solution (50 ml) of Bu$_4$NBr (0.45g, 1.4 mmol) and W(CO)$_5$(CS) (0.5g, 1.36 mmol) was heated at 40° for one hr. The mixture was concentrated to 10 ml and diluted with 10 ml of ethyl ether and 10 ml of hexane. Cooling to -20° overnight gave 0.5g of dark yellow crystals (55%). The product was recrystallized from CH$_2$Cl$_2$-ether.

$\text{IR(}CH_2Cl_2)\ 2065\text{w},\ 1947\text{vs,}\ 1193\text{s}$. Anal. Calcd. for Bu$_4$N[BrW(CO)$_4$(CS)]: C, 38.65; H, 5.52. Found: C, 38.10; H, 5.58.
20. Preparation of \( \text{Bu}_4\text{N}[^{\text{trans}}\text{ClW(CO)}_4\text{(CS)}] \)

A THF solution (25 ml) of \( \text{W(CO)}_5\text{(CS)} \) (0.86g, 2.33 mmol) and \( \text{Bu}_4\text{NCl} \) (0.65g, 2.34 mmol) was stirred at room temperature for 1.5 hr. It was then concentrated to 10 ml and diluted with 10 ml ethyl ether, which caused the formation of an oil. Cooling to -20° solidified the oil, and it was dried under high vacuum. A crude yield of 0.75g was collected (52%). The complex was characterized only by its IR and \(^{13}\text{C}\) NMR spectra.

IR\( (\text{CH}_2\text{Cl}_2) \) 2064w, 1945vs, 1193s.

21. Preparation of \( \text{trans-W(CO)}_4\text{(CS)(PPh}_3\text{)} \)

A solution of \( \text{Bu}_4\text{N}[\text{IW(CO)}_4\text{(CS)}] \) (0.20g, 0.282 mmol) in 5 ml acetone was stirred under \( \text{N}_2 \) while silver trifluoromethanesulfonate (0.073g, 0.284 mmol) in 3 ml acetone was added over a two min period. A voluminous yellow precipitate of AgI immediately formed. Triphenyl-phosphine (0.08g, 0.305 mmol) in 3 ml acetone was then added and the solution was stirred for 1.5 hr at room temperature. After filtering through Celite filter-aid and evaporating the solution to dryness, the residue was extracted with 25 ml of hot hexane. The solution was filtered and cooled to -20° to yield 0.12g of yellow crystals. A second crop of 0.02g was also collected (82%).

IR\( (\text{hexane}) \) 2061w, 1956vs, \((\text{CS}_2)\) 1247vs.

22. Preparation of \( \text{mer-W(CO)}_3\text{(CS)(bipy)} \)

A solution of \( \text{Bu}_4\text{N}[\text{IW(CO)}_4\text{(CS)}] \) (0.20g, 0.282 mmol) in 15 ml acetone was stirred under \( \text{N}_2 \) while AgCF\(_3\)SO\(_3\) (0.0725g, 0.282 mmol) in 2 ml acetone
was added dropwise. The solution became dark red immediately when bipy
(0.044g, 0.282 mmol) was added to the mixture. It was filtered through
Celite, evaporated to dryness, and the residue was dissolved in CH₂Cl₂.
This solution was placed on the top of a 1.5 x 20 cm florisil/CH₂Cl₂
column. Elution with CH₂Cl₂ gave a red band which was collected, con­
centrated, diluted with hexane, and cooled to -20°. Dark red crystals
were collected. (0.075g, 57%).

IR(CS₂) 2004w, 1948vw, 1916vs, 1888m, 1203s. Anal. Calcd. for

23. Preparation of W(CO)₅(CS) from Bu₄N[W(CO)₄(CS)]

A 250 ml beverage bottle containing Bu₄N[W(CO)₄(CS)] (5.1g, 7.2
mmol) in 150 ml acetone was flushed with CO and capped. A solution of
AgCF₃SO₃ (1.85g, 7.2 mmol) in 5 ml acetone was added through a syringe,
with stirring, and the bottle was pressured with 30 psi of CO. The mix­
ture was stirred vigorously with a magnetic stirrer for six hr, with
occasional CO repressuring. The solution was then filtered through Celite
and evaporated to dryness. The residue was extracted with warm hexane,
filtered, concentrated, and run through a 2 x 40 cm florisil/hexane
column. Evaporation of the yellow band gave 2.15g pure W(CO)₅(CS) (83%).

24. Preparation of trans-(¹³CO)W(CO)₄(CS)

A procedure identical to the previous one was used, starting with
0.71g Bu₄N[W(CO)₄(CS)] (1.0 mmol) and 0.26g AgCF₃SO₃ (1.0 mmol) in 60 ml
of acetone contained in a 100 ml bottle. The solution was stirred
vigorously for 8 hr under ~1.5 atm $^{13}$CO. A yield of 0.62g (84%) was collected. Reactions performed with a lower partial pressure of $^{13}$CO or with slow stirring yielded a product which contained more W($^{12}$CO)$_5$(CS) than expected, perhaps by a slow decomposition of the intermediate.

IR(hexane) 2091w, 1989vs, 1967m, (CS$_2$) 1258vs.

25. Reaction of Bu$_4$N[W(CO)$_4$(CS)] with P(4-ClC$_6$H$_4$)$_3$ and preparation of cis-W(CO)$_4$(CS)[P(4-ClC$_6$H$_4$)$_3$]

Ten ml of a dioxane solution of Bu$_4$N[W(CO)$_4$(CS)] (0.25g, 0.35 mmol) and P(4-ClC$_6$H$_4$)$_3$ (0.14g, 0.38 mmol) were stirred at 75° while N$_2$ bubbled through the solution. After 30 min the IR showed that most of the starting complex had been converted to a new compound, presumably Bu$_4$N[mer-W(CO)$_3$(CS)]{P(4-ClC$_6$H$_4$)$_3$]}. IR(CH$_2$Cl$_2$) 2012m, 1914vs, 1175m.

The above solution was cooled to room temperature and saturated with CO while AgCF$_2$SO$_2$ (0.09g, 0.35 mmol) in 3 ml acetone was added dropwise. Stirring and CO saturation were continued for 1.5 hr. The solution was then filtered through Celite and evaporated to dryness on a rotary evaporator under reduced pressure. The residue was extracted four times with hot hexane. These extracts were combined, concentrated, and placed on the top of a florisil/hexane column (1.5 x 30 mm). Development with 1:2 CH$_2$Cl$_2$-hexane brought down a yellow band which was concentrated and cooled to -20°. Large yellow crystals found to be mainly cis-W(CO)$_4$(CS)[P(4-ClC$_6$H$_4$)$_3$] were collected (0.025g, 10%).
IR(hexane) 2053m, 1981w, 1963m, 1955s, (CS) 1245s. Mass spectrum
parent ion m/e 704. Anal. Calcd. for W(CO)₄(CS)[P(4-ClC₆H₄)₃]:
C, 39.12; H, 1.70. Found: C, 40.00; H, 1.72.

A reaction of this product with CH₃NH₂ was quite rapid; the cis
isomer was converted in about 15 min to cis-W(CO)₄(CNCH₃)[P(4-ClC₆H₄)₃],
according to the IR spectrum.
IR(hexane) 2020m, 1936m, 1917s.

The fact that some of the trans isomer is present in the mixture
(~25%) is apparent from this reaction, since it reacts more slowly with
CH₃NH₂. Thus, after one day there is still some unreacted trans-
W(CO)₄(CS)[P(4-ClC₆H₄)₃].
IR(hexane) 1956vs.

26. Reaction of Et₄N[W(CO)] with P(4-ClC₆H₄)₃ and preparation of
   cis-W(¹³CO)₄[P(4-ClC₆H₄)₃]

The Et₄N[W(CO)]₅ was prepared according to the literature method.¹⁰⁷
A modification of the method of Allen and Barrett¹⁰⁸ was used in the
phosphine reaction. Ten ml of a dioxane solution of Et₄N[W(CO)]₅
(0.25g, 0.42 mmol) was stirred with P(4-ClC₆H₄)₃ (0.16g, 0.435 mmol) at
100°C with continuous purging of the solution by N₂. After 1.5 hr the
IR showed nearly complete consumption of the starting complex, so the
mixture was cooled to room temperature. Some formation of
W(CO)₅[P(4-ClC₆H₄)₃] was evident, but the major product is presumed to
be Et₄N[cis-W(CO)]₄[P(4-ClC₆H₄)₃], based on the similarity of its IR
spectrum to those reported for similar Cr and Mo complexes.¹⁰⁸
IR(CH₂Cl₂) 2007m, 1893vs, 1876m, sh, 1818m.

The above solution was saturated for a short time with ¹³CO and the flask was stoppered with a serum cap. A solution of AgCF₃SO₃ (0.1079 g, 0.415 mmol) in 3 ml acetone was added dropwise with stirring. The pressure of ¹³CO over the solution was increased to about 1.5 atm, and vigorous stirring was continued for one hr. The solution was then filtered through Celite and evaporated to dryness on a rotary evaporator. The residue was extracted with several 10 ml portions of hot hexane. The combined extracts were concentrated and placed on a 1.5 x 30 cm florisil/hexane column. Developing with 1:1 hexane-CH₂Cl₂ brought down a very pale yellow band, which was collected, concentrated, and cooled to -20°. Cream-colored crystals (0.125 g, 43%) were obtained.

IR(hexane) 2066w, 1975vw, 1953m, 1945s, 1914m, br.

27. Preparation of W(CO)_5[P(4-C₁₆H₁₃)₃]

A solution of Et₄N[W(CO)_₅] (0.208 g, 0.347 mmol) in 20 ml acetone was stirred while Ag CF₃SO₃ (0.09 g, 0.35 mmol) in 2 ml acetone was added dropwise. Excess phosphine (0.26 g, 0.71 mmol) in 5 ml acetone was then introduced, and stirring was continued for 2 hr. The mixture was evaporated to dryness and extracted with hot hexane. The hexane solution was concentrated and put on top of a florisil/hexane column. Developing the column with 1:1 hexane-CH₂Cl₂ gave a very pale yellow band which was collected, concentrated, and cooled at -20°. Light crystals of the product resulted (0.12 g, 50%).
IR(hexane) 2073w, 1953m, 1945s. Anal. Calcd. for
W(CO)\(_5\)\([\text{P(4-ClC}_6\text{H}_4\text{)}_3]\): C, 40.03; H, 1.74. Found: C, 40.53; H, 1.76.

28. Preparation of preferentially cis\(^{13}\text{CO}\)-enriched [(Ph\(_3\)P)\(_2\)N][ClW(CO)\(_5\)]

The complex, prepared according to the literature method,\(^{107}\) was stirred in CH\(_2\)Cl\(_2\) solution at room temperature under a pressure of about 1.5 atm 90\% \(^{13}\text{CO}\). The appearance of the enriched species was followed in the infrared spectrum by comparing the intensities of the 2063 (all \(^{12}\text{CO}\) complex) and 2054 cm\(^{-1}\) (mono-\(^{13}\text{CO}\) complex) bands. After 2 hr the enrichment was approximately 40-50\%, and the mixture was evaporated to dryness.

IR(CH\(_2\)Cl\(_2\)) 2063w, 2054w, 1914vs, 1838m.

29. Preparation of W(CO)\(_2\)(CS)(PPh\(_3\))\(_2\)Br\(_2\)

A solution of W(CO)\(_5\)(CS) (0.10g, 0.27 mmol) in 3 ml CH\(_2\)Cl\(_2\) was cooled to -80\° and Br\(_2\) (0.05g, 0.62 meq) in 1 ml CH\(_2\)Cl\(_2\) was added dropwise. The Schlenk tube reaction vessel was then removed from the cooling bath and allowed to warm to room temperature. A solution of PPh\(_3\) (0.20g, 0.76 mmol) in 2 ml CH\(_2\)Cl\(_2\) was added to this mixture, which caused immediate gas evolution. The solution was concentrated on a rotary evaporator and crystallized by the addition of hexane and cooling to -20\°. A yield of 0.25g (92\%) of dark yellow crystals was obtained.

IR(CH\(_2\)Cl\(_2\)) 2014m, 1959s, (CS\(_2\)) 1245s. Anal. Calcd. for
Attempts to decarbonylate this complex by refluxing in CH₂Cl₂ for 10 hr or refluxing in CHCl₃ for 4 hr led only to decomposition.

30. Preparation of W(CO)(CS)(diphos)₂Br₂

A solution of W(CO)(CS) (0.10g, 0.27 mmol) in 5 ml CHCl₃ was cooled to -80°, treated with Br₂ (0.05g, 0.62 meq) in 1 ml CHCl₃, and allowed to warm to room temperature. A solution of diphos (0.25g, 0.63 mmol) in 3 ml CHCl₃ was then introduced and the mixture was refluxed for 1 hr. It was diluted with pentane and cooled to -20° to yield a rust-colored precipitate. The compound was reprecipitated from CH₂Cl₂-hexane (0.15g, 44%). The elemental analyses were very poor, perhaps because the complex could not be crystallized.

IR(CH₂Cl₂) 1929s, 1216s. Molar conductivity λ=2.7 ohm⁻¹cm²mole⁻¹.

Found: C, 50.32; H, 3.83; Br, 14.61.


A solution of 0.15g W(CO)₅(CS) (0.41 mmol) in 5 ml CH₂Cl₂ was cooled to -80° and reacted with Br₂ (0.075g, 0.94 mmol) as it warmed to room temperature. Then a solution of P(2-totyl)₃ (0.28g, 0.92 mmol) in 2 ml CH₂Cl₂ was added, which caused immediate evolution of a gas. After standing 10 min, approximately 10 ml of hexane was added and the mixture was filtered. Addition of 10 ml more hexane and cooling to -20° gave metallic yellow crystals (0.15g, 45%). The complex was recrystallized from CH₂Cl₂-hexane.
IR(KBr) 2078 w, 2028 s, 1992 s, 1260 s. NMR(DCCl₃): 8 2.50 (m), 7.50 (s).
Molar conductivity \( \Lambda = 20.0 \text{ ohm}^{-1} \text{cm} \text{mole}^{-1} \).
Anal. Calcd. for [\((2-\text{CH}_3\text{C}_6\text{H}_4)_3\text{PH}\)\]W(CO)₃(CS)Br₃]: C, 34.97; H, 2.56; Br, 27.97. Found: C, 35.36; H, 2.88; Br, 28.50.

32. Preparation of W(CO)₂(CS)(diphos)₁₂

A solution of W(CO)₃(CS)(diphos) (0.07g, 0.98 mmol) and I₂ (0.027g, 2.12 meq) in 10 ml CH₂Cl₂ was stirred at room temperature for 4 hr. The solution was then filtered, diluted with hexane and cooled to \(-20^\circ\). The powder was reprecipitated from CH₂Cl₂-hexane several times and dried 12 hr at 85° under high vacuum. The analytical data were poor, and a chlorine analysis showed the presence of some chlorine, perhaps as CH₂Cl₂.

IR(CH₂Cl₂) 2036 s, 1972 s, (CS) 1245 s. Anal. Calcd. for W(CO)₂(CS)(diphos)₁₂: C, 37.18; H, 2.56; I, 27.14. Found: C, 35.82; H, 2.51; I, 24.38; Cl, 1.42.

33. Reaction of W(CO)(CS)(diphos)₂ with I₂

Reactions were carried out in CH₂Cl₂ between the two reactants in equivalent ratios of 1:1, 1:2, and 1:3. The mixtures containing two- or three-fold amounts of I reacted similarly, but the reaction with one equivalent of I showed consumption of only half of the W(CO)(CS)(diphos)₂.

A mixture of W(CO)(CS)(diphos)₂ (0.073g, 0.069 mmol) and I₂ (0.028g, 0.22 meq) was stirred for approximately 30 min. The solution was filtered, diluted with hexane, and cooled to \(-20^\circ\). The dark yellow crystals
(0.014g, 13%) were recrystallized from CH$_2$Cl$_2$-hexane and dried one hr at 50° under high vacuum.


Another product was produced in this reaction, and was also found to form from the above complex on standing in CH$_2$Cl$_2$ in IR cells. This product had IR bands at 2037s and 1971s. These are attributable to W(CO)$_2$(CS)(diphos) I$_2$. Infrared bands were also seen in some reactions at 1934 and 1218 cm$^{-1}$. These are very close to those of W(CO)(CS)(diphos)$_2$Br$_2$ and suggest the presence of W(CO)(CS)(diphos)$_2$I$_2$.

34. Preparation of [HW(CO)(CS)(diphos)$_2$]CF$_3$SO$_3$

Trifluoromethanesulfonic acid (0.086g, 0.57 mmol) in 2 ml CH$_2$Cl$_2$ was added to a suspension of W(CO)(CS)(diphos)$_2$ (0.60g, 0.57 mmol) in 20 ml CH$_2$Cl$_2$. After stirring 10 min, the solution was filtered, diluted with 35 ml of ethyl ether, and cooled to 0°. Orange crystals of the CH$_2$Cl$_2$-solvated complex (0.64g, 87%) were collected. After three recrystallizations from CH$_2$Cl$_2$-ether the crystals were dried in a high vacuum at 100° for five hours.

IR(CH$_2$Cl$_2$) 1958s, 1207s. NMR(DCCl$_3$) (recorded with a Bruker HX-90 Fourier transform instrument) $\tau$: 2.67 (m), 7.30 (m), 12.79 (triplet of triplets, J$_{PW}$=72 Hz, J$_{P'WH}$=13 Hz). Molar conductivity $\Lambda =$ 19.8 ohm$^{-1}$ cm$^2$ mole$^{-1}$. Anal. Calcd. for [HW(CO)(CS)(diphos)$_2$] CF$_3$SO$_3$: C, 54.91; H, 4.08; P, 10.88. Found: C, 54.50; H, 4.03; P, 10.64.
35. Preparation of W(CO)$_2$(diphos)$_2$

A different procedure from that in the literature was used to prepare this compound. A mixture of W(CO)$_6$ (1.5g, 0.425 mmol) and diphos (4.0g, 1.0 mmol) in 50 ml of decalin was refluxed for seven days. The solid mass which had formed was crushed, and the hot mixture was filtered and washed well with CH$_2$Cl$_2$ and hexane. A crude yield of 3.8g (86%) was thus obtained.

IR(CH$_2$Cl$_2$) 1847s, 1782s.

36. Preparation of [HW(CO)$_2$(diphos)$_2$]CF$_3$SO$_3$

A suspension of W(CO)$_2$(diphos)$_2$ (1.0g, 0.97 mmol) in 30 ml of CH$_2$Cl$_2$ was stirred with CF$_3$SO$_3$H (0.16g, 1.07 mmol) for 15 min. The solution was then filtered, diluted with 60 ml of ether, and cooled to 0° to yield 1.09g (89%) of pale yellow crystals containing CH$_2$Cl$_2$ of solvation. After recrystallization the product was dried for 12 hr at 100° under high vacuum.

IR(CH$_2$Cl$_2$) 1968w, 1862vs. NMR(DCC$_3$) (recorded with a Bruker HX-90 Fourier transform instrument) 2.80 (m), 7.35 (d), 14.91 (triplet of triplets, $J_{pwh} = 74$ Hz, $J_{p'wh} = 13$ Hz). Molar conductivity

Λ = 19.8 ohm$^{-1}$ cm$^2$ mole$^{-1}$. Anal. Calcd. for [HW(CO)$_2$(diphos)$_2$]CF$_3$SO$_3$:

C, 56.07; H, 4.16; P, 10.88. Found: C, 55.40; H, 3.84; P, 10.64.

37. Reaction of W(CO)(CS)(diphos)$_2$ with BCl$_3$

A suspension of W(CO)(CS)(diphos)$_2$ (0.54g, 0.51 mmol) in 20 ml of CH$_2$Cl$_2$ was exposed to BCl$_3$ gas and stirred until all of the complex
had dissolved. The mixture was filtered and diluted with ether, which caused the powdery product to precipitate (0.45g, ~80%). The product was reprecipitated three times from BC\textsubscript{3}-saturated solutions and dried in a high vacuum. Attempts to crystallize the product were not successful, and precipitation in the absence of excess BC\textsubscript{3} yielded some W(CO)(CS)(diphos)\textsubscript{2}. A magnetic susceptibility measurement with a Guoy balance showed the compound to be diamagnetic.

IR(\text{CH}_2\text{Cl}_2) 1960s, 2012s. Molar conductivity $\Lambda = 18.6$ ohm$^{-1}$ cm$^2$ mole$^{-1}$. Anal. Calcd. for W(CO)(CS)(diphos)\textsubscript{2}•BC\textsubscript{3}: C, 55.41; H, 4.10; Cl, 9.11. Found: C, 53.45; H, 4.13; Cl, 8.06.

38. Reaction of W(CO)\textsubscript{2}(diphos)\textsubscript{2} with BC\textsubscript{3}

A suspension of W(CO)\textsubscript{2}(diphos)\textsubscript{2} (0.50g, 0.48 mmol) was stirred under a BC\textsubscript{3} atmosphere until all of the complex had dissolved. The solution was then filtered and diluted with ethyl ether until precipitation began. Cooling to -20° gave a yellow precipitate (0.42g, ~75%). The product was reprecipitated several times from CH\textsubscript{3}Cl\textsubscript{2}-ether and dried under high vacuum. A magnetic susceptibility measurement showed this complex to be diamagnetic.

IR(\text{CH}_2\text{Cl}_2) 1967vw, 1863vs. Molar conductivity $\Lambda = 20.5$ ohm$^{-1}$ cm$^2$ mole$^{-1}$. Anal. Calcd. for W(CO)\textsubscript{2}(diphos)\textsubscript{2}•BC\textsubscript{3}: C, 56.67; H, 4.20; Cl, 9.31. Found: C, 55.38; H, 4.09; Cl, 9.52.

39. Preparation of [W(CO)\textsubscript{2}(diphos)\textsubscript{2}(C\textsubscript{2}H\textsubscript{2})]BF\textsubscript{4}

A mixture of W(CO)\textsubscript{2}(diphos)\textsubscript{2} (0.50g, 0.48 mmol) and [Et\textsubscript{3}O]BF\textsubscript{4} (0.09g, 0.475 mmol) in 50 ml CH\textsubscript{2}Cl\textsubscript{2} was stirred until the complex had
dissolved (~4hr). The solution was filtered and ethyl ether was added until it became cloudy. Cooling to -20° gave a yellow crystalline product (0.55g, ~90%) which contained CH₂Cl₂ of solvation. After two recrystallizations the product was dried under high vacuum at 100° for 6 hr. Magnetic susceptibility measurements showed that this complex is diamagnetic, as expected for a W(II) complex.

\[ \text{IR}(\text{CH}_2\text{Cl}_2) \, 1970\text{w}, 1864\text{vs.} \]

\[ \text{NMR}(\text{DCCl}_3) \, \tau 2.74 \text{ (m)}, 6.51 \text{ (q, J=7 Hz)}, \]

\[ 8.30 \text{ (s)}, 8.79 \text{ (t, J=7 Hz)}. \]

Molar conductivity \( \Lambda = 24.0 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \).

Anal. Calcd. for \( \text{[W(CO)}_2(\text{diphos})_2(\text{C}_2\text{H}_5)]\text{BF}_4 \): C, 58.84; H, 4.64; P, 10.86. Found: C, 57.63; H, 4.37; P, 10.49.

40. Preparation of (diphos)₃(\text{CO})\text{WCS·HgCl₂}

A suspension of W(CO)(CS)(diphos)₂ (0.10g, 0.095 mmol) and HgCl₂ (0.026g, 0.096 mmol) in 8 ml of CH₂Cl₂ was stirred (in air) for approximately 10 min. The solution was filtered, diluted with 7 ml of hexane and cooled to -20° to complete the crystallization. The orange solid (0.11g, 87%) was recrystallized from CH₂Cl₂-hexane.

\[ \text{IR}(\text{CH}_2\text{Cl}_2) \, 1885\text{s}. \]

Molar conductivity \( \Lambda = 5.4 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1} \). Anal. Calcd. for W(CO)(CS)(diphos)₂·HgCl₂: C, 46.84; H, 3.55; S, 2.42. Found: C, 46.59; H, 3.44; S, 2.37

41. Preparation of (diphos)₃(\text{CO})\text{WCS·Hgl₂}

A suspension of W(CO)(CS)(diphos)₂ (0.10g, 0.095 mmol) and Hgl₂ (0.045g, 0.099 mmol) in 10 ml of CH₂Cl₂ was stirred for five min, and the resultant red solution was filtered. Diluting with 10 ml hexane and cooling to -20° gave red crystals (0.14g, ~93%). These were recrystallized
from CH₂Cl₂-hexane. An NMR spectrum in DCCl₃, after drying in a high vacuum, showed the presence of CH₂Cl₂.

IR(CH₂Cl₂) 1872s. Molar conductivity Α = 5.4 ohm⁻¹ cm² mol⁻¹.

Anal. Calcd. for W(CO)(CS)(diphos)_2·Hgl₂·CH₂Cl₂: C, 41.45; H, 3.14; S, 2.05. Found: C, 40.98; H, 2.99; S, 1.91.

42. Preparation of [(diphos)_2(CO)WCS]_2AgBF₄

A suspension of W(CO)(CS)(diphos)_2 (0.39g, 0.37 mmol) in 30 ml acetone was stirred while AgBF₄ (0.036g, 0.185 mmol) in 2 ml acetone was added dropwise. The clear yellow solution, after stirring 10 min, was filtered, concentrated, and diluted with 20 ml of ethyl ether. Cooling to -20° completed the precipitation. The yellow powder (0.38g, 89%) was crystallized by dissolving in 30 ml CH₂Cl₂, filtering through Celite, adding hexane with warming, and allowing to cool to -20°. A magnetic susceptibility measurement showed the complex to be diamagnetic.

IR(CH₂Cl₂) 1869s, 1106s. Molar conductivity Α = 26.4 ohm⁻¹ cm² mol⁻¹.


43. Preparation of (diphos)_2(CS)W-CS-W(CO)₅

A solution of W(CO)₅ (acetone) was prepared by adding dropwise a solution of AgBF₄ (0.033g, 0.17 mmol) in 2 ml acetone to Et₄N[W(CO)₅] (0.10g, 0.167 mmol) in 10 ml acetone. This solution was drawn into a syringe and added slowly to a stirred suspension of W(CO)(CS)(diphos)_2 (0.15g, 0.142 mmol) in 80 ml CH₂Cl₂. The suspension gradually became a clear orange solution. After 30 min of stirring, the solution was
filtered and concentrated to 50 ml. Hexane (30 ml) was added, and the evaporation was continued until precipitation was nearly complete. Cooling to -20° gave 0.19g of orange solid (96%). The complex was crystallized by dissolving in 10 ml of warm CS₂, filtering, diluting with 10 ml pentane, and cooling to -20°.

IR(CS₂) 2062w, 1925vs, 1878m. Anal. Calcd. for W(CO)(CS)(diphos)₂: W(CO)₅: C, 51.45; H, 2.87; S, 2.32. Found: C, 51.76; H, 3.54; S, 1.75.

44. Preparation of [(diphos)₂(CO)W(CSCH₂)]F₃O₇

A suspension of W(CO)(CS)(diphos)₂ (0.10g, 0.095 mmol) in 10 ml CH₂Cl₂ was stirred as MeSO₃F (0.011g, 0.096 mmol) was added to the mixture. The complex dissolved very rapidly, and the clear solution was filtered and diluted with 15 ml hexane. Cooling to -20° gave pink-orange crystals of the product (0.10g, 86%).

IR(CH₂Cl₂) 1898s. NMR(DCCl₃) τ 2.7 (m), 7.9 (s,-CH₂), 8.4 (s).

Molar conductivity Λ = 21.6 ohm⁻¹ cm² mole⁻¹. Anal. Calcd. for [W(CO)(diphos)₂(CSCH₂)]F₃O₇: C, 56.60; H, 4.37; S, 5.49. Found: C, 56.35; H, 4.42; S, 5.71.

45. Preparation of [(diphos)₂(CO)W(CSCH₂)]BF₄

A suspension of W(CO)(CS)(diphos)₂ (0.425g, 0.404 mmol) in 25 ml CH₂Cl₂ was stirred as [Et₃O]BF₄ (0.078g, 0.41 mmol) in 2 ml CH₂Cl₂ was added. After 10 min of stirring, the solution was filtered and concentrated to 10 ml. Addition of hexane (~40 ml) and cooling to 0° gave dark pink crystals (0.43g, 91%).
IR(CH₂Cl₂) 1898. NMR(DCCl₃) 2.7 (m), 7.9 (q), 8.6 (s), 9.25 (t).
Molar conductivity Λ = 25.6 ohm cm⁻¹ mol⁻¹. Anal. Calcd. for
\([W(CO)(diphos)₂(CSCH₂)]BF₄\): C, 57.53; H, 4.54; S, 2.74. Found:
C, 57.72; H, 4.90; S, 2.27.

46. Preparation of \([W(CO)]₄CSCH₃\)

A suspension of Bu₄N[\([W(CO)]₄CS\)] (0.58g, 0.82 mmol) in a mixture of 50 ml pentane and 5 ml CH₂Cl₂ at 0° was stirred while CH₃SO₃F (0.10g, 0.88 mmol) in 2 ml CH₂Cl₂ was added dropwise. After stirring 30 min the solution was decanted from the dark oil which had formed. The oil was extracted once with pentane, and the combined solutions were evaporated. The residue was extracted with pentane (~20 ml) and the solution concentrated under a stream of N₂ to ~3 ml. Cooling to -80° gave yellow crystals (0.07g, 18%). The product is quite pure at this stage. Recrystallization using Schlenk techniques causes a large product loss and does not appear to increase the purity significantly.

IR(pentane) 2115w, 2033vs, 1118m. NMR(DCCl₃) 7.40 (s). Mass spectrum parent ion m/e 482. Anal. Calcd. for \([W(CO)]₄CSCH₃\): C, 14.93; H, 0.62; I, 26.35. Found: C, 14.19; H, 0.7; S, 25.99.

47. Preparation of \([W(CO)]₄CSC(0)CF₃\)

A suspension of Bu₄N[\([W(CO)]₄CS\)] (0.50g, 0.705 mmol) in a mixture of 3 ml CH₂Cl₂ and 50 ml of pentane was vigorously stirred for 30 min after the addition of trifluoroacetic anhydride (0.25g, 1.19 mmol).
The yellow solution was then decanted from the dark oil and concentrated
to about 5 ml. This solution was filtered under \(N_2\) and cooled to \(-80^\circ\). Yellow crystals formed which became dark brown when the solution was decanted. The product was dried in a high vacuum. An elemental analysis was not attempted because of the apparent instability of the complex.

\[
\text{IR (pentane)} \ 2137w, 2080w, sh, 2057vs, 2052vs, 1737m. \quad \text{Mass spectrum parent ion } m/e \ \text{Calcd. for } ^{182}\text{W}(\text{CO})_4\text{CSC(O)CF}_3: \ 561.7905. \ \text{Found: } 561.7924 \pm 0.0028.
\]

46. **Preparation of \(\text{W}(\text{CO})_4\text{CSC(O)CH}_3\)**

Acetic anhydride (1.0g, 9.8 mmol) in 10 ml \(\text{CH}_2\text{Cl}_2\) was treated with excess gaseous \(\text{BF}_3\), and the saturated solution was added to \(\text{Bu}_4\text{N[\text{W}(\text{CO})_4\text{CS})] (4.0g, 5.65 mmol) in 125 ml \text{CH}_2\text{Cl}_2.\) The mixture was stirred for 30 min, and then diluted with 100 ml pentane, which caused a dark oil to precipitate. The supernatant solution was decanted under \(N_2\), evaporated to dryness, and extracted with pentane. Crystallization of the solution at \(-80^\circ\) using Schlenk techniques gave bright yellow crystals. After two recrystallizations, the yield of the product was 0.28g (10%). The solid is slightly air-sensitive and was stored under vacuum at \(-20^\circ\).

\[
\text{IR (pentane)} \ 2124w, 2065w, sh, 2057vs, 2052vs, 1753m, 1081m. \quad \text{NMR (DCCl}_3) \ 7.60 \ (s). \quad \text{Mass spectrum parent ion } m/e \ 510. \quad \text{Anal. Calcd. for } \text{W}(\text{CO})_4\text{CSC(O)CH}_3: \ C, 16.47; H, 0.59; I, 24.90. \ \text{Found: } C, 16.15; H, 0.54; I, 25.70.
49. **Preparation of $\text{W(CO)}_5\text{CNCH}_3$ from $\text{W(CO)}_5\text{(CS)}$**

A solution of $\text{W(CO)}_5\text{(CS)}$ (0.60g, 1.67 mmol) in 50 ml of ethyl ether was saturated with $\text{CH}_3\text{NH}_2$. After five min the solution was evaporated to dryness. Sublimation of the residue at $35^\circ$ under high vacuum gave quite pure $\text{W(CO)}_5\text{CNCH}_3$ (0.55g, 92%).

IR (pentane) 2177w ($\nu_{\text{CN}}$), 2069w, 1956vs. NMR ($\text{DCCl}_3$) $\tau 6.55$ (s).

Mass spectrum parent ion m/e 365. Anal. Calcd. for $\text{W(CO)}_5\text{CNCH}_3$:
C, 23.60; H, 0.85. Found: C, 23.07; H, 0.73.

An identical reaction with trans-$(^{13}\text{CO})\text{W(CO)}_4\text{(CS)}$ gave $\text{trans-}$(^{13}\text{CO})$\text{W(CO)}_4\text{CNCH}_3$.

IR (pentane) 2177w ($\nu_{\text{CN}}$), 2064w, 1955vs, 1916m.

50. **Preparation of $\text{W(CO)}_5\text{CNCy}$ from $\text{W(CO)}_5\text{(CS)}$**

A solution of $\text{W(CO)}_5\text{(CS)}$ (0.20g, 0.56 mmol) and cyclohexylamine (0.065g, 0.66 mmol) in 25 ml of pentane was allowed to stand at room temperature for three hours. The mixture was evaporated, extracted with pentane, filtered, concentrated, and cooled to $-20^\circ$. A yield of 0.22g $\text{W(CO)}_5\text{CNCy}$ was collected (91%).

IR (pentane) 2154w ($\nu_{\text{CN}}$), 2065w, 1953vs.

An identical preparation with trans-$(^{13}\text{CO})\text{W(CO)}_4\text{(CS)}$ gave $\text{trans-}$(^{13}\text{CO})$\text{W(CO)}_4\text{CNCy}$.

IR (pentane) 2154w ($\nu_{\text{CN}}$), 2058w, 1952vs, 1912m.

51. **Preparation of $\text{W(CO)}_5\text{CNCH}_2\text{CO}_2\text{CH}_3$ from $\text{W(CO)}_5\text{(CS)}$**

A methanol solution of sodium methoxide was prepared by adding Na (0.10g, 4.35 mmol) to 25 ml methanol. To this solution was added
glycine methyl ester hydrochloride (0.70 g, 5.6 mmol). This solution was added to a mixture of W(CO)$_5$(CS) (0.70 g, 1.90 mmol) in 200 ml methanol, and the solution was stirred for 12 hr. Evaporation of the solution, extraction several times with hexane, filtration, concentration to about 20 ml, and cooling to -20$^\circ$ gave 0.25 g of the product (31%). The complex was recrystallized three times from hexane.

IR(hexane) 2159 (v$_{CN}$), 2063 w, 1957 vs. NMR(DCCl$_3$) 5.60 (-CH$_2$-), 6.20 (-CH$_3$-). Mass spectrum parent ion m/e 423.

52. Reaction of W(CO)$_5$(CS) with piperidine

A mixture of W(CO)$_5$(CS) and W(CO)$_6$ containing 2.0 g of W(CO)$_5$(CS) (5.45 mmol) was dissolved in 200 ml hexane. A solution of piperidine (0.514 g, 6.05 mmol) in 10 ml hexane was added, which caused the solution to become cloudy immediately; a precipitate soon formed. The solution was stirred at room temperature for five days, but the IR spectrum showed that much W(CO)$_5$(CS) was still present. More piperidine (0.35 g, 4.1 mmol) was added and the solution was stirred one more day. It was then evaporated to dryness, slurried in 1:1 CH$_2$Cl$_2$-hexane, and put on the top of a 2 x 35 cm florisil/hexane column. Washing with hexane removed the W(CO)$_6$. Developing with 1:1 CH$_2$Cl$_2$-hexane brought down a broad yellow band, the front of which was mainly W(CO)$_5$(piperidine). The remainder of the band was W(CO)$_5$(SC(H)N(CH$_2$)$_3$). This solution was concentrated with warming and cooled to -20$^\circ$ to yield 0.8 g of the complex (33%).

IR(hexane) 2070 w, 1974 vs, 1937 s, 1929 s, 1915 m. NMR(DCCl$_3$)
8.1 (s, C-H), 6.15 (m, -CH$_2$-), 6.40 (m, -CH$_2$-), 8.28 (s, -CH$_2$CH$_2$CH$_2$-).
Mass spectrum parent ion m/e 453. Anal. Calcd. for W(CO)$_5$(SC(H)N(CH$_2$)$_5$): C, 29.2; H, 2.43; S, 7.05. Found: C, 29.42; H, 2.13; S, 6.86.

53. **Reaction of W(CO)$_5$(CS) with dimethylamine**

A mixture of W(CO)$_5$(CS) and W(CO)$_6$ containing 1.1g W(CO)$_5$(CS) (3.0 mmol) was dissolved in 100 ml hexane which was then saturated with dimethylamine. After standing six hr, the solution was stored at -20° overnight. The solution and precipitate were put on a 2 x 35 cm florisil/hexane column and washed with hexane. Developing the column with 1:1 CH$_2$Cl$_2$-hexane gave two yellow bands; the first was found to be W(CO)$_5$(NHMe$_2$). The second band was collected, concentrated, and cooled to -20° to yield 0.20g W(CO)$_5$(SC(H)NMe$_2$) (16%).

IR(hexane) 2071w, 1975vw, 1938s, 1932s, 1916m. NMR(DCCl$_3$) δ1.05 (C-H), 6.60 (-CH$_3$), 6.72 (-CH$_3$). Mass spectrum parent ion m/e 413. Anal. Calcd. for W(CO)$_5$(SC(H)N(CH$_2$)$_2$): C, 23.2; H, 1.69; S, 7.75. Found: C, 22.89; H, 1.88; S, 7.40.

54. **Preparation of W(CO)$_5$(SC(H)N(CH$_2$)$_2$) from N,N-dimethylthioformamide**

A solution of W(CO)$_6$ (1.5g, 4.25 mmol) and SC(H)N(CH$_2$)$_2$ (0.4g, 4.5 mmol) in 40 ml THF was stirred and irradiated with ultraviolet light for seven hr at room temperature. The mixture was evaporated to dryness, dissolved in 1:2 CH$_2$Cl$_2$-hexane, put on a 2 x 35 cm florisil column, and washed with hexane. Developing with 1:1 CH$_2$Cl$_2$-hexane brought down a yellow band of the product (0.40g, 23%). This complex had IR and NMR spectra identical to those of the complex prepared from W(CO)$_5$(CS) and dimethylamine.
55. Reaction of W(CO)$_4$(CS)(PPh$_3$) with CH$_3$NH$_2$

The mixture of cis and trans isomers of W(CO)$_4$(CS)(PPh$_3$) which is obtained by the thermal preparation (0.30 g, 0.50 mmol) was dissolved in 150 ml of hexane saturated with methylamine. After five hr all of the cis isomer had reacted, so the solution was concentrated and placed on the top of a 1.5 x 35 cm florisi1/hexane column. After washing with hexane and developing with 1:1 CH$_2$Cl$_2$-hexane, a broad yellow band containing the trans isomer was eluted. Developing with CH$_2$Cl$_2$ brought off the isocyanide product, W(CO)$_4$(CNCH$_2$)$_2$(PPh$_3$), mainly the cis isomer. Concentration, addition of hexane, and cooling to -20° gave the colorless product (0.044 g, 14.5%).

IR(n-hexane) 2148 (v$_{CN}$), 2018m, 1932m, 1913vs. NMR(DCCl$_3$)
2.70 (m), 7.10 (d, $^5J_{P-H}=1.5$Hz). Mass spectrum parent ion m/e 599.

Anal. Calcd. for W(CO)$_4$(CNCH$_2$)$_2$(PPh$_3$): C, 48.10; H, 3.00; N, 2.43.
Found: C, 48.08; H, 3.01; N, 2.43.

56. Preparation of W(CO)$_5$NCS$^-$ from W(CO)$_5$(CS)

A mixture of W(CO)$_5$(CS) (0.05 g, 0.136 mmol) and [(Ph$_3$P)$_2$N][N$_3$] (0.08 g, 0.14 mmol) in a flask under N$_2$ was dissolved in 3 ml THF. Gas evolution began immediately. After 45 min of standing at room temperature, the IR spectrum of the solution showed that all of the W(CO)$_5$(CS) had reacted. The infrared spectrum of the product was identical to that of [(Ph$_3$P)$_2$N][W(CO)$_5$(NCS)] prepared from W(CO)$_6$ and [(Ph$_3$P)$_2$N][NCS] according to the method of Wojcicki and Farona. The complex was isolated by precipitation with ethyl ether and cooling to -20° (0.10 g, 95%).
IR($\text{CH}_2\text{Cl}_2$) 2102 m ($\nu_{\text{CN}}$), 2066 w, 1921 vs, 1862 s.

An identical reaction with trans-$^{13}$W(CO)$_2$(NCS) gave [trans-$^{13}$W(CO)$_2$(NCS)]$^-$.

IR($\text{CH}_2\text{Cl}_2$) 2102 m ($\nu_{\text{CN}}$), 2061 w, 1921 vs, 1822 s.

57. Reaction of W(CO)$_5$(CS) with MeLi and [Me$_3$O]PF$_6$

A solution of W(CO)$_5$(CS) (1.0 g, 2.72 mmol) in 20 ml of THF was stirred at 0° while a 2.0 M ether solution of CH$_3$Li (1.35 ml, 2.70 mmol) was added dropwise. The mixture was stirred for five min and then evaporated to dryness. The dark residue was dissolved in 10 ml of CH$_2$Cl$_2$ and added dropwise to [Me$_3$O]PF$_6$ (0.76 g, 3.7 mmol) in 10 ml CH$_2$Cl$_2$. After stirring 10 min, 5 g of florisil was added and the solution was evaporated to dryness. The florisil was placed on top of a 1.5 x 35 cm florisil/hexane column and washed with hexane. Developing with 2:1 hexane-CH$_2$Cl$_2$ brought off a broad yellow band containing several poorly separated fractions. The major fraction was collected and evaporated to an oil under high vacuum. Distillation at room temperature onto a water-cooled probe gave a yellow liquid (~0.05 g, 20%). This was redistilled to yield yellow crystals, which melt at 25.5°. The compound was found to be W(CO)$_5$(CH$_3$)$_2$.

IR(n-hexane) 2075 w, 1980 v, 1942 v, 1935 m. NMR($\text{DCCl}_3$) $\tau$ 7.38 (s).

IV. RESULTS AND DISCUSSION

A. Attempts to Prepare Thiocarbonyl Complexes

1. Reactions of metal complexes with \( \text{CS}_2 \)

Since it had been found earlier that the nucleophilic addition of \( \text{CpFe(CO)}_2^- \) to \( \text{CS}_2 \) provided a convenient route to a metal thiocarbonyl complex,\(^80\) this reaction was investigated in detail in the hope that this sequence might prove to be a general route to metal thiocarbonyls. Reactions carried out according to the method reported in the literature\(^80\) gave several products and low yields of the desired \([\text{CpFe(CO)}_2(\text{CS})]^-\) complex. It was found that the addition of \( \text{CS}_2 \) to \( \text{CpFe(CO)}_2^- \) is a rapid reaction, and that the introduction of methyl iodide to form the dithioester complex, \( \text{CpFe(CO)}_2\text{CS}_2\text{CH}_3 \), could follow the addition of \( \text{CS}_2 \) by just seconds. Using this procedure, the dithioester complex was formed very cleanly and could be isolated in good yield.\(^111\) When longer reaction times between \( \text{CpFe(CO)}_2^- \) and \( \text{CS}_2 \) are employed, one of the products is \([\text{CpFe(CO)}_2]\)^{2-}, which apparently results from oxidation of the iron anion.

Several reactions of \( \text{CpFe(CO)}_2\text{CS}_2\text{CH}_3 \) were investigated to find the best method of converting the complex to the thiocarbonyl cation. The literature method,\(^80,111\) which uses HCl gas, is rather slow and although satisfactory in this system, may not be applicable to other metal systems. Reactions of the dithioester with acetyl chloride, trichloroacetic acid, mercuric chloride, and stannic chloride were all quite slow and yielded other carbonyl products in addition to the thiocarbonyl. Methyl
fluorosulfonate and [Et₂O]BF₄ reacted more rapidly, but did not yield the desired product. Similar complexes were produced by the two reagents, as indicated by the infrared spectra (ν(CO) at 2056, 2016 and 2057, 2016 cm⁻¹, respectively). Although these products were not isolated and characterized, their identification as dithiocarbene complexes, [CpFe(CO)₂C(SR)₂]⁺, seems reasonable in light of the preparation of similar complexes of platinum. The fact that products other than [CpFe(CO)₂(CS)]⁺ were formed in these reactions meant, however, that no acceptable substitute for HCl was found.

When a large excess of CS₂ is added to a THF solution of Mn(CO)₅⁻, the color immediately becomes dark yellow. Addition of CH₃I causes the formation of one major product, which was found to be Mn(CO)₅CH₃. An identical reaction between Re(CO)₅⁻ and CS₂ yields little, if any, Re(CO)₅CH₂, and only one major product is observed in the infrared spectrum of the reaction mixture. Treatment of this product with HCl gas and anion metathesis with [NH₄]PF₆ yielded a light powder which may have been [Re(CO)₅(CS)]PF₆. The infrared spectrum and a rapid reaction with cyclohexylamine led to this assignment. Unfortunately, several attempts to repeat this preparation met with no success. These reactions all produced the same product which had been observed in the first preparation upon reaction of the Re(CO)₅⁻-CS₂ mixture with CH₃I. However, the following reaction with HCl is apparently the non-reproducible step.
Carbon disulfide added to a THF solution of \( \text{CpW(CO)}_3^- \) causes an immediate color change to dark yellow. However, addition of \( \text{CH}_3\text{I} \) gives only \( \text{CpW(CO)}_2\text{CH}_3^- \). The use of \( \text{CH}_3\text{SO}_3\text{F} \) instead of \( \text{CH}_3\text{I} \) produces another compound as well, which was shown to be \( \text{CpW(CO)}_3^-\text{OSO}_2\text{F} \) by its elemental analysis and mass spectrum. The \( \text{CS}_2 \) is not essential in the formation of this product, which apparently results from oxidation of the tungsten species by \( \text{CH}_3\text{SO}_3\text{F} \). Eaborn et al. have recently reported other reactions in which this reagent oxidizes metal complexes.\(^\text{113}\)

An attempt was made to prepare \([\text{CpRu(CO)}_2\text{CS}]^+\) in a manner analogous to that used to obtain the iron complex. Although there is good evidence that the dithioester complex is obtained cleanly upon reaction of \( \text{CpRu(CO)}_2^- \) with \( \text{CS}_2 \) followed by \( \text{CH}_3\text{I} \), the further reaction of this complex with \( \text{HCl} \) was not very successful. Much of the dithioester did not react, and only small quantities of the desired product were seen in the infrared spectrum.

These results may be partially interpreted in terms of the nucleophilicities of the metal anions. Dessy, Pohl, and King\(^\text{114}\) have determined that the nucleophilicities of these anions decrease in the order\(^\text{115}\)

\[
\text{CpFe(CO)}_2^- \gg \text{Re(CO)}_5^- \gg \text{CpW(CO)}_3^- \gg \text{Mn(CO)}_5^- .
\]

Color changes in solutions of all of the anions upon the addition of \( \text{CS}_2 \) suggest that there is some interaction with \( \text{CS}_2 \) in all cases. However, only \( \text{CpFe(CO)}_2^- \), \( \text{CpRu(CO)}_2^- \), and \( \text{Re(CO)}_5^- \) show any evidence for the formation of a \( \text{M-CS}_2\text{CH}_3 \) complex on addition of \( \text{CH}_3\text{I} \). These results indicate that there may be an equilibrium situation (Eq. 13) in the \( \text{CS}_2^- \)-containing solutions.

\[
\text{M}^- + \text{CS}_2 \rightleftharpoons \text{M} - \text{CS}_2^S
\]  
(13)
The stronger nucleophiles drive the equilibrium to the right, but the poor nucleophiles exist mainly as the free metal anions. Ellis has shown recently that (Cy₃P)Mn(CO)₄⁻ (which is expected to be substantially more nucleophilic than Mn(CO)₅⁻) and Re(CO)₅⁻ react with CS₂ to form intermediates (presumably of the type in Eq. 13) which can be metallated to produce metal carbonyl dithiolate complexes.¹¹⁶

Very recently it has been found that the conversion of CpFe(CO)₂CS₂CH₃ to [CpFe(CO)₂(CS)]⁺ may be carried out rapidly and cleanly with trifluoromethanesulfonic acid.¹¹⁷ The thiocarbonyl cation may be conveniently isolated as the CF₃SO₃⁻ salt. Since HCl reacts only poorly with the dithioester intermediates presumed to be formed in several of the metal anion -CS₂-CH₃ reactions, CF₃SO₃H may make it possible to isolate thiocarbonyl complexes from these intermediates. However, it is apparent that the preparation of these dithioester complexes is limited to those metal complexes which form strongly nucleophilic metal anions.

In a reaction related to these, infrared evidence was seen for the formation of small amounts of CpFe(CO)₂CSe₂CH₃ from CpFe(CO)₂⁻, CSe₂⁻, and CH₃I. Reaction with HCl did not appear to convert this complex to the desired selenocarbonyl. However, the use of CF₃SO₃H may also be advantageous in this reaction.

The reaction of a metal carbonyl complex containing a weakly bound ligand such as an olefin¹¹⁸ or THF¹¹⁹ with CS₂ and a sulfur acceptor (triphenylphosphine) has been used to prepare several metal thiocarbonyl complexes. In an attempt to use this type of reaction, W(CO)₅NCCH₃
(prepared by refluxing $\text{W(CO)}_6$ in acetonitrile for two days and crystal-
izing the hexane-soluble portion) was refluxed in $\text{CS}_2$ with equimolar $\text{PPh}_3$ for 19 hr. The infrared spectrum showed that a large amount of $\text{W(CO)}_5\text{PPh}_3$ had formed. There were also two very weak IR peaks (2096, 2007 cm$^{-1}$) which could be those of $\text{W(CO)}_5\text{(CS)}$. It was concluded, however, that this was not a satisfactory method of preparation for the complex. Metal complexes which do react with $\text{CS}_2$ to yield thiocarbonyl complexes apparently form an intermediate $\pi$-$\text{CS}_2$ complex by the oxidative addition of $\text{CS}_2$ to the metal. $\text{72,74,81-83}$ Such an oxidative addition to a $\text{W(CO)}_5$ moiety is perhaps unfavorable because of low metal electron density.

2. **Reactions of organometallic anions with thiophosgene and its derivatives**

The reaction of $\text{CpFe(CO)}_2^-$ with $\text{Cl-C(S)OR}$ ($\text{R=CH}_3$, $\text{C}_2\text{H}_5$) has been reported to yield $\text{CpFe(CO)}_2^-$-$\text{C(S)OR}$, which may be converted to the thiocarbonyl cation with $\text{HCl}$. $\text{85}$ A similar procedure was attempted by reacting $\text{CpW(CO)}_3^-$ with $\text{ClC(S)OCH}_3$, but the major product of this reaction was $\text{CpW(CO)}_3\text{Cl}$. To investigate the reaction further, phenyl chlorothioformate $\text{118}$ ($\text{ClC(S)OPh}$) was prepared and reacted with several organometallic anions. The reaction with $\text{CpFe(CO)}_2^-$ appeared to give the desired product, and its reaction with $\text{HCl}$ produced some of the thiocarbonyl cation. However, the reaction of $\text{Re(CO)}_5^-$ with $\text{ClC(S)OPh}$ yielded only $\text{Re(CO)}_5\text{Cl}$, and the reaction with $\text{Mn(CO)}_5^-$ gave a mixture
of many products. Ethylene trithiocarbonate was also reacted with 
\( \text{CpFe(CO)}_2^- \) and \( \text{Mn(CO)}_5^- \). Only \( [\text{CpFe(CO)}_2]_2 \) was produced in the first reaction, and the latter combination showed no evidence of reaction after refluxing in THF for two days.

Reactions of \( \text{CpFe(CO)}_2^- \) with \( \text{Cl}_2\text{CS} \) in THF were performed using molar ratios of 2:1 and 1:2. In both cases the product was \( [\text{CpFe(CO)}_2]_2 \). Some \( \text{CpFe(CO)}_2\text{Cl} \) was also seen in the latter reaction. The tetracarbonylferrate anion, \( \text{Fe(CO)}_4^- \), was also treated with thiophosgene. The infrared spectrum of one reaction mixture showed a strong band at 1259 cm\(^{-1}\), indicative of a metal thiocarbonyl, but several attempts to repeat this reaction failed. Another unsuccessful venture was the reaction of \( \text{Cl}_2\text{CS} \) with \( \text{Na}_2\text{Cr(CO)}_5 \).\(^{119}\) No IR bands indicative of a thio-carbonyl complex were seen.

The successful preparation of the group VI \( \text{M(CO)}_5 \) (CS) complexes by the reaction of reduced metal species with thiophosgene is discussed in another section (vide infra).

3. Reactions of metal carbonyls with boron sulfide

The conversion of organic ketones to thioketones may be accomplished quite smoothly with \( \text{B}_2\text{S}_3 \).\(^{120}\) Several attempts were made to extend this reaction to a carbonyl coordinated to a transition metal. Refluxing a \( \text{CHCl}_3 \) solution of \( [\text{CpFe(CO)}_2]_2 \) or \( \text{CpFe(CO)}_2\text{CH}_3 \) with \( \text{B}_2\text{S}_3 \) caused little reaction to occur. After heating a diglyme solution of \( \text{W(CO)}_6 \) and \( \text{B}_2\text{S}_3 \) at 120\(^\circ\) for one day, no thio-carbonyl formation was observed. Boron sulfide did react with \( \text{W(CO)}_2(\text{diphos})_2 \) in refluxing \( \text{CHCl}_3 \), but the product
apparently results from an oxidative addition to the metal and does not contain a thiocarbonyl. Reactions of B₃S₃ with organic carbonyls appear to involve nucleophilic attack by the carbonyl oxygen at boron. Apparently the lower nucleophilicity of a metal carbonyl prevents it from reacting in this manner.

B. The Group VI M(CO)₅(CS) Complexes

1. Preparation

Reduction of the group VI hexacarbonyls by sodium amalgam in refluxing tetrahydrofuran has been recently shown to produce mainly the M₂(CO)₁₀⁻ binuclear dianions along with smaller amounts of the mononuclear M(CO)₅⁻ species. The reactions of these products with organic or organometallic halides give products (generally in low yields) which could arise from either the mononuclear or dimeric dianions. For example, reactions with 3, 4-dichlorocyclobutenes give cyclobutadiene-tetracarbonylmetal complexes (M=W, 1%; M=Mo, 35%); a reaction of the molybdenum species with 3-chloro-2-(chloromethyl)-propene gives a 1% yield of trimethylenemethanetetracarbonylmolybdenum; the chromium and tungsten reduced species react with 2-bromo-2-nitrosopropane to give 3-5% yields of dimethylketimine complexes; the chromium species react with dialkyl germanium and tin dihalides to produce THF adducts of dialkylgermylene and dialkylstannylene complexes; and the chromium species also react with 1,1-dichloro-2,3-diphenylcyclopropene, forming a cyclopropylcarbene complex in 19.5% yield. The product-yielding species
in these reactions now appears to be the \( M_2(CO)_{10} \) \(^{2-}\) anions, through a reaction such as that of Eq. 14.

\[
Na_2M_2(CO)_{10} + LX_2 \rightarrow M(CO)_nL + M(CO)_5 + 2NaX + (5-n)CO
\]

(The \( M(CO)_5 \) fragment may react with \( NaX \) to form \( NaM(CO)_5X \) or with \( CO \) to form \( M(CO)_6 \).) Indeed, some of the above reactions do give product yields higher than would be expected if the small amount of \( M(CO)_5 \) \(^{2-}\) is the precursor.

Excess thiophosgene (\( Cl_2CS \)) was found to react with THF solutions of reduced group VI carbonyls, presumably in a reaction of the type of Eq. 14. The products of these reactions are the thiocarbonyl complexes, \( M(CO)_5(CS) \) (\( M=Cr, Mo, W \)). The mononuclear dianion, \(^{119}Cr(CO)_5 \) \(^2-\), prepared in liquid ammonia and redissolved in THF does not give any \( Cr(CO)_5(CS) \) on reaction with \( Cl_2CS \), which is a further indication that the \( M_2(CO)_{10} \) \(^{2-}\) species is the anionic intermediate important in the thiocarbonyl preparation.

In addition to the thiocarbonyl complexes formed in these reactions, a large amount of the metal hexacarbonyls is regenerated; from one to eight times as much \( M(CO)_6 \) as \( M(CO)_5(CS) \) is produced. This product could be formed if some of the unstable \( M(CO)_5 \) generated in a reaction such as Eq. 14 were to decompose, thus releasing \( CO \) which may be captured by the remaining \( M(CO)_5 \). Other products which may be produced in these reactions were not investigated. The overall yields of thiocarbonyl complexes were estimated by gas chromatographic analysis of the product mixtures from small reactions (1-10g \( M(CO)_6 \) starting complex). Excellent separations
of \( M(CO)_{6} \) and \( M(CO)_{5}(CS) \) were obtained for the chromium and tungsten complexes (Figure 1). The yields, assuming a reaction of the type in Eq. 14, are in the range of 10-12\% for \( Cr(CO)_{5}(CS) \) and 20-25\% for \( W(CO)_{5}(CS) \). The \( Mo(CO)_{5}(CS) \) could not be detected gas chromatographically, presumably because of its lower stability, but yields of 3-5\% are estimated from the infrared spectra of product mixtures. Scaling the reactions up to 30 to 50g of \( M(CO)_{6} \) gave somewhat reduced yields of \( Cr(CO)_{5}(CS) \) (6-8\%) and \( W(CO)_{5}(CS) \) (12-18\%). Scale-up of the molybdenum preparation proved to be impossible; reactions of solutions containing more than approximately 2 meq of the molybdenum anion (derived from \( \sim 1g \) \( Mo(CO)_{6} \)) with thiophosgene gave little or no \( Mo(CO)_{5}(CS) \). Thus many small reactions were necessary to prepare even a small quantity of this complex.

The low yields obtained in these preparations may be partially a result of the high reactivity of the thiocarbonyl complexes. For example, \( W(CO)_{5}(CS) \) has been found to react rapidly with chloride ion in THF solutions even at room temperature. Based on a comparison of the reactivities of the \( M(CO)_{6} \) complexes with halide ions,\(^{127}\) this reaction is expected to have a similar rate for \( Cr(CO)_{5}(CS) \) and to be much more rapid for \( Mo(CO)_{5}(CS) \). Since free chloride ion is presumably generated in these preparations, its reaction with the \( M(CO)_{5}(CS) \) complexes could be one cause of the low yields.
Fig. 1. Gas chromatographic trace of the product mixture from a typical preparation of \( W(CO)_{5}(CS) \). A 0.25 in x 6 ft 2% SE-30 column was used with an initial temperature of 70\(^\circ\)C, a temperature program of 8\(^\circ\)/min, and a helium flow rate of 30 cc/min. The first large peak is hexane solvent, the next is \( W(CO)_6 \), and the last peak is \( W(CO)_{5}(CS) \).
2. **Purification of the \(\text{M}(	ext{CO})_5(\text{CS})\) complexes**

Upon sublimation of the evaporated reaction mixtures obtained in these preparations, yellow crystals are collected which are found to be composed of \(\text{M}(	ext{CO})_5(\text{CS})\), \(\text{M}(	ext{CO})_6\), and traces of other impurities. The separation of the \(\text{M}(	ext{CO})_5(\text{CS})\) compounds from the hexacarbonyls was found to be a difficult process because of the similar physical properties of the complexes. There was little evidence of any separation during sublimations of mixtures of the complexes. Although gas chromatography separated the complexes very efficiently, column chromatography of pentane solutions of the complexes on florisil, alumina, or silica gel at room temperature (or florisil at \(-70^\circ\)) gave little or no separation. Crystallization of the mixtures from pentane or hexane solutions by slow cooling (1-2 days) was found to be a practicable, although lengthy, separation method. The crystals formed in the first crystallization step were found to contain more than 99% \(\text{M}(	ext{CO})_6\), and the solutions generally contained a mixture of 60-80% \(\text{M}(	ext{CO})_5(\text{CS})\). Repeated concentration of the solution and crystallization by slow cooling yielded, after 4-6 steps, relatively small amounts of \(\text{M}(	ext{CO})_5(\text{CS})\) of approximately 99% purity. Large amounts of \(\text{M}(	ext{CO})_5(\text{CS})\) were contained in the crystals formed during the later crystallization steps. The \(\text{Mo}(	ext{CO})_5(\text{CS})\) complex was not purified beyond about 70% because of the small quantities produced in its preparation.

Very pure \(\text{W}(	ext{CO})_5(\text{CS})\) and \(\text{Cr}(	ext{CO})_5(\text{CS})\) (>99.95%) were attainable in small quantities through preparative gas chromatography, since there were
large differences in the retention times of the thiocarbonyl and hexacarbonyl complexes (Figure 1). It was necessary to operate the gas chromatograph oven and detector at relatively low temperatures to avoid decomposition of the thiocarbonyl complexes; at temperatures above 75°C substantial formation of the hexacarbonyls was evident.

A chemical separation was found to be a more convenient method of obtaining pure \( \text{W(CO)}_5(\text{CS}) \); although this method was not used with \( \text{Mo(CO)}_5(\text{CS}) \) and \( \text{Cr(CO)}_5(\text{CS}) \), it would be expected to work equally well with these complexes. This separation sequence involves the conversion of the \( \text{W(CO)}_5(\text{CS}) \) in a mixture with \( \text{W(CO)}_6 \) to \( \text{W(CO)}_4(\text{CS})^- \) by reaction with \( \text{Bu}_4\text{N}^- \). The \( \text{W(CO)}_6 \) does not react under the mild conditions employed and may be easily separated from the thiocarbonyl salt. The \( \text{Bu}_4\text{N}[\text{W(CO)}_4(\text{CS})]^- \) is then reconverted in high yields to \( \text{W(CO)}_5(\text{CS}) \) by reaction with \( \text{Ag}^+ \) and CO.

3. **Spectroscopic studies of the \( \text{M(CO)}_5(\text{CS}) \) complexes and their derivatives**

The infrared spectra of the \( \text{M(CO)}_5(\text{CS}) \) complexes (Table 2) exhibit the three carbonyl bands expected of pentacarbonyl complexes with \( C_{5v} \) symmetry, although the positions of these bands are higher than normal for \( \text{M(CO)}_5\text{L} \) derivatives. This increase in frequency is presumably due largely to a decrease in metal electron density caused by the strong \( \pi \)-acidity of the \( \text{CS} \) ligand. This in turn causes a diminishing of the \( \pi \) back-bonding from the metal to the carbonyl \( \pi^* \) orbitals and increases the C-O bond order. In general, all of the thiocarbonyl derivatives
### Table 2. Infrared CO and CS peaks of group VI thiocarbonyl complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(\text{CO}), \text{cm}^{-1} )</th>
<th>( \nu(\text{CS}), \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cr(CO)}_5(\text{CS}) )</td>
<td>( 2091 \text{w}, 2023 \text{m}, 1997 \text{vs}^a )</td>
<td>( 1253 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{Mo(CO)}_5(\text{CS}) )</td>
<td>( 2096 \text{w}, 2020 \text{m}, 1995 \text{vs}^a )</td>
<td>( 1247 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{W(CO)}_5(\text{CS}) )</td>
<td>( 2096 \text{w}, 2007 \text{m}, 1989 \text{vs}^a )</td>
<td>( 1258 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{trans-Cr(CO)}_4(\text{CS})(\text{PPh}_3) )</td>
<td>( 2063 \text{vww}, 1960 \text{vs}^a )</td>
<td>( 1230 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{cis-Cr(CO)}_4(\text{CS})(\text{PPh}_3) )</td>
<td>( 2044 \text{w}, 1992 \text{w}, 1960 \text{vs}^a )</td>
<td>( 1230 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{trans-W(CO)}_4(\text{CS})(\text{PPh}_3) )</td>
<td>( 2061 \text{vwv}, 1956 \text{vs}^a )</td>
<td>( 1247 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{cis-W(CO)}_4(\text{CS})(\text{PPh}_3) )</td>
<td>( 2052 \text{w}, 1981 \text{w}, 1956 \text{vs}^a )</td>
<td>( 1247 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{trans-W(CO)}_4(\text{CS})[\text{P(4-CIC}_6\text{H}_4)_3] )</td>
<td>( 2056 \text{vs}^a )</td>
<td>( 1245 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{cis-W(CO)}_4(\text{CS})[\text{P(4-CIC}_6\text{H}_4)_3] )</td>
<td>( 2053 \text{m}, 1981 \text{w}, 1863 \text{m}, 1955 \text{s}^a )</td>
<td>( 1245 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{trans-W(CO)}_4(\text{CS})(\text{py}) )</td>
<td>( 2062 \text{vw}, 1950 \text{vs}^a )</td>
<td>( 1224 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{Bu}_4\text{N[trans-W(CO)}_4(\text{CS})] )</td>
<td>( 2064 \text{w}, 1945 \text{vs}^c )</td>
<td>( 1193 \text{vs}^c )</td>
</tr>
<tr>
<td>( \text{Bu}_4\text{N[trans-BrW(CO)}_4(\text{CS})] )</td>
<td>( 2064 \text{w}, 1947 \text{vs}^c )</td>
<td>( 1193 \text{vs}^c )</td>
</tr>
<tr>
<td>( \text{Bu}_4\text{N[trans-iW(CO)}_4(\text{CS})] )</td>
<td>( 2062 \text{w}, 1947 \text{vs}^c )</td>
<td>( 1195 \text{vs}^c )</td>
</tr>
<tr>
<td>( \text{mer-Cr(CO)}_3(\text{CS})(\text{diphos}) )</td>
<td>( 2006 \text{w}, 1924 \text{vs}^b )</td>
<td>( 1209 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{mer-W(CO)}_3(\text{CS})(\text{diphos}) )</td>
<td>( 2013 \text{w}, 1925 \text{vs}^c )</td>
<td>( 1215 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{mer-W(CO)}_3(\text{CS})(\text{diars}) )</td>
<td>( 2010 \text{w}, 1928 \text{m}, 1919 \text{vs}^a )</td>
<td>( 1213 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{mer-W(CO)}_3(\text{CS})(\text{bipy}) )</td>
<td>( 2004 \text{w}, 1956 \text{vs}, 1916 \text{vs}, 1888 \text{m}^b )</td>
<td>( 1203 \text{vs}^b )</td>
</tr>
<tr>
<td>( \text{Bu}_4\text{N[mer-iW(CO)}_3(\text{CS})[\text{P(4-CIC}_6\text{H}_4)_3] )</td>
<td>( 2012 \text{m}, 1914 \text{vs}^c )</td>
<td>( 1175 \text{m}^c )</td>
</tr>
</tbody>
</table>

\(^a\text{Recorded in n-hexane solution.}\)

\(^b\text{Recorded in CS}_2\text{ solution.}\)

\(^c\text{Recorded in CH}_2\text{Cl}_2\text{ solution.}\)
Table 2. continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(CO), cm⁻¹</th>
<th>ν(CS), cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(CO)₂(CS)(triphos)</td>
<td>1933 s, 1974b</td>
<td>1197 s, 1185mb</td>
</tr>
<tr>
<td>W(CO)(CS)(diphos)₂</td>
<td>1838 c</td>
<td>1161 sc</td>
</tr>
<tr>
<td>[HW(CO)(CS)(diphos)₂]CF₃SO₃</td>
<td>1958 c</td>
<td>1207 c</td>
</tr>
<tr>
<td>[(2-CH₃C₆H₄)₃PH][W(CO)₃(CS)Br₃]</td>
<td>2078 w, 2028 s, 1992d</td>
<td>1260 d</td>
</tr>
<tr>
<td>W(CO)₂(CS)(PPh₃)₂Br₂</td>
<td>2014 m, 1959 c</td>
<td>1249 b</td>
</tr>
<tr>
<td>W(CO)₂(CS)(diphos)Br₂</td>
<td>2036 s, 1972 c</td>
<td>1245 b</td>
</tr>
<tr>
<td>W(CO)(CS)(diphos)₂Br₂</td>
<td>1929 c</td>
<td>1216 c</td>
</tr>
</tbody>
</table>

Recorded in a KBr disk.

Prepared from these complexes also exhibit infrared carbonyl absorptions (Table 2) at higher average frequencies than those of the analogous carbonyl complexes. The CS stretching absorptions of the complexes range from 1260 to 1160 cm⁻¹, and are easily recognizable in most cases because of the intensity and sharpness of the band. As expected, increasing the number or donor strength of noncarbonyl substituent ligands causes the CS absorption to shift to lower frequencies, parallel with the carbonyl absorption shift.

The mass spectra of all of the thiocarbonyl complexes investigated with this technique have abundant parent ion peaks and the expected fragments due to loss of the individual ligands. In general, however, fragments resulting from the loss of CS were of low abundance, and the MCS⁺ fragment could always be observed (with fragmenting electron beam...
energies). A mass spectrometric ion appearance potential study carried out at this institution showed that the W-CS bond energy in $\text{W(CO)}_5(\text{CS})$ is approximately twice as large as the average W-CO bond energy. 128

The $^{13}$C NMR spectra of the thiocarbonyl derivatives (Table 3) all exhibit a low-field thiocarbonyl carbon resonance; a low-field position was also found for the CS carbon resonances of the two metal thiocarbonyls previously studied by $^{13}$C NMR. 102 The position of this resonance changes, although not greatly, on changing the metal ligands. There appears to be no obvious correlation between the ligand properties and the direction of this shift. The positions of the carbonyl carbon resonances are very close to those of the carbonyl analogs.

C. Reactions at the Metal Center

1. Photochemical substitution

Photolytic dissociation of carbonyl ligands is a general method used in metal carbonyl chemistry whereby another ligand may be substituted for the carbonyl. 129 The photolytic substitution of CO has also been successful in thiocarbonyl-containing complexes. 81-83 It was therefore expected that the photolytic replacement of a carbonyl by another ligand would provide a useful synthetic route to substituted derivatives of $\text{W(CO)}_5(\text{CS})$ and $\text{Cr(CO)}_5(\text{CS})$. However, irradiation with a low-pressure Hg lamp of THF solutions of $\text{W(CO)}_5(\text{CS})$ in Vycor vessels, in the presence of $\text{PPh}_3$ or py, gave little evidence of reaction under conditions that cause substitution with $\text{W(CO)}_6$. Solutions containing very low concentrations of
Table 3. $^{13}$C NMR data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta(^{13}\text{CO})^a$</th>
<th>$\delta(^{13}\text{CS})^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)$_6$</td>
<td>-212.1</td>
<td></td>
</tr>
<tr>
<td>Cr(CO)$_5$(CS)</td>
<td>-211.4</td>
<td>-331.1</td>
</tr>
<tr>
<td>W(CO)$_6$</td>
<td>-191.1</td>
<td></td>
</tr>
<tr>
<td>W(CO)$_5$(CS)</td>
<td>-192.4 (cis), -189.3 (trans)</td>
<td>-298.7</td>
</tr>
<tr>
<td>[(Ph$_3$P)$_2$N][WIW(CO)$_5$]</td>
<td>-198.7$^b$ (cis), -201.6 (trans)</td>
<td></td>
</tr>
<tr>
<td>Et$_4$N[W(CO)$_5$]</td>
<td>-197.8$^c$ (cis), -202.2 (trans)</td>
<td></td>
</tr>
<tr>
<td>Bu$_4$N[trans-C1W(CO)$_4$(CS)]</td>
<td>-199.2</td>
<td>-287.3</td>
</tr>
<tr>
<td>Bu$_4$N[trans-BrW(CO)$_4$(CS)]</td>
<td>-198.5</td>
<td>-287.4</td>
</tr>
<tr>
<td>Bu$_4$N[trans-IW(CO)$_4$(CS)]</td>
<td>-196.5$^d$</td>
<td>-285.7</td>
</tr>
<tr>
<td>mer-W(CO)$_3$(CS)(diars)</td>
<td>-210.2 (trans to As), -201.9 (cis)</td>
<td>-306.9</td>
</tr>
<tr>
<td>trans-IW(CO)$_4$CSC$_2$H$_5$</td>
<td>-188.8</td>
<td>-252.7</td>
</tr>
<tr>
<td>trans-IW(CO)$_4$CSC=0CH$_3$</td>
<td>-188.1, -186.7 (C=0)</td>
<td>-233.9</td>
</tr>
<tr>
<td>W(CO)$_5$NC$_2$</td>
<td>-194.0$^d$ (cis), -196.2$^f$ (trans)</td>
<td></td>
</tr>
<tr>
<td>W(CO)$_5$P(4-CIC$_6$H$_4$)$_3$</td>
<td>-196.4$^d,^g$ (cis), -197.9$^h$ (trans)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ ppm downfield from TMS.
$^b$ $J_{183\text{W}}^{13\text{C}} = 129Hz$.
$^c$ $J_{183\text{W}}^{13\text{C}} = 126Hz$.
$^d$ $J_{183\text{W}}^{13\text{C}} = 128Hz$.
$^e$ Recorded at -30°.
$^f$ $J_{183\text{W}}^{13\text{C}} = 137Hz$.
$^g$ $J_{\text{PWC}} = 6Hz$.
$^h$ $J_{\text{PWC}} = 22Hz$. 
W(CO)$_5$(CS) (~$10^{-2}$ M), however did react, yielding some of the substituted complexes, trans-LW(CO)$_4$(CS) (L=PPh$_3$, py), as well as other unidentified complexes. Reasons for the lack of reaction of the more concentrated solutions are not clear, but there is some formation of a deposit on the glass surface in these reactions. This deposit may screen the wavelengths required for carbonyl dissociation. The necessity of using small amounts of starting materials and the fact that other products form means that this process has little synthetic utility.

2. Thermal carbonyl substitution

As expected by analogy with the hexacarbonyl complexes, Cr(CO)$_5$(CS) and W(CO)$_5$(CS) react with donor ligands at elevated temperatures to form substituted complexes. However, the geometry of these complexes could not be predicted a priori since no similar thiocarbonyl complexes had ever been prepared. The chromium and tungsten thiocarbonyl complexes were found to react with ligands at lower temperatures than their hexacarbonyl analogs, and the products were found to be the M(CO)$_4$(CS)L complexes, of mainly trans geometry.

For example, Cr(CO)$_5$(CS) in refluxing toluene (110°) reacts with PPh$_3$ to yield a mixture of largely trans-Cr(CO)$_4$(CS)(PPh$_3$), along with some of the cis isomer. Likewise, W(CO)$_5$(CS) in xylene at 130° is substituted by PPh$_3$ to yield a similar mixture of isomers. Column chromatography did not separate the isomers, and fractional crystallization gave only a slightly greater proportion of the trans isomer in the crystals than is present in an equilibrium mixture. Reactions performed in the
presence of excess phosphine and allowed to proceed after most of the first substitution had occurred showed some evidence of forming $M(CO)_3(CS)(PPh_3)_2$ complexes. However, the main products were $M(CO)_5(PPh_3)$ and some $M(CO)_4(PPh_3)_2$, even when no $M(CO)_6$ was present in the starting material. The $M(CO)_3(CS)(PPh_3)_2$ may be an intermediate in the formation of these complexes, since it only appears in small amounts and eventually disappears.

The trans-$W(CO)_4(CS)(py)$ complex is the only thiocarbonyl product observed in the reaction of $W(CO)_5(CS)$ with pyridine at 135° in xylene; no cis isomer was detected. It may be worth noting that, unlike $W(CO)_5(CS)$ and $W(CO)_4(CS)(PPh_3)$, which could not be separated from their carbonyl analogs by column chromatography, $W(CO)_4(CS)(py)$ and $W(CO)_5(py)$ did separate on the column. The $\nu(CS)$ of this complex is also much lower than in the previous two complexes. A reaction of $W(CO)_5(CS)$ with 2,2'-bipyridine surprisingly yielded no thiocarbonyl-containing products, and only $W(CO)_4(bipy)$ was produced. The o-phenanthroline ligand gave similar results. On the other hand, the bidentate diphos ligand reacts with $W(CO)_5(CS)$ at 130° or with $Cr(CO)_5(CS)$ at 110° in xylene to yield the mer-$M(CO)_3(CS)(diphos)$ complexes. The geometry of these complexes was determined from the fact that only two infrared carbonyl bands are seen, and one is a weak, high-frequency band characteristic of an $A_1$ mode involving two nearly-trans carbonyls. No $M(CO)_4(diphos)$ is detected in these preparations, even after extended reaction times with excess ligand.
The intermediate in these reactions, \( M(\text{CO})_4(\text{CS})(\text{diphos}) \) (identified by the similarity of its infrared spectrum to that of \( W(\text{CO})_4(\text{CS})(\text{PPh}_3) \)), can be detected, but the second phosphorus atom coordinates quite rapidly under the conditions used. An analogous reaction carried out between \( W(\text{CO})_5(\text{CS}) \) and diars gave large amounts of the \( W(\text{CO})_4(\text{CS})(\text{diars}) \) complex, and the closing of the chelate ring was accomplished only by extended heating. A reaction between \( W(\text{CO})_5(\text{CS}) \) and triphos yielded a trisubstituted complex, \( W(\text{CO})_2(\text{CS})(\text{triphos}) \), which is apparently a mixture of isomers since two CS infrared absorptions are observed. Going to even higher substitution, a mixture of \( W(\text{CO})_3(\text{CS})(\text{diphos}) \) and equimolar diphos when heated at 200\(^\circ\) evolves CO and soon solidifies on formation of the tetrasubstituted \( W(\text{CO})(\text{CS})(\text{diphos})_2 \). The structure of this complex is presumed to have the CO and CS groups mutually \textit{cis}, based on the geometry of the \( W(\text{CO})_3(\text{CS})(\text{diphos}) \) precursor and the carbonyl analog, \( W(\text{CO})_2(\text{diphos})_2 \). No products resulting from the loss of CS could be detected. A similar reaction was attempted between \( \text{Cr}(\text{CO})_3(\text{CS})(\text{diphos}) \) and the diphos ligand, but no further substitution was detected, perhaps because of steric effects. Attempts to replace all five of the carbonyl ligands in \( W(\text{CO})_5(\text{CS}) \) by reacting \( W(\text{CO})_2(\text{CS})(\text{triphos}) \) with diphos were also not successful.

Tetrahydrofuran solutions of \( W(\text{CO})_5(\text{CS}) \) and tetrabutylammonium halides react with gas evolution even at room temperature. The tetrabutylammonium halides do not react at such low temperatures, perhaps because of stronger
ion-pair interaction. Sufficiently high temperatures to give a reaction lead to decomposition. The products of the Bu₄NX reactions were determined by IR and ¹³C NMR spectroscopy to be exclusively

Bu₄N[trans-XW(CO)₄(CS)] (X=Cl, Br, I). Remarkably, the reaction of trans-(¹³CO)W(CO)₄(CS) (vide infra) with the halides showed that there is a very high, if not complete, preference for the loss of the trans carbonyl in this substitution process. To avoid exchange of the free ¹³CO with the relatively labile carbonyls in [XW(CO)₄(CS)]⁻ it was necessary to continually purge the reaction mixture with N₂. A separate experiment showed that the carbonyls in [IW(CO)₄(CS)]⁻ exchange with ¹³CO quite rapidly under the reaction conditions.

Several reactions were done in an attempt to substitute a carbonyl in [trans-IW(CO)₄(CS)]⁻ with PPh₃. At temperatures of about 100° in dioxane solution, some carbonyl substitution was observed, but a large amount of iodide substitution (yielding W(CO)₄(CS)(PPh₃)) was also seen. However, the use of P(4-ClC₆H₄)₃ instead of PPh₃ led to the production of mainly [mer-IW(CO)₃(CS)][P(4-ClC₆H₄)₃]⁻. This product was not isolated but was characterized by its infrared spectrum and its reactions in situ.

Several attempts were made to prepare an arene complex from W(CO)₅(CS) and mesitylene (1,3,5-trimethylbenzene) by heating the reactants under N₂; but only decomposition was observed. Why an arene complex does not form is unknown, since W(CO)₆ does give such complexes under these conditions.

Since there seemed to be a great preference for the formation of trans-substituted derivatives by the thermal substitution of the
M(CO)$_5$(CS) complexes, experiments were performed to determine whether $^{13}CO$ exchange would preferentially label the trans site. At 100-112° in decalin solution, Cr(CO)$_5$(CS) and W(CO)$_5$(CS) do exchange with $^{13}CO$, but the enrichment is statistical between the cis and trans sites.

3. Preparation of complexes by silver ion abstraction of coordinated halide ions

The abstraction of a halide ion from group VI $[XM(CO)_5]^{-}$ complexes has been effected by $[Et_3O]BF_4$, Ag$^+$, or AlCl$_3$. This reaction may be followed by the addition of a ligand to yield M(CO)$_5$L complexes. (The intermediate in these reactions is presumably a M(CO)$_5$(solvent) complex.) Therefore, it was expected that the $[XM(CO)_4(CS)]^{-}$ complexes might also undergo halide abstraction and subsequent ligand substitution. Indeed, the addition of Ag$^+$ to solutions of $[IW(CO)_4(CS)]^{-}$ followed by addition of a ligand gives good yields of W(CO)$_4$(CS)L complexes. Moreover, all of the complexes thus formed are observed to have exclusively a trans geometry. For example, the addition of PPh$_3$ to an acetone solution of W(CO)$_4$(CS)(acetone) yields only trans-W(CO)$_4$(CS)(PPh$_3$). This contrasts with the thermal preparation, which yields a mixture of cis and trans isomers. In fact, heating a toluene solution of trans-W(CO)$_4$(CS)(PPh$_3$) to 105° for a few minutes yields an identical mixture of isomers.

The W(CO)$_4$(CS)(solvent) (solvent=THF, acetone) intermediate provides a route to complexes unobtainable by other routes. Thus, reactions with 2,2'-bipyridine yield mer-W(CO)$_3$(CS)(bipy) in good yields. The reaction
is quite rapid and the presumed intermediate, W(CO)$_4$(CS)(bipy), cannot be detected. This complex could not be prepared by the thermal reaction of W(CO)$_5$(CS) with bipy. Another diamine, tetramethylethylenediamine (TMEDA), reacts with the W(CO)$_4$(CS)(solvent) intermediate to yield, apparently, W(CO)$_4$(CS)(TMEDA). Refluxing a THF solution of this complex for two hr causes the formation of another complex, which is tentatively identified as W(CO)$_3$(CS)(TMEDA).

A very useful reaction of W(CO)$_4$(CS)(solvent) is its reconversion to W(CO)$_5$(CS) by interaction with CO. Since the [W(CO)$_4$(CS)]$^-$ salt may be easily purified, this reaction provides a simple route to pure W(CO)$_5$(CS). The entire process is easily carried out on a large scale and is much less time-consuming than other purification methods.

Attempts to form complexes by reactions between W(CO)$_4$(CS)(solvent) and toluene or thallium cyclopentadienide were unsuccessful. Likewise, reactions between [W(CO)$_4$(CS)]$^-$ and TICp did not give any new thio-carbonyl complexes. The purity of the cyclopentadienide salt, however, is questionable.

The in situ reaction of Bu$_4$N[mer-W(CO)$_3$(CS)[P(4-ClC$_6$H$_4$)$_3$] with Ag$^+$ and CO yielded largely cis-W(CO)$_4$(CS)[P(4-ClC$_6$H$_4$)$_3$]. The small amount of trans product observed may have been present in the mixture before the addition of Ag$^+$, as a result of a side reaction in the preparation of the phosphine iodide complex. This is the only reaction found which produces mainly a cis-M(CO)$_4$(CS)L complex. Heating a solution of this complex to 105° for a few minutes gives a mixture of isomers containing mainly the trans complex.
The surprising result of the reaction of W(CO)$_4$(CS)(acetone) with $^{13}$CO was that only trans-( $^{13}$CO)W(CO)$_6$(CS) was produced. This compound was characterized by its infrared spectrum (Figure 2), which is entirely consistent with such a C$_4$V complex. Carbon monoxide of 90% $^{13}$CO enrichment was used in the preparation of the complex; thus a small amount of W($^{12}$CO)$_5$(CS) was observed, but the mass spectrum confirmed that there was only 10% of this product present. The cis isomer was not detectable in the infrared spectrum. However, heating a xylene or decalin solution of the trans isomer to 100° for several hr gave an equilibrium mixture of the cis and trans forms (Figure 2). No other products were observed except trace amounts of W($^{12}$CO)$_5$(CS) and W($^{13}$CO)$_2$( $^{12}$CO)$_3$(CS). From such an equilibrium mixture ([cis]=4 [trans]) it was possible to determine the extinction coefficients of all of the IR bands of the cis isomer (Table 4).

4. Stereospecific $^{13}$CO enrichment studies

There are very few examples in the literature of reactions that yield metal carbonyl complexes in which one bonding site is preferentially labeled by an isotopically enriched carbonyl ligand,$^{131-133}$ particularly when the labeling is close to being totally specific.$^{134-135}$ The surprising observation that the reaction of W(CO)$_4$(CS)(acetone) with $^{13}$CO led to the stereospecific generation of trans-( $^{13}$CO)W(CO)$_4$(CS) stimulated a further investigation of this and similar reactions. It was believed that the actual reacting species in solutions of M(CO)$_5$(solvent) and M(CO)$_4$L(solvent) complexes were the coordinatively unsaturated species
Fig. 2. Carbonyl region of the infrared spectra of (A) W(CO)$_5$(CS), (B) trans-$^{13}$CO-W(CO)$_4$(CS), and (C) an equilibrium mixture of cis- and trans-$^{13}$CO-W(CO)$_4$(CS). All solutions are $7.5 \times 10^{-4}$ M in decalin. Band positions and extinction coefficients are given in Table 4.
Table 4. Positions and extinction coefficients of infrared carbonyl bands of $\text{W(CO)}_5(\text{CS})$, $\text{trans-}(^{13}\text{CO})\text{W(CO)}_4(\text{CS})$, and $\text{cis-}(^{13}\text{CO})\text{W(CO)}_4(\text{CS})$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band Assignment</th>
<th>Position, cm$^{-1}$</th>
<th>$\varepsilon$, M$^{-1}$ cm$^{-1}$</th>
</tr>
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<tr>
<td>$\text{W}(^{12}\text{CO})_5(\text{CS})$</td>
<td>$A_1^{(1)}$</td>
<td>2096</td>
<td>4200</td>
</tr>
<tr>
<td></td>
<td>$A_1^{(2)}$</td>
<td>2007</td>
<td>6500</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>1989</td>
<td>35000</td>
</tr>
<tr>
<td>$\text{trans-}(^{13}\text{CO})\text{W(CO)}_4(\text{CS})$</td>
<td>$A_1^{(1)}$</td>
<td>2031</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>1989</td>
<td>35000</td>
</tr>
<tr>
<td></td>
<td>$A_1^{(2)}$</td>
<td>1967</td>
<td>6500</td>
</tr>
<tr>
<td>$\text{cis-}(^{13}\text{CO})\text{W(CO)}_4(\text{CS})$</td>
<td>$A'$</td>
<td>2089</td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>$A'$</td>
<td>2010</td>
<td>$\sim$1000</td>
</tr>
<tr>
<td></td>
<td>$A'$</td>
<td>2005</td>
<td>6000</td>
</tr>
<tr>
<td></td>
<td>$A''$</td>
<td>1988</td>
<td>10000</td>
</tr>
<tr>
<td></td>
<td>$A'$</td>
<td>1957</td>
<td>10000</td>
</tr>
</tbody>
</table>

$[\text{M(CO)}_5]$ and $[\text{M(CO)}_4\text{L}]$, since the solvent ligand is only weakly bound. Thus, a situation such as that shown in Eq. 15 was envisioned for the reaction process of $[\text{XM(CO)}_5]^-$ with $\text{Ag}^+$ and $\text{L}$.

$$
\text{XM(CO)}_5^- + \text{Ag}^+ \rightarrow [\text{M(CO)}_5]^- + \text{AgX} \\
\text{L} [\text{M(CO)}_5]^- \rightarrow \text{M(CO)}_5\text{L} \quad (15)
$$

$\text{H(CO)}_5(\text{S})$ (S=solvent)
The \([\text{M(CO)}_5]\) or \([\text{LM(CO)}_4]\) intermediates were presumed to be the same intermediates as those which are apparently formed in photochemical\(^{136,137}\) and \(\text{S}_1\) thermal substitutions\(^{138,139}\) of the group VI carbonyls. A study of \([\text{M(CO)}_5]\) and \([\text{M(CO)}_4\text{L}]\) intermediates generated as in Eq. 15, it was thought, might give information about the structure and properties of these intermediates. For example, if it could be shown that the intermediate which reacts with \(^{13}\text{CO}\) to give trans-(\(^{13}\text{CO}\))\(\text{W(CO)}_4\text{(CS)}\) is actually the free \([\text{W(CO)}_4\text{(CS)}]\) species, it might be concluded that this pentacoordinate structure has a square pyramidal geometry with the CS ligand at the apex. No isomer of a trigonal bipyramidal geometry would be expected to give the observed product with such high specificity.

Most investigations of pentacoordinate group VI complexes have been low-temperature matrix spectroscopic studies.\(^{140-143}\) Both square pyramidal and trigonal bipyramidal structures have been observed. Evidence has been presented for a \(\text{D}_{3h}\) structure of \([\text{Cr(CO)}_5]\) at low temperatures which converts to a \(\text{C}_{4v}\) structure on slight warming.\(^{141,143}\) Square pyramidal \([\text{W(CO)}_5]\) is observed in a frozen hydrocarbon medium.\(^{140}\) The initial conclusion that melting the glass gave a \(\text{D}_{3h}\) structure\(^{140}\) has been suggested to be spurious.\(^{144}\) Pearson has predicted that a square pyramidal geometry is the most stable configuration for a group VI \([\text{M(CO)}_5]\) complex.\(^{145}\) The substitution of a carbonyl in such a complex by another strong field ligand such as CS or a phosphine should not affect the relative stabilities of the \(\text{D}_{3h}\) and \(\text{C}_{4v}\) structures.\(^{145}\) Thus, information about the structure of an \([\text{M(CO)}_4\text{L}]\) complex should also be applicable to that of \([\text{M(CO)}_5]\).
To determine whether the CS ligand is unique in directing the specific introduction of $^{13}$CO into one position of a [W(CO)$_4$L] moiety, two similar reactions were investigated. By modifying the method of Allen and Barrett, who prepared similar Cr and Mo complexes, P(4-ClC$_6$H$_4$)$_3$ was stirred with $\text{Et}_4\text{N}[\text{IW(CO)}_5]$ in dioxane at 100$^\circ$ for 1.5 hr while $\text{N}_2$ was bubbled through the solution. The major product was not isolated, but the similarity of its IR spectrum to those reported for similar complexes supports its formulation as $\text{Et}_4\text{N}[\text{ cis- W(CO)}_4\{\text{P(4-ClC}_6\text{H}_4\}_3\}$. Some W(CO)$_5$[P(4-ClC$_6$H$_4$)$_3$] was also formed by iodide substitution. Reaction of this dioxane solution with Ag$^+$ and $^{13}$CO yielded a mixture containing largely ($^{13}$CO)W(CO)$_4$[P(4-ClC$_6$H$_4$)$_3$] and some of the unlabeled phosphine complex, which is presumably that formed by iodide substitution. The $^{13}$C NMR spectrum of the mixture showed that the product of the $^{13}$CO substitution is almost exclusively $\text{cis-}(^{13}\text{CO})\text{W(CO)}_4\{\text{P(4-ClC}_6\text{H}_4\}_3\}$. 

A similar reaction was investigated with [(Ph$_3$P)$_2$N]
$[\text{ cis-ClW(CO)}_4(\text{CNCy})]$, which was prepared according to the method of Murdoch and Henzi. The reaction of this complex with Ag$^+$ and $^{13}$CO gave, again, almost exclusively the $\text{ cis-}^{13}$CO-enriched product. The $^{13}$C NMR showed a very strong resonance at -194.0 ppm due to the $\text{cis}$ carbonyls and a barely observable peak at -196.2 ppm, where the $\text{trans}$ carbonyl of W(CO)$_5$CNCy is known to occur. Thus, the reaction of [trans-IW(CO)$_4$CS]$^-\text{Ag}^+$ and $^{13}$CO leads to a $\text{trans}$ product, and reactions of [cis-IW(CO)$_4$P(4-ClC$_6$H$_4$)$_3$]$^-\text{Ag}^+$ and [cis-ClW(CO)$_4$(CNCy)]$^-\text{Ag}^+$ give $\text{cis}$ products.
Fig. 3. Carbonyl carbon resonances in the $^{13}$C NMR spectra of $\text{W(CO)}_5[\text{P(4-ClC}_6\text{H}_4)_3]$. (A) $^{13}$CO-enriched sample prepared from $[\text{cis-W(CO)}_4\text{I[P(4-ClC}_6\text{H}_4)_3}]^-$, $\text{Ag}^+$ and $^{13}$CO. (B) $^{13}$CO-enriched sample prepared from preferentially cis ($^{13}$CO)-enriched $[\text{W(CO)}_5\text{Cl}]^-$, $\text{Ag}^+$ and $\text{P(4-ClC}_6\text{H}_4)_3$. (C) Natural abundance $^{13}$C sample. The strong doublet is the cis carbonyl resonance; the less intense doublet to the left is the trans resonance. Positions and coupling constants are given in Table 3.
These results could lead to two possible conclusions: first, the reactions may proceed through intermediates in which stereochemical rearrangement is impossible, and thus the geometry of the precursor is maintained in the final product. This could involve, for example, a stereochemically rigid square pyramidal intermediate, or a seven-coordinate intermediate resulting from solvent or ligand association during the substitution process. It has previously been shown that $\text{W(CO)}_5(\text{acetone})$ reacts with alkenes in a totally dissociative substitution process, so an $S_N^2$ attack by CO seems unlikely in view of its low nucleophilicity. The possibility of a stereochemically rigid square pyramidal intermediate seems unlikely, since both $D_{3h}$ and $C_{4v}$ structures have been observed spectroscopically for the $[\text{M(CO)}_5]$ species, and the barrier to interconversion through a Berry or "reverse-Berry" pseudorotation is expected to be small. Monosubstitution should not substantially alter the barrier to rearrangement, by analogy with other pentacoordinate systems. However, if the lifetime of the free pentacoordinate complex (the time between ligand dissociation and ligand association) is short relative to the time required for rearrangement, then retention of geometry could be observed even though the five-coordinate intermediate would not normally be classified as being "rigid".

A second possible conclusion based on the results of the above reactions is that a stereochemically nonrigid intermediate may form which is free to rearrange, but maintains one geometry because of steric or
electronic effects. The energy barrier to such rearrangements in octahedral complexes is quite high,\textsuperscript{150} and a process such as the isomerization of a solvent-bound octahedral intermediate would not appear to be favorable under the reaction conditions. A stereochemically non-rigid square pyramidal system, however, could rearrange to the most stable isomer. Recent studies have shown that electronegativity\textsuperscript{151} and $\pi$-bonding\textsuperscript{152} effects are important in determining which isomers of substituted square pyramidal structures are most stable.

Experiments were sought which would help distinguish among the various possible reasons for the observed stereospecificity. One such experiment was designed to ascertain whether the substituent ligand on the $[\text{W(CO)}_4\text{L}]$ moiety was responsible for determining the stereochemistry of the product. This experiment was done by labeling one position in the reactant with $^{13}$CO instead of a noncarbonyl ligand, and was based on a reaction reported by Darensbourg, Darensbourg, and Dennenberg.\textsuperscript{153} They found that the reaction of preferentially labeled cis-$(^{13}$CO)$\text{Mo(CO)}_4$(piperidine) with $\text{AsPh}_3$ gave, in an $S_{N1}$ process, $(^{13}$CO)$\text{Mo(CO)}_4$(As$\text{Ph}_3$) with the labeled carbonyl statistically scrambled between the cis and trans positions. It was concluded that, under the conditions used (38° in hexane), the equatorial and axial carbonyls equilibrate in a trigonal-bipyramidal or highly distorted square pyramidal structure. To carry out a similar experiment, preferentially cis $^{13}$CO-labeled $[\text{ClW(CO)}_5]$ was prepared by stirring $[(\text{Ph}_3\text{P})_2\text{N}][\text{ClW(CO)}_5]$ under about 1.5 atm of $^{13}$CO in CH$_2$Cl$_2$ for two hr. The enriched product was
found by $^{13}$C NMR to have approximately three times as much $^{13}$CO in the 
**cis** positions as in the **trans** position, after the statistical correction.
This product was dissolved in acetone and the chloride ion was abstracted 
with silver ion. The addition of a donor ligand then gives $^{13}$CO-enriched 
$\text{W(CO)}_5\text{L}$ complexes. The $\text{W(CO)}_5[\text{P(4-ClC}_6\text{H}_4\text{)}_3]$ complex thus obtained was 
found by $^{13}$C NMR to still possess preferential enrichment in the **cis** 
positions. Although some scrambling had occurred, the doublet of the 
**trans**-$^{13}$CO was still less than one-half as large as that in the natural 
abundance spectrum (Figure 3). Enriched $\text{W(CO)}_5\text{CNCy}$ prepared similarly 
also showed retention of the preferential **cis** enrichment. However, the 
use of excess CyNC caused formation of another product as well, believed 
to be **cis**-$\text{W(CO)}_4(\text{CNCy})_2$. The appearance of this product points out the 
fact that although an $S_N^1$ substitution involving prior loss of the sol­
vent molecule seems likely, an $S_N^2$ attack at the intermediate is also 
possible by these stronger nucleophiles. Such a process, as in Eq. 16, 
could be responsible for the observed retention of geometry in the final, 
product forming step.

\begin{align*}
\begin{array}{c}
\text{M} \hspace{1cm} \downarrow \hspace{1cm} \text{L} \\
\text{S} \hspace{1cm} \text{L} \\
\end{array}
\rightarrow \\
\begin{array}{c}
\text{M} \hspace{1cm} \downarrow \hspace{1cm} \text{S} \\
\text{S} \hspace{1cm} \text{L} \\
\end{array}
\rightarrow \\
\begin{array}{c}
\text{M} \hspace{1cm} \downarrow \hspace{1cm} \text{L} \\
\text{S} \hspace{1cm} \text{L} \\
\end{array}
\end{align*}
(16)

However, the geometry must also be maintained in the **first** step, the 
halide ion removal. This process may be considered as the first-order 
loss of an Ag-X ligand. Therefore, the addition of a solvent molecule 
to the $[\text{M(CO)}_5]$ complex thus generated must be rapid enough to occur
before the pentacoordinate complex can rearrange. This experiment shows that an $S_N$ ligand exchange may occur with retention of geometry of a group VI $M(CO)_5$ complex; the Daresbourg experiment showed that it need not.

In conclusion, the reason that retention of geometry of the $W(^{13}CO)(CO)_4$ moiety is observed appears to be that the lifetime of this free intermediate in coordinating solvents is too short to allow it to rearrange (Eq. 17).

![Diagram](image)

This same reason may also explain the retention of the original geometry of $[W(CO)_4L]$ intermediates. However, that the influence of the non-carbonyl ligand in the latter complex may also stabilize a certain geometry cannot be discounted or proved with the present evidence.

5. **Kinetic studies of isomerization and substitution reactions of $W(CO)_5(CS)$**

The discovery that trans-$^{13}COW(CO)_4(CS)$ isomerizes upon heating in solution to a mixture of the cis and trans isomers prompted a thorough study of this process. The barrier to intramolecular rearrangements in octahedral complexes is very high, and its occurrence in nonchelate complexes has only been studied in three classes of compounds:
H₂ML₄ (M=Fe, Ru; L=phosphine or phosphite)¹⁵⁴, M(CO)₄(M'₃R₂)₂ (M=Ru, Os; M'=Si, Sn; R=CH₃, C₂H₅)¹⁵⁵, and (CO)₄Cr(PR₃)[C(OCH₃)CH₃] (R=Et, Cy).¹⁵⁶ Therefore, it was of interest to determine whether this isomerization was actually intramolecular. Heating a decalin solution of trans-¹³COW(CO)₄(CS) at about 100° for a few hr gives an equilibrium mixture of the cis and trans complexes. Only very little W(¹²CO)₅(CS) and W(¹³CO)₂(¹²CO)₃(CS) is produced in these reactions. Performing the reaction in ¹²CO-saturated decalin under a ¹²CO atmosphere gives no significant increase in W(¹²CO)₅(CS). These observations indicate that the isomerization is not accompanied by CO dissociation. A mechanism involving CS dissociation can also be discounted; no W(CO)₆ was ever observed to form in these reactions.

In contrast to the reactions in decalin solution, isomerizations carried out in 1, 4-dioxane at about 100° gave large amounts of W(¹²CO)₅(CS) and W(¹³CO)₂(¹²CO)₃(CS) as products, indicating that CO dissociation is occurring in this solvent. Dioxane has previously been observed to greatly enhance "S₅₇" substitution rates of metal carbonyls; this effect may be attributed to nucleophilic displacement of carbonyl ligands by the dioxane.¹⁵⁷ The isomerization and intermolecular ¹³CO scrambling appeared to approach equilibrium at approximately the same rate in this solvent. Furthermore, substitution reactions carried out in dioxane solutions saturated with ¹³CO showed that the labeled CO was incorporated relatively rapidly into W(CO)₅(CS). An analysis of the IR spectra showed that the rate of formation of trans-¹³COW(CO)₄(CS) under
these conditions was approximately four times the rate of formation of the cis isomer. This experiment also shows that the rate of trans exchange is faster than the rate of isomerization in dioxane. The rates of cis exchange and isomerization are similar, but a good comparison was impossible because of infrared carbonyl band overlap.

A kinetic study of the isomerization of trans-(¹³CO)W(CO)₄(CS) was carried out in decalin solvent under N₂ at temperatures from 80-100.5°C (Table 5).

Table 5. Kinetic data for the intramolecular isomerization of trans-(¹³CO)W(CO)₄(CS) in decalin

<table>
<thead>
<tr>
<th>Temperature</th>
<th>10³ [complex], M</th>
<th>10⁴ kₗₐₜₐₚₜₜ, sec⁻¹</th>
<th>Average kₖₐₚₜₜ^a</th>
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<tr>
<td>80.0°C</td>
<td>1.08</td>
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<td>1.00</td>
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<td>2.08</td>
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<tr>
<td>100.5°C</td>
<td>0.54</td>
<td>3.28</td>
<td>2.60 x 10⁻⁴ sec⁻¹</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.35</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.35</td>
<td>3.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.70</td>
<td>3.28</td>
<td></td>
</tr>
</tbody>
</table>

^aΔH° = 31.8 ± 1 kcal/mole; ΔS° = 9.8 ± 3 cal/deg mole.
The rate of appearance of the 2005 cm\(^{-1}\) band of the cis isomer was followed in the infrared spectrum. As expected, the reaction was observed to be first-order in the complex. The data were analyzed using the McKay equation for isotopic exchange\(^{158,159}\) (for exchange between the trans and cis positions). This equation gives Eq. 18,

\[
\ln \left[ 1 - \frac{A(\text{cis}^*)}{A(\text{cis}^*)_e} \right] = -\frac{5}{4} k_f t
\]

where \(A(\text{cis}^*)\) is the absorbance of the cis isomer at time \(t\), \(A(\text{cis}^*)_e\) is the absorbance of the cis isomer when equilibrium is reached, and \(k_f\) is the rate of conversion of the trans to the cis isomer. Rearrangement of the equation shows that a plot of \(-\ln[A(\text{cis}^*)_e - A(\text{cis}^*)]\) vs. \(t\) gives a line of slope \(5/4 k_f\) (thus \(k_f = \frac{4}{5} k_{\text{obs}}\)).

A preliminary investigation was also carried out on the isomerization of \(\text{trans-}(^{13}\text{CO})\text{W(CO)}_4\text{CNCH}_3\) (prepared from \(\text{trans-}(^{13}\text{CO})\text{W(CO)}_4\text{(CS)}\) and \(\text{CH}_3\text{NH}_2\)). This isomerization was found to be considerably slower; \(k_{\text{obs}} \approx 1.0 \times 10^{-5}\) sec\(^{-1}\) at 112°. It is not known whether this is also an intramolecular process.

Several reactions were carried out at 100.5° in decalin to determine the rate of CO exchange of \(\text{W(CO)}_5\)(CS). A \(^{12}\text{CO}\) atmosphere was maintained over an equilibrium mixture of cis and \(\text{trans-}(^{13}\text{CO})\text{W(CO)}_4\text{(CS)}\), and the rate of disappearance of the \(^{13}\text{CO}\)-enriched trans-isomer was followed. Since the rate of CO exchange is slower than the rate of isomerization, an equilibrium mixture of the cis and trans isomers was always maintained. The values of \(k_{\text{obs}}\) obtained in these reactions were multiplied by a factor
of five to account for the fact that only one out of every five carbynyls being replaced was labeled. This gave an approximate rate constant for the CO exchange of $1 \times 10^{-5}$ sec$^{-1}$, which is about twenty times slower than the rate of isomerization. This comparison provides further proof that the isomerization process is actually intramolecular.

The gas-phase isomerization of trans-$^{13}$CO$_4$W(CO)$_4$(CS) was also studied. Vials of the solid complex (in amounts corresponding to approximately $2 \times 10^{-4}$ M gas-phase concentrations) were evacuated and filled with $^{12}$CO (140 torr) at room temperature. After sealing, the vials were heated in an oil bath at 100.5°C. The samples were withdrawn at recorded times, immediately cooled, and the contents dissolved in a measured quantity of decalin. No decomposition was detected, and only a small amount of W($^{12}$CO)$_5$(CS) was observed in the samples. From a comparison of the length of time required for the gas-phase samples to reach the point at which two IR bands were of equal intensity (the 1967 cm$^{-1}$ band of the trans isomer (decreasing) and the 1957 cm$^{-1}$ band of the cis isomer (increasing)) and the time observed for parallel solution samples to reach the identical point, it was determined that the gas-phase reaction rate constant is related to the rate constant of the solution isomerization by a factor of 0.595. This is analogous to comparing half-lives of first-order reactions; the fractional-life in this case is approximately one-half. Gas-phase reactions carried out in a vacuum (no added CO) gave variable amounts of decomposition. However, infrared analysis of the products showed that isomerization had also occurred in these samples, and there was no formation of W($^{12}$CO)$_5$(CS).
These gas-phase isomerizations prove that CO dissociation is not involved in the isomerization process. Furthermore, the fact that the isomerization rates are so similar in the gas phase and in solution indicates that there is little solvent interaction during the process.

Several mechanisms have been proposed for the nondissociative isomerization of octahedral complexes. These all involve twisting the octahedron through a trigonal prismatic structure. However, there is no experimental evidence to support any particular mechanism for this isomerization. It was noted, though, that the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of the isomerization process are of the magnitude normally associated with dissociation of a carbonyl from a group VI metal complex.

To obtain kinetic data and activation parameters for the dissociation of CO from $\text{W(CO)}_5(\text{CS})$, the reaction between this complex and triphenylphosphine was investigated. The disappearance of $\text{W(CO)}_5(\text{CS})$ was followed in the IR spectrum ($2096 \text{ cm}^{-1}$ band) in decalin solutions containing known concentrations of $\text{PPh}_3$ in at least a ten-fold excess. Reactions were studied at temperatures of 120-146° (Table 6). Plots of $k_{\text{obs}}$ vs. $[\text{PPh}_3]$ gave intercepts and slopes corresponding to rate constants of the phosphine-independent (Eq. 19) and phosphine-dependent reactions (Eq. 20).

$$\text{W(CO)}_5(\text{CS}) \xrightarrow{k_1} [\text{W(CO)}_4(\text{CS})] + \text{CO} \xrightarrow{\text{fast}} \text{W(CO)}_4(\text{CS})(\text{PPh}_3)$$

(Eq. 19)

$$\text{W(CO)}_5(\text{CS}) \xrightarrow{k_2[\text{PPh}_3]} \text{W(CO)}_4(\text{CS})(\text{PPh}_3) + \text{CO}$$

(Eq. 20)
Table 6. Kinetic data for the reaction of W(CO)$_5$(CS) with PPh$_3$ in decalin

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$10^2$[PPh$_3$], M</th>
<th>$10^4 k_{obs}$, sec$^{-1}$</th>
<th>Rate constants$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120.0°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.302</td>
<td>1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.031</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.863</td>
<td>1.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.626</td>
<td>1.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.733</td>
<td>1.68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.164</td>
<td>1.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.649</td>
<td>1.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.569</td>
<td>2.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.47</td>
<td>2.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1 = 1.17 \times 10^{-4}$ sec$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2 = 8.70 \times 10^{-4}$ M$^{-1}$ sec$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>135.0°</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2.882</td>
<td>6.38</td>
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<td>3.844</td>
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<td>4.889</td>
<td>7.02</td>
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<td>5.733</td>
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<td></td>
</tr>
<tr>
<td>7.695</td>
<td>7.75</td>
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<td></td>
</tr>
<tr>
<td>9.542</td>
<td>8.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.50</td>
<td>8.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1 = 5.60 \times 10^{-4}$ sec$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2 = 2.91 \times 10^{-3}$ M$^{-1}$ sec$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>146.0°</td>
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</tr>
<tr>
<td>3.885</td>
<td>18.1</td>
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<tr>
<td>5.771</td>
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<td>9.584</td>
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<td>11.54</td>
<td>23.0</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1 = 1.54 \times 10^{-3}$ sec$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2 = 6.30 \times 10^{-3}$ M$^{-1}$ sec$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a\Delta H_1^* = 32.0 \pm 1$ kcal/mole; $\Delta S_1^* = 4.4 \pm 3$ cal/deg mole. $\Delta H_2^* = 24.1 \pm 1$ kcal/mole; $\Delta S_2^* = -11.7 \pm 3$ cal/deg mole.
Several results of this study are noteworthy. First, it is apparent that the activation parameters for the carbonyl dissociation are very close to those determined for the intramolecular isomerization; they are equal within experimental error. This may be an indication that there is a great deal of bond-breaking in the isomerization process even though complete dissociation does not occur. In any event, it is apparent that the energy barrier to intramolecular isomerization of an octahedral complex is indeed high. Secondly, extrapolation of an Arrhenius plot of the first-order carbonyl dissociation to 100.5° gives a predicted rate constant at that temperature of $1.25 \times 10^{-5}\text{sec}^{-1}$, in excellent agreement with the approximate rate constant, $1 \times 10^{-5}\text{sec}^{-1}$, determined by CO exchange. This confirms that the dissociation is approximately twenty times slower than the isomerization.

Finally, it is interesting to compare the kinetic data from this reaction with that of the analogous reaction of $\text{W(CO)}_6$ and $\text{PPh}_3$. Extrapolation of the Arrhenius plot for the first-order reaction of $\text{W(CO)}_5(\text{CS})$ to 165.7°, the temperature at which the $\text{W(CO)}_6$ reaction was performed, shows that $\text{W(CO)}_5(\text{CS})$ reacts by this process approximately 80 times faster than $\text{W(CO)}_6$. A similar comparison of the second-order processes shows that $\text{W(CO)}_5(\text{CS})$ reacts about 200 times faster than $\text{W(CO)}_6$ by the phosphine-dependent route. Therefore, not only does $\text{W(CO)}_5(\text{CS})$ undergo CO substitution markedly faster than its carbonyl analog, but there also seems to be a preferential increase in the $k_2$ term over the $k_1$ rate constant.
Another kinetic study was carried out on the reaction between $\text{W(CO)}_5(\text{CS})$ and $\text{Bu}_4\text{NI}$ (Table 7).

Table 7. Kinetic data for the reaction of $\text{W(CO)}_5(\text{CS})$ with $\text{Bu}_4\text{NI}$ in chlorobenzene

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$10^2 x [i^-]$</th>
<th>$10^4 x k_{obs}$</th>
<th>Rate constants$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>38.2$^\circ$</td>
<td>3.604</td>
<td>2.34</td>
<td>$k_1 \approx 3 \times 10^{-5}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>4.412</td>
<td>2.86</td>
<td>$k_2 = 5.87 \times 10^{-3}$ M$^{-1}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>5.420</td>
<td>3.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.821</td>
<td>4.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.211</td>
<td>5.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.49</td>
<td>6.45</td>
<td></td>
</tr>
<tr>
<td>48.2$^\circ$</td>
<td>2.694</td>
<td>4.81</td>
<td>$k_1 \approx 6 \times 10^{-5}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>3.252</td>
<td>5.60</td>
<td>$k_2 = 1.53 \times 10^{-2}$ M$^{-1}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>5.407</td>
<td>8.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.146</td>
<td>10.3</td>
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</tr>
<tr>
<td></td>
<td>10.80</td>
<td>17.2</td>
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</tr>
<tr>
<td>58.2$^\circ$</td>
<td>3.285</td>
<td>14.8</td>
<td>$k_1 \approx 1.5 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>4.369</td>
<td>19.1</td>
<td>$k_2 = 4.05 \times 10^{-2}$ M$^{-1}$ sec$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>5.431</td>
<td>23.4</td>
<td></td>
</tr>
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<td></td>
<td>6.802</td>
<td>29.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.179</td>
<td>34.2</td>
<td></td>
</tr>
</tbody>
</table>

$^a \Delta H_2^\circ = 19.0 \pm 1$ kcal/mole; $\Delta S_2^\circ = -8.0 \pm 3$ cal/deg mole.
This study was of interest because of the observation that there is a high preference for the loss of the trans carbonyl. This selectivity suggested that perhaps the halide ion attacks the carbon atom of the trans carbonyl in the substitution process. The reactions were performed in chlorobenzene solutions containing known concentrations of Bu$_4$NI in at least a ten-fold excess. Plots of $k_{obs}$ vs. $[I^-]$ show that the reaction is almost totally associative; very small iodide-independent terms are seen. These results are similar to those found for the reactions of W(CO)$_6$ with halides.$^{127}$ It is interesting to note that by extrapolating the Arrhenius plot of the W(CO)$_5$(CS) reaction to 120°, where the analogous W(CO)$_6$ reaction was performed, it was found that W(CO)$_5$(CS) should react more than 10$^3$ times faster with I$^-$ than does W(CO)$_6$.

The values of the enthalpy and entropy of activation do not allow an unequivocal assignment of the site of attack (W atom or trans-carbonyl carbon), but the values are reasonably close to those reported for a similar reaction; the activation parameters of the W(CO)$_6$-Br$^-$ reaction,$^{127}$ in which the site of attack is believed to be the metal, are $\Delta H^* = 26.5$ kcal/mole; $\Delta S^* = -0.3$ cal/deg mole. Thus, it seems likely that the iodide ion adds to the metal atom in the transition state of its reaction with W(CO)$_5$(CS). The trans-(13CO)W(CO)$_4$(CS) experiment (in which it was shown that the trans CO is specifically lost with iodide substitution) requires that the seven-coordinate intermediate formed in such an attack must largely maintain the mutually trans arrangement of the CS and the...
unique CO. This is necessary to prevent scrambling of the trans, labilized carbonyl with the others before it has left the complex.

6. Oxidative addition reactions to tungsten thiocarbonyl and related complexes

Tungsten hexacarbonyl reacts at low temperatures with halogens in chlorinated solvents to produce the unstable W(II) halocarbonyls, \( [\text{W(CO)}_4^X_2] \). These complexes then react with donor ligands to yield seven-coordinate \( \text{W(CO)}_3^X_2^L_2 \) complexes, which are stable and well-characterized. In a similar reaction, \( \text{W(CO)}^5^X^2^S \) was found to react with gas evolution at about -40° in \( \text{CH}_2\text{Cl}_2 \) or \( \text{CHCl}_3 \) with \( \text{Br}_2 \). Presumably the product is \( [\text{W(CO)}_3^X_2^S^2^X_2^S] \), but no attempt was made to isolate this complex. However, the addition of \( \text{PPh}_3 \) to these solutions at room temperature causes the immediate liberation of CO and formation of \( \text{W(CO)}_2^X_2^L_2^X_2^P^2 \). The analogous tricarbonyl complex, \( \text{W(CO)}_3^X_2^L_2^P^X_2^2 \), upon heating to 40° in \( \text{CH}_2\text{Cl}_2 \) for 2-3 hr loses CO and forms a six-coordinate complex, \( \text{W(CO)}_2^X_2^L_2^P^2 \). The steric requirements of the phosphine ligand are presumably the reason for the tendency to revert to a hexacoordinate complex. This coordinatively unsaturated species may also be readily reconverted to the seven-coordinate complex by exposure to CO. It was expected that \( \text{W(CO)}_2^X_2^L_2^P^X_2^2 \) might also undergo carbonyl loss. However, this was never observed, even on heating at 60° in chloroform for many hours. The complex simply decomposed slowly to yield insoluble, non-carbonyl-containing products. It was reported that \( \text{W(CO)}_3^X_2^L_2^P^2 \), which contains a highly sterically hindered...
phosphine, was even less stable than the triphenylphosphine derivative, and yielded the corresponding six-coordinate decarbonylated complex at temperatures little above room temperature. Therefore, a similar preparation was carried out using \([W(CO)_3(CS)Br_2]^{\text{3}}\) and \(P(3\text{-toly})_3\). From the similarity of the IR spectrum of the product to that of \(W(CO)_2(CS)(PPh_3)_2Br_2\), it was determined that the product was the analogous tritolylphosphine complex. Heating this complex in \(CHCl_3\) for several hr also did not cause any new compounds to form. A synthesis using a phosphine with even higher steric hindrance, \(P(2\text{-toly})_3\), did not yield an analogous complex (vide infra).

The result that the \(W(CO)_2(CS)L_2Br_2\) complexes do not lose CO even though the \(W(CO)_3L_2Br_2\) complexes easily do so is surprising in view of the kinetic studies of carbonyl loss from \(W(CO)_5(CS)\). There may be two reasons that decarbonylation is not observed for the \(W(\text{II})\) thio-carbonyl complexes. First, the different oxidation state of the metal will certainly cause a difference in the \(W-CO\) bond strengths in \(W(CO)_5(CS)\) and \(W(CO)_2(CS)(PPh_3)_2Br_2\). It is also expected that \(M-CO\) pi back-bonding will be less important and \(OC-M\) sigma bonding will be more important in the \(W(\text{II})\) complexes. The stronger \(\pi\)-acidity of CS relative to CO should make the W atom in \(W(CO)(CS)(PPh_3)_2Br_2\) (if it were possible to form this decarbonylated product) a considerably stronger Lewis acid than in the \(W(CO)_2(PPh_3)_2Br_2\) complex. This effect would make the addition of a Lewis base, such as CO, a more favorable process. Thus, the reverse of this reaction, the loss of CO, would be less favorable.
A second possible cause for the stability of the \( W(\text{CO})_2(\text{CS})(\text{PPh}_3)_2\text{Br}_2 \) complex may involve the structure of this complex and the analogous tricarbonyl complex. If a carbonyl is specifically lost from one coordination site in the carbonyl complex, it is possible that CS occupies specifically that position in the thiocarbonyl complex. If this is the case, then thiocarbonyl dissociation would be necessary to form a six-coordinate complex. However, CS dissociation has always been observed to be much less favorable than CO dissociation in an analogous complex. There is some literature evidence which supports this possibility. The crystal structure of a complex closely related to \( W(\text{CO})_3(\text{PPh}_3)_2\text{Br}_2 \) has been determined. The seven-coordinate complex \( W(\text{CO})_3(\text{dam})_2\text{Br}_2 \) has one carbonyl in a unique site, capping a face of the octahedron. Only one end of each potentially bidentate arsenic ligand is coordinated to the W atom.

The carbonyl infrared spectra of this complex and the PPh\(_3\) analog are quite similar, in support of an isostructural assignment (Table 8).
Table 8. Carbonyl infrared spectra of some tungsten (II) carbonyl halides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium</th>
<th>ν(CO)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(CO)₃(PPh₂)₂Br₂</td>
<td>nujol</td>
<td>2015m, 1940s, 1900m</td>
<td>162</td>
</tr>
<tr>
<td>W(CO)₃(dam)₂Br₂</td>
<td>nujol</td>
<td>2027s, 1948s, 1911s</td>
<td>166</td>
</tr>
<tr>
<td>W(CO)₂(CS)(PPh₃)₂Br₂</td>
<td>CH₂Cl₂</td>
<td>2014m, 1959s</td>
<td></td>
</tr>
<tr>
<td>W(CO)₂(PPh₃)₂Br₂</td>
<td>nujol</td>
<td>1955w, 1870s</td>
<td>162</td>
</tr>
</tbody>
</table>

The infrared spectra, when compared to the spectrum of W(CO)₂(CS)Br₂, also suggest that the CS ligand may occupy the capping position. There is no evidence, however, that it is specifically the capping carbonyl which dissociates from W(CO)₃(PPh₂)₂Br₂.

A reaction performed between the [W(CO)₃(CS)Br₂] intermediate and the very bulky P(2-tolyl)₃ ligand in CH₂Cl₂ solution did not lead to a phosphine-substituted complex. Instead an ionic complex with high bromine content was isolated in a 45% yield. This was shown by IR spectroscopy (νₚ₋ₕ at 2350 in KBr) and elemental analyses to be [(2-tolyl)₃PH][W(CO)₃(CS)Br₂]. The mechanism of formation of this product is unknown, but it seems likely that the CH₂Cl₂ solvent is the source of the proton. Analogous [W(CO)₄X]⁻ complexes have been prepared either by oxidizing the [W(CO)₅X]⁻ anions with halogens or by reacting [W(CO)₄X₂] with halide salts.
Excess diphos reacts with \([W(CO)_3(CS)Br_2]\) to yield a complex which is apparently \(W(CO)(CS)(\text{diphos})_2Br_2\). Presumably, the complex is seven-coordinate, which implies that one of the diphos ligands is acting as a monodentate ligand. A conductivity measurement showed that the complex is in fact molecular; both bromine atoms are thus coordinated to the metal as in the dicarbonyl analog. The complex could not be made to crystallize; only powder-like precipitates could be isolated, and the elemental analyses of this material were very poor.

The oxidation of \(W(CO)_3(CS)(\text{diphos})\) with \(I_2\) gives a complex identified as \(W(CO)_2(CS)(\text{diphos})I_2\), which also could only be obtained as a powdery precipitate. Reactions of \(W(CO)(CS)(\text{diphos})_2\) with excess \(I_2\) appear to be more complex. Experiments with varying quantities of iodine showed that two equivalents of \(I\) are necessary for all of the \(W(CO)(CS)(\text{diphos})_2\) to react. However, the initial product was quite unstable, and was only isolated in a crystalline state in very small amount from one reaction. Other attempts to isolate the product were unsuccessful. The crystals obtained from the one reaction, however, analyzed for carbon and hydrogen as \([W(CO)(CS)(\text{diphos})_2I]\)\(_2\). An infrared analysis of other products formed in these reactions and of the decomposition products formed from the initial complex showed that in both cases the major IR peaks were attributable to \(W(CO)_2(CS)(\text{diphos})I_2\). Therefore, it seems likely that any CO which is released by decomposition is trapped by the \([W(CO)(CS)(\text{diphos})_2I]\)\(_2\)\(_I\) to form this complex. Carbonyl abstraction is also a possibility which could account for the rapid reaction.
Another product observed in small amounts in these reactions has an IR spectrum very similar to that of \( W(CO)(CS)(\text{diphos})_2\text{Br}_2 \). This suggests that small amounts of \( W(CO)(CS)(\text{diphos})_2\text{I}_2 \) may be present. A possible reaction sequence which would lead to these products is shown in Eq. 21

\[
\begin{align*}
  \text{W(CO)(CS)(diphos)$_2$} & \xrightarrow{\text{I}_2} \text{[W(CO)(CS)(diphos)$_2$I]} (\text{or I$_3$}) \\
  \text{W(CO)(CS)(diphos)}(\text{P}) & \xrightarrow{\text{CO}} \text{W(CO)$_2$(CS)(diphos)$_2$} \\
\end{align*}
\]

This reaction of \( \text{W(CO)(CS)(diphos)$_2$} \) with \( \text{I}_2 \) may be contrasted with the reported reaction of \( \text{W(CO)$_2$(diphos)$_2$} \) with \( \text{I}_2 \). In the latter reaction only one equivalent of \( \text{I} \) is reduced, and a stable \( \text{W(I)} \) complex, \( \text{[W(CO)$_2$(diphos)$_2$I]} \), is isolated in good yields as the only product. Presumably a \( \text{W(I)} \) species is an intermediate in the oxidation of \( \text{W(CO)(CS)(diphos)$_2$} \) by \( \text{I} \). A complex such as \( \text{[W(CO)(CS)(diphos)$_2$I]}^+ \) would be expected to have a higher metal acidity as compared to the dicarbonyl analog, because of the greater \( \pi \)- acidity of \( \text{CS} \). This property may allow the complex to coordinate \( \text{I}^- \), giving a seven-coordinate complex which could be oxidized further.

The oxidative addition of other reagents to \( \text{W(CO)(CS)(diphos)$_2$} \) was studied in connection with reactions taking place at the thiocarbonyl sulfur atom (vide infra). The two most nucleophilic sites in this molecule are the metal atom and the sulfur atom, and addition to one or
the other is possible, depending on the particular electrophile. Comparative reactions were also done with W(CO)$_2$(diphos)$_2$, since these reactions had been studied little previously.

Both W(CO)(CS)(diphos)$_2$ and W(CO)$_2$(diphos)$_2$ react with trifluoromethanesulfonic acid to yield stable metal-protonated complexes. That the metal is the site of protonation is confirmed by the NMR spectra of the products, which both exhibit a high-field metal hydride resonance. The position of the resonance in the thiocarbonyl complex (2.79 ppm upfield from TMS), however, is shifted considerably downfield from the resonance in the dicarbonyl analog (4.91 ppm upfield from TMS). This is some evidence that the thiocarbonyl complex may have lower metal electron density than the carbonyl complex.

The geometries of these complexes may also be determined from the NMR spectra. Both metal hydride resonances are split into a triplet of triplets by coupling through the metal to two sets of two equivalent phosphorus atoms. This suggests a structure in which the phosphorus atoms are all in one plane with the proton coordinating through an octahedral face. Which faces are protonated has not been established.

The structure of the isoelectronic complex HTa(CO)$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$ has recently been determined$^{171}$ and a similar protonated complex of molybdenum, [HMo(CO)$_2$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]HCl$_2$, has been reported.$^{172}$ The
proton NMR spectra of both complexes exhibit high-field metal hydride resonances, and each is split into a triplet of triplets. The fact that the Mo and W complexes exhibit trans geometries is surprising, since the unprotonated complexes have cis configurations. However, Bond has also observed this isomerization during the electrochemical oxidation of W(CO)$_2$(diphos)$_2$ and presents molecular orbital-based arguments to explain the rearrangement.

The W(CO)$_2$(diphos)$_2$ and W(CO)(CS)(diphos)$_2$ complexes are also protonated by HCl, as shown by the infrared spectra. However, the low stability of the presumed [HW(CO)(CS)(diphos)$_2$]HCl$_2$ complex prevented its purification; crystallization in the absence of excess HCl always led to the formation of some W(CO)(CS)(diphos)$_2$. The complex was also easily deprotonated by cyclohexylamine, although the dicarbonyl analog could not be deprotonated similarly. This is another indication of low electron density on the metal caused by the strong $\pi$-acceptor capacity of CS.

Both W(CO)(CS)(diphos)$_2$ and W(CO)$_2$(diphos)$_2$ react with BCl$_3$ in solution to yield complexes which analyze approximately as W(CO)(CS)(diphos)$_2$·BCl$_3$ and W(CO)$_2$(diphos)$_2$·BCl$_3$. The elemental analyses were not very satisfactory; reproducibility and accuracy were low. Both complexes are 1:1 electrolytes in nitrobenzene, which suggests that in this solution the complexes dissociate to M·BCl$_2$ and Cl$^-$. The thio-carbonyl complex loses BCl$_3$ on recrystallization without excess boron halide although the dicarbonyl analog does not. As was also observed in
the IR spectra of the metal-protonated thiocarbonyl complexes, the frequency of the CS stretching absorption has increased by more than 40 cm\(^{-1}\). This is one indication that addition to the metal has occurred.

Although CH\(_3\)SO\(_3\)F and [Et\(_3\)]BF\(_4\) attack W(CO)(CS)(diphos)\(_2\) at the sulfur atom (vide infra), they add to the metal atom in W(CO)\(_2\)(diphos)\(_2\). Both reagents react slowly with the complex, and the reactions appear to give analogous products. Only the ethylated complex, [W(CO)\(_2\)(diphos)\(_2\)(C\(_2\)H\(_5\))]BF\(_4\), was characterized. A similar complex, [Mo(o-phenanthroline)(PF\(_3\))\(_2\)(CO)\(_2\)(CH\(_3\))]SO\(_3\)F, has been reported.\(^{174}\)

A reaction of W(CO)\(_2\)(diphos)\(_2\) with AgBF\(_4\) gives a paramagnetic W(I) complex, [W(CO)\(_2\)(diphos)\(_2\)]BF\(_4\). This complex could also be prepared from the reported [W(CO)\(_2\)(diphos)\(_2\)]BF\(_4\)\(_3\) by treatment with AgBF\(_4\).\(^{170}\)

The reaction of W(CO)(CS)(diphos)\(_2\) with several other reagents appears to give oxidation or oxidative addition products, although they were not characterized. Thus, reactions with NOPF\(_6\) and tetracyanoethylene yield solutions which exhibit high-frequency \(\nu\)(CO) and \(\nu\)(CS) absorptions in their infrared spectra. The reaction of W(CO)(CS)(diphos)\(_2\) with excess AgBF\(_4\) involves an oxidation, since silver metal is plated out in the process. A diamagnetic complex is produced but it could not be isolated in a pure form. The \(^{19}\)F NMR spectrum of the mixture exhibits two resonances (89.7 and 153.9 ppm above CFCl\(_3\)), so it seems possible that fluorine abstraction from BF\(_4\) has occurred, possibly to form [W(CO)(CS)(diphos)\(_2\)F]BF\(_4\).
D. Reactions at the Thiocarbonyl Sulfur Atom

There have been several examples reported in the literature of metal carbonyl complexes in which a terminal carbonyl ligand bonds through the oxygen to a Lewis acid. The complexes which form these adducts have carbonyl ligands possessing high electron density, as evidenced by low CO stretching frequencies. Because of the lower electronegativity of sulfur as compared to oxygen, it was expected that thiocarbonyls might also react with Lewis acids, perhaps even more readily than do analogous carbonyls. Therefore, many attempts were made to react $\text{W(CO)}_5(\text{CS})$ and $\text{W(CO)}_4(\text{CS})(\text{PPh}_3)$ with a variety of Lewis acids, including $\text{BF}_3$, $\text{B}_2\text{H}_6$, $\text{HgCl}_2$, $[\text{Et}_3\text{O}]\text{BF}_4$, $\text{MeSO}_3\text{F}$, and $\text{HCl}$. No new products or changes in the infrared spectra were observed. Likewise, $\text{W(CO)}_3(\text{CS})(\text{diphos})$, which is expected to have higher sulfur electron density, did not react with $\text{MeSO}_3\text{F}$ or $\text{HgCl}_2$. Although $\text{W(CO)}_3(\text{CS})(\text{bipy})$ and $\text{W(CO)}_2(\text{CS})(\text{triphos})$ do react with $\text{HgCl}_2$ and $\text{MeSO}_3\text{F}$ or $[\text{Et}_3\text{O}]\text{BF}_4$, the reactions appear to be complex and may involve oxidation or oxidative addition to the metal; these reactions were not thoroughly investigated.

However, $\text{W(CO)(CS)(diphos)}_2$, which has the lowest CS stretching frequency yet reported for a terminal thiocarbonyl complex and thus should have high sulfur electron density, does react with a variety of Lewis acids to form sulfur-bound adducts. Mercuric chloride or mercuric iodide in $\text{CH}_2\text{Cl}_2$ cause the complex, which is only slightly soluble in $\text{CH}_2\text{Cl}_2$, to dissolve rapidly. Infrared spectra of these solutions show
that the carbonyl band has shifted to higher frequency by about 40 cm⁻¹ (Table 9).

Table 9. Infrared CO and CS absorption positions of W(CO)(CS)(diphos)₂ and its Lewis acid adducts in CH₂Cl₂ solution

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(CO), cm⁻¹</th>
<th>ν(CS), cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(CO)(CS)(diphos)₂</td>
<td>1838</td>
<td>1161</td>
</tr>
<tr>
<td>[W(CO)(CS)(diphos)₂H]CF₃SO₃</td>
<td>1958</td>
<td>1207</td>
</tr>
<tr>
<td>W(CO)(diphos)₂-CS-HgCl₂</td>
<td>1885</td>
<td>~1100</td>
</tr>
<tr>
<td>W(CO)(diphos)₂-CS-Hgl₂</td>
<td>1872</td>
<td>~1100</td>
</tr>
<tr>
<td>[[W(CO)(diphos)₂CS]₂Ag]BF₄</td>
<td>1869</td>
<td>1106</td>
</tr>
<tr>
<td>W(CO)(diphos)₂-CS-W(CO)₅</td>
<td>2062w, 1925vs, 1878m</td>
<td>~1100</td>
</tr>
<tr>
<td>[W(CO)(diphos)₂(CSCH₃)]FSO₃</td>
<td>1898</td>
<td>~1095</td>
</tr>
<tr>
<td>[W(CO)(diphos)₂(CSC₂H₅)]BF₄</td>
<td>1898</td>
<td>~1095</td>
</tr>
</tbody>
</table>

In contrast, complexes in which addition to the metal has occurred (by H⁺, BCl₃, etc.) show carbonyl shifts to higher frequency of more than 100 cm⁻¹. Furthermore, the CS stretching mode has apparently shifted to lower frequencies upon reaction with the mercuric halides. No new bands are detectable for 200 cm⁻¹ above the 1161 cm⁻¹ position of the original band, but a strong diphos ligand absorption at about 1095 cm⁻¹ has become more intense, indicating that the CS band overlaps at this position (Figure 4).
Fig. 4. Carbonyl and thiocarbonyl regions of the infrared spectra of (A) $\text{W(CO)(CS)(diphos)}_2$, (B) $(\text{diphos})_2(\text{CO})\text{W-CS-HgCl}_2$, and (C) $[(\text{diphos})_2(\text{CO})\text{W(CSCH}_3)]\text{SO}_3\text{F}$. All spectra recorded in KBr disks.
Shoulders are discernable on the high-frequency side of this composite band, which suggests that the CS stretching frequencies of the mercuric halide adducts occur at about 1100 cm$^{-1}$. This represents a lowering by about 60 cm$^{-1}$ from its position in W(CO)(CS)(diphos)$_2$. Metal carbonyls which are adducted through oxygen to a Lewis acid also show decreases in their stretching frequencies.

Both the HgCl$_2$ and HgI$_2$ adducts are isolable in high yields as stable, crystalline solids. No decomposition to the starting complex is observed either in solution or in the solid state. However, the addition of PPh$_3$ to their solutions gives rapid regeneration of the starting complex. The adducts are poor conductors in nitrobenzene, indicating little or no ionic dissociation. Thus, all of the available evidence points to their formulation as (diphos)$_2$(CO)W-CS-HgX$_2$ complexes. By way of contrast, the carbonyl complex W(CO)$_2$(diphos)$_2$ reacts with mercuric halides to form ionic [W(CO)$_2$(diphos)$_2$HgX]HgX$_3$ complexes.$^{183}$

Methylmercuric chloride was found not to react with W(CO)(CS)(diphos)$_2$, apparently because the Hg atom is less electrophilic than in the dihalides. The addition of AgBF$_4$ to a mixture of CH$_3$HgCl and W(CO)(CS)(diphos)$_2$ did not lead to any new complexes.

Silver ion alone, however, does react instantly with W(CO)(CS)(diphos)$_2$. A stoichiometric study showed that only one-half mole of Ag$^+$ is required per mole of the complex. The product is not the result of an oxidation, since no silver metal is produced and addition of PPh$_3$ to the solution gives back the starting complex.
Conversion to the \(\text{W(CO)(CS)(diphos)_2}\) complex is also observed within a few minutes when an infrared spectrum of a \(\text{CH}_2\text{Cl}_2\) solution of the material is recorded in a NaCl cell. These reactions apparently occur because of coordination of \(\text{PPh}_3\) and chloride ion to the silver ion. A crystalline product is isolable from the 2:1 \(\text{W(CO)(CS)(diphos)_2-Ag}^+\) reactions which has an infrared spectrum similar to those of the \(\text{HgX}_2\) adducts. This complex, however, shows a definite peak at 1106 cm\(^{-1}\) which is assigned to the CS stretch. The stoichiometry of the reaction, the elemental analyses and the molar conductivity of the complex indicate a composition of \([\{(\text{diphos})_2(\text{CO})\text{W-CS}_2\text{Ag}\}]_4\text{BF}_4\). In contrast, \(\text{W(CO)_2(diphos)_2}\) reacts with \(\text{AgBF}_4\) in any proportions in an oxidation-reduction process (vide supra).

A novel complex, \((\text{diphos})_2(\text{CO})\text{W-CS-W(CO)_5}\), was synthesized by reacting \(\text{W(CO)(CS)(diphos)_2}\) with \(\text{W(CO)_5(acetone)}\). The complex undergoes noticeable decomposition in the solid state after several days, and its reaction in solution with \(\text{PPh}_3\) is quite rapid, yielding \(\text{W(CO)(CS)(diphos)_2}\) and \(\text{W(CO)_5(PPh}_3)\). Nevertheless, it can be isolated as a crystalline solid. An X-ray crystal structure determination was attempted using one of the crystals. A triclinic crystal habit was observed with unit cell parameters \(a, b, c\) of 13.7, 19.0, and 12.5 Å, and angles \(\alpha, \beta, \gamma\) of 95.4, 116.1, and 81.7°. Two molecules were computed per unit cell. Both tungsten atoms of the molecule were found by a Patterson synthesis, and all other nonhydrogen atoms were located in the three-dimensional electron density map. Refinement to an R factor of about 17.5 showed
that the two tungsten atoms are separated by approximately 5.2 Å, and a sulfur atom is placed between them at a distance of about 2.6 Å from the W(CO)₅ portion and about 3.5 Å from the other W atom. The WSW angle was approximately 115° to 120°. The CS carbon atom was located, but its position did not refine. All attempts to refine the positions to give a lower R factor were unsuccessful, and other phenyl carbon atoms seemed to appear in the electron density map. It is possible that some disorder is present in the crystal, or that other isomers of the complex are present in small amounts.

Methyl fluorosulfonate and [Et₂OBF₄ react very rapidly with W(CO)(CS)(diphos)₂. Although these reagents add to the metal in W(CO)₂(diphos)₂, in this reaction they alkylate the sulfur atom. These S-alkylthiocarbonylium complexes form crystalline solids which may be recrystallized many times with no decomposition. In fact, the complexes do not react with PPh₃; they do, however, react very slowly with n-BuNH₂ to yield W(CO)(CS)(diphos)₂. An X-ray crystal structure determination was also attempted on [(diphos)₂(CO)W(CSC₂H₅)]BF₄. The monoclinic crystals had unit cell parameters a, b, and c of 11.9, 20.4, and 12.9 Å with β=109.7°. Two molecules were observed per unit cell. Although the atoms could be located, refinement below about R=17 was again not possible; disorder or isomerism may also be the cause in this instance.

The exposure of W(CO)(CS)(diphos)₂ to SO₂, either in solution or in the solid state, causes an immediate color change from yellow to dark brown. Bubbling N₂ through the solution, subjecting the solid to a high
vacuum, or allowing either to stand in air for several hours brings back the yellow color of the unchanged complex. The infrared spectrum of an SO₂-saturated solution shows a large amount of W(CO)(CS)(diphos)₂ but a shoulder is evident on the ν(CO) band at 1950 cm⁻¹, a shift of about 10 cm⁻¹ to higher frequency. This small shift is indicative of a weak interaction at the thiocarbonyl sulfur, which is consistent with the facile reversibility of SO₂ absorption. An attempt was made to trap the SO₂ adduct by reaction with MeSO₃F, but only [(diphos)₂(CO)W(CSCH₂)]SO₃F seemed to be produced. Although SO₂ has been observed to bond to the metal in several organometallic complexes, it seems unlikely the metal is the site of coordination in this complex because of the IR spectrum. Furthermore, W(CO)₂(diphos)₂, which appears to have higher metal electron density, does not react with SO₂. Sulfur trioxide does not appear to react with W(CO)(CS)(diphos)₂.

Another thiocarbonyl complex which was expected to have high electron density on the sulfur is the [IW(CO)₄(CS)]⁻ ion. Therefore, reactions of several electrophiles were performed with this complex. Contact with SO₂ causes this complex also to darken rapidly, and the change is rapidly reversible. The action of [Et₃O]BF₄ on the complex in the presence of PPh₃ yields two products in approximately equal amounts. One is trans-W(CO)₄(CS)(PPh₃), presumably formed by the abstraction of I⁻ by the [Et₃O]⁺ ion, similar to the Ag⁺ reaction (vide supra). The second product is also formed by reaction with [Et₃O]⁺ in the absence of PPh₃. A very similar complex is produced by the addition of MeSO₃F to
[IW(CO)₄(CS)]⁻, and this product was isolated in 15-20% crude yields. The complex is air-sensitive in solution, but is more stable in the solid state, and was fully characterized. Only a singlet is observed in the proton NMR spectrum of the complex, and an abundant mass spectrum parent ion is observed which corresponds to IW(CO)₄(CS)(CH₃)⁺. The infrared evidence establishes that the alkylation has occurred at the sulfur, since the thiocarbonyl CS stretch has been lowered in this complex by nearly 80 cm⁻¹ from the starting complex, although the ν(CO) absorptions have shifted to higher frequencies. The carbonyl infrared spectrum and the ¹³C NMR data show that this IW(CO)₄(CSCH₃) complex has a trans geometry, as does the starting complex.

The [IW(CO)₄(CS)]⁻ complex also reacts with trifluoroacetic anhydride to give a complex with a similar infrared carbonyl spectrum. The thiocarbonyl region is unfortunately obscured by C-F absorptions. All of the starting material is consumed when reacted in CH₂Cl₂ solution with (CF₃CO)₂O, as indicated by the IR spectrum. However, removal of the solvent under reduced pressure also causes regeneration of the starting complex, presumably by removal of the trifluoroacetic anhydride (Eq. 22).

\[
\text{Bu}_4\text{N}[\text{IW(CO)}_4(\text{CS})] + \text{CF}_3\text{O}-\text{C}-\text{CF}_3 \rightleftharpoons \text{IW(CO)}_4\text{CSCF}_3 + \text{Bu}_4\text{N}[\text{CF}_3\text{CO}_2^-] \quad (22)
\]

The acylated complex could be isolated when the reaction was performed in a pentane suspension, since the trifluoroacetate salt product is insoluble
in this solution. The complex formed is rather unstable, and the yellow crystals obtained by cooling a pentane solution to -80° darken even on standing in the mother liquor at this temperature. An elemental analysis was not attempted, but the exact mass of the parent ion in the high resolution mass spectrum supports the assigned formula. Fragment ions were seen as a result of the loss of CF₃CO and CF₃CSC, as well as those due to carbonyl dissociation.

A similar reaction between [IW(CO)₄(CS)]⁻ and acetic anhydride was attempted, but there was no evidence of any reaction. However, in the presence of BF₃ a reaction does take place (Eq. 23), and a 15-20% yield of the crude product could be isolated. The neutral S-acetylthiocarbonylum complex has a thiocarbonyl stretching absorption in its IR spectrum which has been lowered by more than 100 cm⁻¹ relative to that of the starting complex. The use of BF₃ in this reaction presumably enhances the electrophilic character of the acetic anhydride and prevents the reverse reaction from occurring. Although the trifluoroacetic anhydride reaction was not attempted in the presence of BF₃, it is presumed that a similar effect would be observed in its reaction.

Both IW(CO)₄CSCCF₂ and IW(CO)₄CSCCH₂ have infrared carbonyl spectra indicative of four carbonyls in a C₄ᵥ structure, except that the strong E mode is split into a doublet and a weak B₁ absorption band appears.
The IR spectrum of the ethylthiocarbonylum complex, $\text{W(CO)}_4\text{CSC}_2\text{H}_5$, also exhibits this splitting and $B_1$ band, but the methyl analog does not. These effects suggest that there is a distortion of the local $C_{4v}$ symmetry of the carbonyl ligands caused by the thiocarbonylum ligand. That the distortion is a steric rather than an electronic effect is suggested by the fact that the methylthiocarbonylum complex does not exhibit either splitting of the sharp E mode or a $B_1$ band. Similar effects have been observed in complexes of the type $R-\text{Mn(CO)}_5$ in which large substituents are bent back toward the carbonyl ligands. This apparent distortion of the carbonyl geometry by steric interaction with the thiocarbonylum ligands gives information about the structure of the ligand. A linear C-S-C bond would seem to prohibit such interaction by placing the alkyl or acyl groups too far from the carbonyls. However, a bent C-S-C linkage brings an atom separated from the sulfur by three bonds quite close to the carbonyl plane.

The methylthiocarbonylum substituent has atoms no further than two bonds from the sulfur, and shows no such interaction. Adducts of $\text{W(CO)(CS)(diphos)}_2$ with alkyl cations presumably also have bent C-S-C bonds, and the metal-containing Lewis acids probably bond in this fashion also. Metal carbonyl-Lewis acid adducts have been observed to form bent carbonyl-acid bonds; the angles observed are in the range of 140-160°.
0-Alkylcarbonylium and 0-acylcarbonylium analogs of these sulfur-bound complexes are unknown. This fact indicates that the sulfur atom of a thiocarbonyl complex is indeed a stronger nucleophile than the oxygen atom of an analogous carbonyl.

The S-alkyl- and S-acylthiocarbonylium complexes are formally analogous to the "carbyne" ligands in group VI metal complexes prepared by Fischer and co-workers \(^{186-188}\) (Eq. 24). It is certain, however,

\[
\text{(CO)}_3 M = C = O'_R + 8X_3 \rightarrow X(\text{CO})_4 M = C = R + CO + X_2 O' X
\]

that there is considerable \(\pi\)-bonding between the metal-bound carbon and the \(-SR\) substituent (Eq. 25). For example, the CS stretching frequency

\[
M = C = SR \rightarrow M = C = S'R
\]

in these complexes is much higher than is observed in alkyl sulfide complexes, which have a C-S single bond.\(^{189}\) A similar \(\pi\)-bonding effect is probably also important in some of the "carbyne" complexes of Eq. 24, when \(R\) is, for example, \(-NR'\_2\), \(-C = C - R''\), \(-C(H)\_CR''\_2\) and \(-Ph\). Infrared and \(^{13}\)C NMR data obtained for the S-alkyl- and S-acylthiocarbonylium complexes are listed in Table 10. For comparison, values measured for some of the "carbyne" complexes are also given.

The fact that the \(\nu(CO)\) frequencies of the thiocarbonylium complexes occur at relatively high frequencies as compared to those of the carbyne complexes indicates that the thiocarbonylium ligand has a very strong
<table>
<thead>
<tr>
<th>X</th>
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<th>¹³C NMR data b</th>
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<tr>
<td></td>
<td></td>
<td>A₁</td>
<td>E</td>
<td>δ(CO)</td>
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<tr>
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<tr>
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<td>-CH₃</td>
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<td>2125</td>
<td>2038</td>
</tr>
</tbody>
</table>

a Recorded in n-pentane or n-hexane solutions, unless specified otherwise.
b ppm downfield from TMS.
c Recorded in DCCl₃.
d A B₁ band is also observed.
e Recorded in D₂CCl₂.
<table>
<thead>
<tr>
<th>X</th>
<th>R</th>
<th>Infrared carbonyl peaks, cm(^{-1})</th>
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<tr>
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<td>-Ph</td>
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<td>2037</td>
<td>-192.3(^{e})</td>
</tr>
<tr>
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<tr>
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<td>-C(H)=C(Ph)NMe(_2)</td>
<td>2101</td>
<td>1988(^{d, f})</td>
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</tbody>
</table>

\(^{f}\)Recorded in CH\(_2\)Cl\(_2\).
electron-withdrawing ability. This is also reflected in the $^{13}$C NMR spectra of the complexes. Studies of $^{13}$C NMR spectra of metal complexes have shown that the carbonyl resonances shift to higher field with decreasing electron density.\textsuperscript{190,191} The carbonyls in the thiocarbonylium complexes do indeed exhibit unusually high-field resonances. These peaks occur at even higher field than the resonances in $W(CO)_6$ (-191.1 ppm) and $W(CO)_5(CS)$ (-192.4, -189.3 ppm).

E. Reactions at the Thiocarbonyl Carbon Atom

1. Reactions with amines

Because of the earlier work of Busetto et al.,\textsuperscript{95} it was expected that group VI thiocarbonyl complexes might be reactive toward nucleophiles. In fact, all three of the $M(CO)_5(CS)$ complexes ($M$=Cr, Mo, W) were found to react very rapidly with methylamine to yield the methyl isocyanide complexes, $M(CO)_5CNCH_3$ (Eq. 26). This reaction differs from that of $M(CO)_5(CS) + RNH_2 \rightarrow M(CO)_5CNR + H_2S$ (or $RNH_2 \cdot H_2S$)\textsuperscript{26}

\[ [CpFe(CO)_2(CS)]^+ + CH_3NH_2 \rightarrow CpFe(CO)_2 - C\cdot NHCH_3.\textsuperscript{95} \]

However, small amounts of $[CpFe(CO)_2CNCH_3]^+$ have also been observed in the iron reaction.\textsuperscript{192}

The reactions of $W(CO)_5(CS)$ with several other primary amines were observed to give analogous products. Thus isocyanide complexes were formed on reaction with cyclohexylamine, benzylamine, and $n$-butylamine. A much slower reaction was observed with the highly hindered $t$-butylamine.
A reaction with glycine methylester, $\text{H}_2\text{NCH}_2\text{CO}_2\text{CH}_3$, proceeded to the expected $(\text{CO})_5\text{WCNCH}_2\text{CO}_2\text{CH}_3$ product. Even the glycinate anion, $\text{H}_2\text{NCH}_2\text{CO}_2^-$, appeared to form the isocyanide product, which was isolated in the protonated form after addition of acid. As expected, **trans**- $(^{13}\text{CO})\text{W(\text{CO})}_4(\text{CS})$ reacts with primary amines to give the **trans**- $(^{13}\text{CO})\text{W(\text{CO})}_4\text{CNR}$ complexes; the stereochemistry at the metal center is unchanged.

Hydrazine and aniline, however, do not react with $\text{W(\text{CO})}_5(\text{CS})$ or $\text{Cr(\text{CO})}_5(\text{CS})$. Ammonia also does not react; the thiocarbonyl complexes may be dissolved in liquid NH$_3$ and recovered unchanged. Addition of sodium or sodium amide to these solutions did not produce any isolable or recognizable products.

Secondary amines also react with $\text{W(\text{CO})}_5(\text{CS})$ in a process which involves rearrangement, to give thioformamide complexes in 20–40% yields (Eq. 27). Identical products could be prepared by the photochemical

$$\text{W(\text{CO})}_5(\text{CS}) + \text{R}_2\text{NH} \rightarrow (\text{CO})_5\text{W - S=CH}_2\text{NR}_2$$

substitution of a carbonyl in $\text{W(\text{CO})}_6$ by a thioformamide. Aziridine (ethyleneimine) reacts differently, and a $\nu(\text{CN})$ band indicative of an isocyanide complex is observed in the infrared spectrum of the product mixture. Although attempts to isolate the product in a pure form were unsuccessful, the mass spectrum supports its formulation as $(\text{CO})_5\text{WCNCH}_2\text{CH}_2\text{SH}$. Tertiary amines, including pyridine, triethylamine,
and DABCO, did not cause any changes in the IR spectrum of $W(CO)\textsubscript{5}(CS)$ over long periods of time.

The substituted complex $W(CO)\textsubscript{4}(CS)(PPh\textsubscript{3})$ reacts much more slowly with primary amines. A mixture of the cis and trans isomers in a hexane solution saturated with $CH\textsubscript{3}NH\textsubscript{2}$ was allowed to stand for about five hr. At this time all of the cis isomer had been converted to the cis isocyanide complex, but only a small amount of the trans isomer had reacted. The reaction between $W(CO)\textsubscript{4}(CS)[P(4-CIC\textsubscript{6}H\textsubscript{4})\textsubscript{3}]$ and $CH\textsubscript{3}NH\textsubscript{2}$, however, was relatively rapid. After 15 min in a hexane solution saturated with the amine, all of the cis isomer had reacted. One day later most of the trans isomer had also reacted. A very slow reaction occurred between trans-$W(CO)\textsubscript{4}(CS)(py)$ and $CH\textsubscript{3}NH\textsubscript{2}$, and it did not produce an isocyanide complex. No reaction took place between methylamine and $W(CO)\textsubscript{3}(CS)$(diphos), $Cr(CO)\textsubscript{3}(CS)$(diphos), or $W(CO)(CS)$(diphos). These experiments show that increasing the electron density on the thio-carbonyl ligand by substituting donor ligands for carbonyls greatly lowers the tendency of the CS to undergo nucleophilic attack. Furthermore, the CS stretching frequency gives some indication of the ligand electron density, and thus, reactivity. Similar correlations between the CO stretching frequency and reactivity have been observed.\textsuperscript{193,194}

A kinetic study of the reaction of amines with $W(CO)\textsubscript{5}(CS)$ was undertaken to gain information about the mechanism of this process. The reactions were carried out in n-hexane solution at 25.0° using at least a ten-fold excess of the amine. Primary monoamines react according to an
overall third-order rate expression (Eq. 28),

\[ \text{rate} = k_1[W(CO) \_5(CS)][\text{amine}]^2. \]  

(28)

For example, the data for the reaction between W(CO)\_5(CS) and cyclohexylamine are shown in Table 11. A plot of \( \ln \text{k}_{\text{obs}} \) vs. \( \ln[\text{amine}] \) gives a straight line of slope 2.00 showing that the amine concentration appears in the rate equation with an exponent of 2. Furthermore, a plot of \( \text{k}_{\text{obs}}/[	ext{amine}] \) vs. \( [\text{amine}] \) (Figure 5) shows that there is no reaction first-order in amine. A straight line of slope \( k \) with a zero intercept is seen.

<table>
<thead>
<tr>
<th>( 10^2 \times [\text{cyclohexylamine}], \text{M} )</th>
<th>( 10^4 \times \text{k}_{\text{obs}}, \text{sec}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.053</td>
<td>0.555</td>
</tr>
<tr>
<td>5.079</td>
<td>1.56</td>
</tr>
<tr>
<td>7.051</td>
<td>2.95</td>
</tr>
<tr>
<td>9.081</td>
<td>5.00</td>
</tr>
<tr>
<td>11.11</td>
<td>7.60</td>
</tr>
<tr>
<td>13.12</td>
<td>10.8</td>
</tr>
</tbody>
</table>

\[ k = 6.1 \times 10^{-2} \text{M}^{-2} \text{sec}^{-1} \]
Fig. 5. Plot of $k_{obs}/[\text{amine}]$ vs. $[\text{amine}]$ for the reaction $\text{W(CO)}_5(\text{CS}) + \text{cyclohexylamine}$ at $25.0^\circ$ in n-hexane. The slope gives the rate constant of the term second-order in $[\text{amine}]$; the zero intercept shows that there is no term first-order in $[\text{amine}]$. 
$10^4 \frac{k_{obs}}{[\text{amine}]} \text{M}^{-1}\text{sec}^{-1}$

$10^3 \times [\text{amine}], \text{M}$
The rate constants of the various amines appear to decrease with decreasing basicity and increasing steric bulk of the amine (Table 12).

Table 12. Rate constants of reactions between $W(\text{CO})_5(\text{CS})$ and amines at $25^\circ \text{C}$ in $n$-hexane

<table>
<thead>
<tr>
<th>Amine</th>
<th>$k_1, a \text{ M}^{-2} \text{ sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N,N$-dimethyl-1,3-diaminopropane</td>
<td>$1.9 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ (± 5%)</td>
</tr>
<tr>
<td>n-butylamine</td>
<td>$1.35 \times 10^{-1}$</td>
</tr>
<tr>
<td>piperidine</td>
<td>$1.1 \times 10^{-1}$</td>
</tr>
<tr>
<td>cyclohexylamine</td>
<td>$6.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>benzylamine</td>
<td>$5.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>diethylamine</td>
<td>$3.65 \times 10^{-3}$</td>
</tr>
<tr>
<td>t-butylamine</td>
<td>$1.4 \times 10^{-4}$ (±10%)</td>
</tr>
</tbody>
</table>

*a*Each rate constant is the average of values obtained from at least three runs. Except as noted, all reactions are second-order in [amine].

The secondary amines diethylamine and piperidine also exhibit second-order dependence and give rate constants similar to those of primary amines, even though the products of these reactions differ from those of the primary amine reactions. The diamine 1,1-dimethyl-1,3-diaminopropane showed a first-order dependence; the tertiary amine end of the molecule is presumably also involved in the reaction.

The temperature dependence of the reaction of n-butylamine with $W(\text{CO})_5(\text{CS})$ was also investigated, and the activation parameters were
determined for this reaction (Table 13).

Table 13. Data for the reaction of $W(CO)_5(CS)$ with $n$-BuNH$_2$ at different temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$10^2 \times [n$-BuNH$_2]$</th>
<th>$10^4 \times k_{obs}$, sec$^{-1}$</th>
<th>$k_1$, M$^{-2}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0°</td>
<td>11.75</td>
<td>2.92</td>
<td>1.35 x 10$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>13.07</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.77</td>
<td>4.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15.64</td>
<td>5.64</td>
<td></td>
</tr>
<tr>
<td>35.0°</td>
<td>7.178</td>
<td>1.67</td>
<td>2.15 x 10$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>8.548</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.521</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.92</td>
<td>5.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.82</td>
<td>7.63</td>
<td></td>
</tr>
<tr>
<td>45.0°</td>
<td>6.808</td>
<td>2.25</td>
<td>3.05 x 10$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>8.384</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.877</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.73</td>
<td>8.00</td>
<td></td>
</tr>
</tbody>
</table>

\[
\Delta H^\ddagger = 7.0 \pm 1 \text{ kcal/mole; } \Delta S^\ddagger = -39.0 \pm 3 \text{ cal/deg mole.}
\]

The kinetics of the reactions between cis- and trans-$W(CO)_4(CS)(PPh_3)$ with $n$-butylamine were also studied. The cis isomer (Table 14) reacts approximately 200 times more slowly than does $W(CO)_5(CS)$. The trans isomer reacts even more slowly, approximately 100 times slower than the cis derivative. This reaction does not appear to involve the prior isomerization to the cis isomer; a different product is observed.
Table 14. Kinetic data for the reactions of cis and trans-\(\text{W(CO)}_4(\text{CS})(\text{PPh}_3)\) with n-butylamine at 25.0° in n-hexane

<table>
<thead>
<tr>
<th>[n-butylamine], M</th>
<th>(10^4 \times k_{\text{obs}}(\text{cis}), \text{sec}^{-1})</th>
<th>(10^6 \times k_{\text{obs}}(\text{trans}), \text{sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5188</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>0.5460</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>0.6821</td>
<td>2.82</td>
<td></td>
</tr>
<tr>
<td>0.8205</td>
<td>4.00</td>
<td>4.44</td>
</tr>
<tr>
<td>1.103</td>
<td>7.01</td>
<td>7.94</td>
</tr>
</tbody>
</table>

\(a k(\text{cis}) = 6.0 \times 10^{-4} \pm 0.2 \text{ M}^{-2} \text{ sec}^{-1}\)

\(b k(\text{trans}) = 6.6 \times 10^{-6} \pm 0.4 \text{ M}^{-2} \text{ sec}^{-1}\)

The rate equation (Eq. 28) of these reactions shows that two amine molecules are involved in the transition state although only one amine is incorporated in the product. This suggests that one of the amines is involved in the transition state as a catalyst. To show that this is a general-base catalyzed reaction, various amines were again reacted with \(\text{W(CO)}_5(\text{CS})\), this time in the presence of pyridine as a base catalyst. The rate equation for these reactions comprised two terms (Eq. 29):

\[
\text{rate} = k_1[\text{W(CO)}_5(\text{CS})][\text{amine}]^2 + k_2[\text{W(CO)}_5(\text{CS})][\text{amine}][\text{pyridine}].
\]

Since \(k_1\) had already been determined for these amines, \(k_2\) could also be calculated (Table 15).
Table 15. Rate constants for the pyridine-catalyzed reaction of W(CO)₅(CS) with amines

<table>
<thead>
<tr>
<th>Amine</th>
<th>$k_2$, M⁻² sec⁻¹ᵃ</th>
<th>$k_1/k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butylamine</td>
<td>$1.5 \times 10^{-1}$ (± 10%)</td>
<td>0.91</td>
</tr>
<tr>
<td>benzylamine</td>
<td>$7.0 \times 10^{-2}$</td>
<td>0.73</td>
</tr>
<tr>
<td>cyclohexylamine</td>
<td>$5.7 \times 10^{-2}$</td>
<td>1.08</td>
</tr>
<tr>
<td>diethylamine</td>
<td>$3.8 \times 10^{-3}$</td>
<td>0.96</td>
</tr>
<tr>
<td>t-butylamine</td>
<td>$1.8 \times 10^{-4}$ (± 20%)</td>
<td>0.78</td>
</tr>
</tbody>
</table>

ᵃRate constants are averages from at least three runs at different pyridine concentrations.

The ratios of the rate constants, $k_1/k_2$, are found to be almost invariant, even though the rate constants themselves vary by a factor of nearly $10^3$. Also noteworthy is the fact that a secondary amine, diethylamine, fits well in this series. Thus it seems likely that primary and secondary amines go through the same transition state.

Pyridine appears to be a quite efficient catalyst for this reaction, slightly better in most cases than the amine itself. To determine the catalytic ability of other bases, a series of reactions was performed using cyclohexylamine and a selection of catalysts (Table 16). This series of reactions shows that remarkably weak bases such as tetrahydrofuran and ethyl ether are catalytically active. Indeed, the $K_a$ values of the catalysts span a range of about $10^{12}$, but the rates of
reaction vary by less than a factor of 10^2. This points out that if the catalyst is acting as a base (proton acceptor), then the transfer of the proton to the catalyst is only partially complete in the transition state. This conclusion is based on the empirical Brönsted relationship observed in other acid- and base-catalyzed reactions.\(^{195}\)

Table 16. Rate constants for base-catalyzed reactions of W(CO)\(_5\)(CS) with cyclohexylamine

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(K_a)</th>
<th>(k_2, M^{-2}\ \text{sec}^{-1})(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tributylphosphine</td>
<td>2.3 \times 10^{-9}</td>
<td>1.3 \times 10^{-1} (± 10%)</td>
</tr>
<tr>
<td>4-picoline</td>
<td>9.6 \times 10^{-7}</td>
<td>1.0 \times 10^{-1}</td>
</tr>
<tr>
<td>DABCO</td>
<td>\sim 1 \times 10^{-11}</td>
<td>8.0 \times 10^{-2}(^b)</td>
</tr>
<tr>
<td>cyclohexylamine</td>
<td>2.2 \times 10^{-11}</td>
<td>6.2 \times 10^{-2}</td>
</tr>
<tr>
<td>pyridine</td>
<td>5.6 \times 10^{-6}</td>
<td>5.7 \times 10^{-2}</td>
</tr>
<tr>
<td>2-picoline</td>
<td>1.1 \times 10^{-6}</td>
<td>4.9 \times 10^{-2}</td>
</tr>
<tr>
<td>t-butylamine</td>
<td>1.5 \times 10^{-11}</td>
<td>3.9 \times 10^{-2}</td>
</tr>
<tr>
<td>triethylphosphite</td>
<td>4 \times 10^{-4}</td>
<td>3.0 \times 10^{-2}</td>
</tr>
<tr>
<td>3-bromopyridine</td>
<td>1.45 \times 10^{-3}</td>
<td>2.2 \times 10^{-2}</td>
</tr>
<tr>
<td>2,6-lutidine</td>
<td>2.0 \times 10^{-7}</td>
<td>2.2 \times 10^{-2}</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>1 \times 10^{-2}</td>
<td>1.9 \times 10^{-2}</td>
</tr>
<tr>
<td>benzyldimethylamine</td>
<td>1.2 \times 10^{-9}</td>
<td>1.5 \times 10^{-2}</td>
</tr>
<tr>
<td>triethylamine</td>
<td>9.8 \times 10^{-12}</td>
<td>3.3 \times 10^{-3}</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>4 \times 10^3</td>
<td>1.5 \times 10^{-3}</td>
</tr>
</tbody>
</table>

\(^a\)Each rate constant is an average from at least three runs at different concentrations.

\(^b\)This value is obtained after correcting for the presence of two active sites.
Steric hindrance of the basic site appears to be an important factor in determining catalytic ability. Thus, a methyl group in the 4-position on a pyridine ring (4-picoline) enhances the catalytic ability as compared to pyridine, but a methyl group in the 2-position (2-picoline) lowers the activity. Methylation of both 2-positions (2,6-lutidine) lowers the activity still further. Triethylamine, a strong base containing a highly sterically hindered lone pair, is a much poorer catalyst than DABCO, a bicyclic analog.

Reactions carried out in the presence of octanoic acid were decelerated to the extent predicted if an equimolar quantity of the amine had been converted to a nonactive form. Addition of methanol to several reactions also retarded the rate, but to a smaller extent. Thus, the rate-determining step is base-catalyzed but acid-inhibited.

A kinetic study of a somewhat similar reaction, the aminolysis of a chromium methoxycarbene complex (Eq. 30), has been recently reported.\(^1\)

\[
\text{(CO)₅} \text{Cr} - \text{C}_2\text{OCH}_3 + \text{RNH}_2 \rightarrow \text{(CO)₅} \text{Cr} - \text{C}_2\text{OCH}_3 + \text{CH}_3\text{OH} \quad (30)
\]

This reaction was found to be catalyzed by both acids and bases. A transition state of the form

\[
\text{(CO)₅} \text{Cr} - \text{C}_2\text{OCH}_3 + \text{RNH}_2 + \text{B} + \text{HA} \rightarrow \text{(CO)₅} \text{Cr} - \text{C}_2\text{OCH}_3 \quad (31)
\]

was postulated. This methoxycarbene complex\(^1\) and other similar carbene complexes\(^1\) have been observed to form fairly stable ylide complexes.
of the type

\[
(CO)_5Cr-C=OCH_3 + B \rightarrow (CO)_5Cr-C=B^+ \quad \text{(32)}
\]

in the presence of a phosphine or tertiary amine. Thus, it is known that nucleophilic addition to the carbene carbon is a favorable process which could be involved in the initial step of the aminolysis.

A transition state similar to that proposed for the carbene aminolysis (Eq. 31) could be drawn for the thiocarbonyl reaction. However, the fact that this reaction is acid-inhibited rules such a structure out and suggests that little negative charge has accumulated on the sulfur up to the transition state. A structure of the transition state which is consistent with the evidence is

\[
HRN-H-B
(CO)_5W-CS + RNH_2 + B \rightarrow (CO)_5W-C=S
\quad \text{(33)}
\]

The fact that no interaction between phosphines or tertiary amines and the thiocarbonyl can be observed suggests that a somewhat higher nucleophilicity than that possessed by a free amine is necessary for addition to the thiocarbonyl to take place. The nucleophilicity of a primary or secondary amine, however, may be increased by hydrogen-bonding with another base. All available evidence indicates, therefore, that the rate-determining step in the reaction of \( W(CO)_5(CS) \) with primary and secondary amines is the attack of a hydrogen-bonded amine complex
RR'N - H--B at the thiocarbonyl carbon atom. Such hydrogen-bonded amine complexes have been spectroscopically observed in non-polar solvents such as heptane, acetonitrile, and carbon tetrachloride. Equilibrium constants have been measured for a process of the form

\[(\text{amine} \cdot \text{amine}) + 2 \text{py} \rightleftharpoons 2 (\text{py} \cdot \text{amine}).\]  

(34)

Moreover, even such weak bases as diethyl ether are observed to form hydrogen bonds with amine protons. The relatively low enthalpy of activation of the reaction between n-butylamine and W(CO)\(_5\)(CS) (7 kcal/mole) may also be accounted for by this model, the \(\Delta H\) of the pre-equilibrium involving hydrogen bonding is included in the value determined for \(\Delta H^\ddagger\). This hydrogen-bonding \(\Delta H\) is negative (3 to 7 kcal), and therefore lowers the \(\Delta H^\ddagger\) accordingly. Very similar activation parameters (\(\Delta H^\ddagger = 3.4\) kcal/mole; \(\Delta S = -45.6\) cal/deg mole) were observed for the amine-catalyzed term of the CH\(_3\)NH\(_2\) aminolysis of phenyl acetate.

A possible mechanism for the formation of an isocyanide by the reaction of a primary amine with W(CO)\(_5\)(CS) is shown in Eq. 35. This must be regarded as speculative, since kinetics give information only up to the rate-determining step.

\[
\begin{align*}
\text{(CO\(_2\))W-CS} + \text{R-N-H--B} & \rightleftharpoons \text{R-N-H} \quad \text{(CO\(_3\))W-CN} + \text{H}_2\text{S} \\
\text{R-N-H} \quad \text{(CO\(_3\))W-CN} & \rightleftharpoons \text{R-N-H} \quad \text{(CO\(_3\))W-CN} + \text{H}_2\text{S}
\end{align*}
\]
The last step of the process, the conversion of the aminothiocarbene to the isocyanide, could be acid- and/or base-catalyzed. Evidence exists, however, that it need not be. The carbene complex in Eq. 36

\[
\text{(CO)}_5\text{Cr-C}^- \text{CH}_3 \quad \xrightarrow{80^\circ} \quad \text{(CO)}_5\text{Cr-CN-C}_2 \text{Y} + \text{CH}_3\text{C-H}
\]  

loses acetaldehyde when heated to 80\(^\circ\) in the solid state under vacuum, in the absence of acid or base.\(^{206}\) The aminothiocarbene intermediate proposed above might be expected to be even less stable. In fact, if it does form, its decomposition is very rapid since it was never detected.

According to the mechanism proposed in Eq. 35, it is apparent that secondary amines could react similarly up to the stage where the aminothiocarbene complex is formed. The product finally isolated from these reactions in yields of 20-40\% is the thioformamide complex,

\[
\text{(CO)}_5\text{W} - \text{S=C(H)NR}_2.
\]

An approximately equal amount of the amine complex,

\[
\text{(CO)}_5\text{W} - \text{NHR}_2,
\]

is also produced. Even though the disappearance of \(\text{W(CO)}_5(\text{CS})\) is rapid on contact with secondary amines, the appearance of the thioformamide complex is very slow, which suggests that an intermediate forms in large quantities. Attempts to isolate this intermediate were not very successful; only an unstable gummy solid could be obtained which decomposed in several hours to yield some of the thioformamide complex. However, a partial characterization of the intermediate was possible. Reactions between equimolar \(\text{W(CO)}_5(\text{CS})\) and piperidine in hexane rapidly gave a precipitate of this substance, but only about half
of the \( \text{W(CO)}_5(CS) \) was consumed. A 2:1 molar ratio of the amine to \( \text{W(CO)}_5(CS) \) was required for all of the \( \text{W(CO)}_5(CS) \) to react. An investigation of a reaction between \( \text{W(CO)}_5(CS) \) and equimolar piperidine with excess DABCO as a catalyst gave evidence that both piperidine and DABCO were incorporated in the intermediate which forms. The ratio of areas of the broad resonance of the 3- and 4-carbon alkyl protons (\( \tau 8.25 \)) to the sharp singlet (\( \tau 7.10 \)) observed for the DABCO protons shows that the two bases are present in approximately a 1:1 molar ratio. (The protons on the 2-carbons of the piperidine ring appear as a broad doublet at about \( \tau 6.2 \). No other resonances were observed.) Extraction of the residue with hexane after evaporating this sample did not yield any free DABCO. The fact that only one sharp peak is observed for the DABCO protons, shifted downfield 0.15 ppm from the position in the free base, suggests that there is a rapid exchange of this base in solution. This was confirmed by adding excess DABCO to a solution of the intermediate; an upfield shift of the peak was observed. Addition of more DABCO caused a further shift. The chemical shift of the DABCO protons was unchanged when the base was added to a solution of \( \text{(CO)}_5\text{W−S=C(H)N(CH}_3)_2 \).

This evidence suggests that an intermediate is formed which includes two amine molecules, one of which is involved in a rapid dissociation-association process in solution. Since there are several examples in the literature of the addition of phosphines or tertiary amines to similar carbene complexes,\(^{197-199} \) it seems very probable that the intermediate in this reaction is an aminothiocarbene complex in equilibrium with a
base-coordinated form (Eq. 37). A rearrangement to coordination through sulfur accompanied by proton transfer would lead to the observed product. Such a rearrangement would seem to be more favorable in the base-coordinated ylide complex than in the free carbene because of the greater electron density on carbon and sulfur and possibly a lower strength of the W-C bond.

\[
\text{[Diagram: Reaction (37)]}
\]

\[
\begin{align*}
(CO)_5W-C &+ B \xrightarrow{} (CO)_5W-C-B^+ \\
&\xrightarrow{} (CO)_5W-C-B^+ + B
\end{align*}
\]

A quite similar reaction of an ylide complex has been reported which involves metal migration to phosphorus accompanied by proton transfer (Eq. 38).

\[
\text{[Diagram: Reaction (38)]}
\]

\[
\begin{align*}
(CO)_5Cr-C &+ H(O)C\text{CH}_3 \xrightarrow{} (CO)_5Cr-CO\text{CH}_3 \\
&\xrightarrow{} (CO)_5Cr-CO\text{CH}_3 + B
\end{align*}
\]

2. **Reactions of W(CO)$_5$(CS) with other nucleophiles**

Many attempts were made to add a variety of nucleophiles to W(CO)$_5$(CS). Although it had been found that many amines react readily, H$_2$O or alcohols were observed not to react. Reactions of W(CO)$_5$(CS) with ethoxide ion do apparently involve nucleophilic attack at the
thiocarbonyl. Attempts to characterize the product by reaction with [Et₃O]BF₄ gave several products, none of which was isolated or identified.

Methanethiol, propylene oxide, triphenylphosphine oxide, Ph₂P=CCl₂, and cyclohexylcarbodiimide showed no evidence of reaction. It seems apparent that, although the thiocarbonyl function in W(CO)₅(CS) is more susceptible to nucleophilic attack than the carbonyl groups in W(CO)₆, quite strong nucleophiles are still required to effect addition.

Stronger nucleophiles which do react with W(CO)₆ also react, as expected, at the thiocarbonyl group in W(CO)₅(CS). Thus, azide ion, which reacts with W(CO)₆ to yield [W(CO)₅NCO]⁻, forms [W(CO)₅NCS]⁻ on reaction with W(CO)₅(CS). Presumably a process similar to that proposed in the carbonyl reaction is involved (Eq. 39). An identical complex was prepared by the reaction of NCS⁻ with W(CO)₆, as reported in the literature. The reaction of trans-(¹³CO)W(CO)₅(CS) with N₃⁻ appears to occur with retention of the specific trans label.

The addition of methylmagnesium iodide to W(CO)₅(CS) followed by introduction of MeSO₂F was expected to give an alkylthiocarbene by analogy with the reaction of W(CO)₆. However, several products were formed in low yields and only one of these, (CO)₅W-S(CH₃)₂, was isolated. The mechanism for the formation of this product is unknown.
Amide ions also react at the thiocarbonyl group, but products could not be isolated. Lithium dimethylamide followed by MeSO$_3$F, for example, yields several unidentified products in small amounts. Some reactions with lithium n-butylamide gave (CO)$_5$WCN(n-Bu); others gave other products and little if any of this compound. Phenylphosphide (PhPH$^-$) appeared to react similarly to Me$_2$N$^-$; addition of MeSO$_3$F to the phenylphosphide reaction mixture gave several unidentified products. In general, these reactions with strong nucleophiles give several products in low yields which could not be crystallized. Intermediates which are anticipated in these reactions (Eq. 40) may rearrange to give other

$$\text{(CO)}_5 W - \text{CS} + \text{N}^- \rightarrow \text{(CO)}_5 W - \text{C} \begin{array}{c} S^- \\ N \end{array}^+ \quad (\text{N}^- = \text{nucleophile}) \quad (40)$$

products because of the proximity to the metal of the highly charged, nucleophilic sulfide ion.
V. CONCLUSIONS

The chromium and tungsten \( M(CO)_{5}(CS) \) complexes are the most versatile thiocarbonyl complexes yet studied. Their stability, solubility, and volatility allow them to be studied by a variety of spectroscopic and chemical methods, and the relative simplicity of their structures permits the aid of theoretical methods in the interpretation of these studies. In addition to exhibiting unusual properties themselves, these complexes yield a variety of substituted derivatives which show a range of properties.

The high stability of the metal-thiocarbonyl bond is evident in both mass spectroscopic and ligand substitution studies. For example, \( W(CO)_{5}(CS) \) undergoes replacement of four carbonyl ligands by diphos with no evidence of thiocarbonyl displacement. The few substitution reactions which do give products resulting from thiocarbonyl replacement do not appear to be simple processes, and the products may arise from decomposition of the original thiocarbonyl-containing products.

All of the reactions of the thiocarbonyl complexes are consistent with the CS being a stronger \( \pi \)-acceptor ligand than CO. The metal atom in these complexes thus behaves as if it has less electron density than in an analogous carbonyl complex. For example, the donor ligands studied add to \( W(CO)_{5}(CS) \) at a rate \( 10^2 \) to \( 10^3 \) times faster than to \( W(CO)_{6} \). The reactions of \( W(CO)(CS)(\text{diphos})_{2} \) with Lewis acids and the properties of the adducts also show that the metal has less available electron density than in the corresponding \( W(CO)_{2}(\text{diphos})_{2} \) carbonyl complex. Although CS
has been calculated to be a better $\sigma$ donor than CO, the behavior of its complexes indicates that the electron-withdrawing effect predominates. Some of these results also may be interpretable in terms of a destabilization of metal orbitals as proposed by Lichtenberger.\textsuperscript{103}

Reactions at the sulfur of substituted thiocarbonyl complexes point out the higher nucleophilicity of the sulfur atom relative to that of oxygen in analogous carbonyl complexes. Many reagents which have not been observed to interact with carbonyl oxygen atoms do bond to the sulfur of appropriate thiocarbonyl complexes. This would seem to be a result of both the greater ability of the CS ligand to withdraw electron density from the metal and the lower electronegativity and greater polarizability of the sulfur atom as compared to oxygen.

Nucleophilic addition to the thiocarbonyl carbon is more favorable in the cases studied than is addition to analogous carbonyls. The lower electronegativity of sulfur should allow the carbon in the CS ligand to maintain a higher electron density than in a CO ligand; a dipolar structure such as $\text{M-}\overset{\delta^{-}}{\text{C}}-\overset{\delta^{+}}{\text{S}}$ thus would seem to contribute little to the actual electronic structure of the ligand complex. Calculations have predicted, in fact, that the CS carbon has less positive charge than the carbon in an analogous carbonyl.\textsuperscript{103} The greater susceptibility of CS in its complexes to nucleophilic attack may be due to a relatively low energy of its lowest unoccupied molecular orbital. This orbital is presumably derived from the low-energy CS $\pi^*$ orbital, which is concentrated mainly on the carbon atom.
The preparation and study of these thiocarbonyl complexes has brought to light some previously unobserved properties and reactions of metal thiocarbonyls. The thiocarbonyl ligand in its complexes is very different from the carbonyl ligand. The properties of the metal atom and other ligands in the complexes are also changed somewhat from the corresponding carbonyl complexes, although in most cases these differences are quantitative rather than qualitative.
VI. SUGGESTIONS FOR FURTHER RESEARCH

This research uncovered many areas in which further study is warranted. Some of these were investigated preliminarily; others have come to light in hindsight.

The reaction of strongly nucleophilic metal carbonyl anions with CS$_2$ and an acid appears to have potential, yet unrealized, for producing a variety of metal thiocarbonyl complexes. These reactions would be significant since there are few processes known which form a metal-thiocarbonyl bond.

Many of the reactions of W(CO)$_5$(CS) which were investigated are also expected of Cr(CO)$_5$(CS), but few were actually carried out. A further study of Cr(CO)$_5$(CS) would be important because theoretical calculations can be performed on first-row transition metal complexes much more easily than on second- and third-row complexes.

Some further work may also be possible with Ho(CO)$_5$(CS). The high reactivity of this complex apparently makes its isolation difficult, but many of its derivatives should be more stable. Improved reaction conditions for its preparation may be found; perhaps lowering the temperature would reduce its decomposition. It may also be possible to obtain Na[ClMo(CO)$_4$(CS)] from the preparations.

A study of the cis-trans isomerism of M(CO)$_4$(CS)(L) complexes may give information about the bonding properties of certain ligands. It appears that non-pi-bonding ligands such as amines and halide ions form
exclusively *trans*-M(CO)$_4$(CS)(L) complexes, but phosphines, which have pi-acceptor capacity, give cis isomers as well. A determination of the cis-trans equilibrium constants for a variety of ligands may show which ligand properties are involved in determining the stabilities of the isomers. A correlation between the equilibrium constants and pi-acceptor capacity of the ligands may be found. A unique property of this system is that steric effects presumably have a minimal effect, so that only electronic effects will be observed. The mechanism of isomerization, which appears to be intramolecular, could also be investigated.

Thiocarbonyl complexes containing a cyclopentadienyl or poly-
pyrazolylborate ligand should be preparable from the M(CO)$_4$(CS)(solvent) intermediates. By analogy with the known carbonyl systems, a wide variety of derivatives should be obtainable from such complexes.

Finally, a further investigation of the M(CO)$_5$(solvent) and 
M(CO)$_4$(L)(solvent) intermediates generated by halide ion abstraction should also be fruitful. These complexes were found to react with ligands to give products which largely retain the geometry of the halide precursor. Further studies could be done to determine the effects of varying conditions such as the temperature, solvent, ligands, and metal. These reactions are significant since they may be used to prepare products preferentially substituted in one position by isotopically labeled carbon monoxide. There have been very few such products previously prepared.
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