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# Preparation and reactions of mercapto and sulfido complexes of tungsten carbonyls

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  PREPARATION AND REACTIONS OF MERCAPTC
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  CARBONYLS.

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Preparation and reactions of mercapto and sulfido

complexes of tungsten carbonyls

by

Richard Geoffrey Warmington Gingerich

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## I. INTRODUCTION

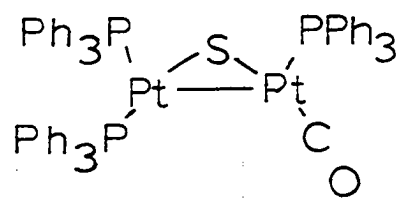### A. Complexes with Sulfur Ligands

Sulfur donor ligands are known to coordinate to metal atoms in a variety of ways which have been described in a recent review (1). In addition to the terminally bonded sulfur atom, I (2), it may act as a two-fold bridge, II (3), a three-fold bridge, III (4), or a four-fold bridge, IV (5) and V (6), between metal atoms. Abel and Crosse (7), Jorgensen (8), and Livingstone (9) have reviewed transition metal complexes that contain organosulfur (RS-) ligands. Metals may be chelated to sulfur chains, VI (10); these complexes have been reviewed by Schmidt (11). Group 6A thiometalates, e.g. $H_2WS_4$ (12), were reviewed by Diemann and Muller (13).

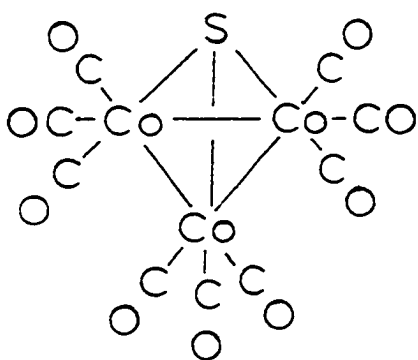### B. Complexes with Hydrogen Sulfide ($H_2S$)

Complexes with the $H_2S$ ligand are $[TiX_4 \cdot nH_2S]$ where X = Cl, Br and n = 1,2 (14), $[(h^5-C_5H_5)Mn(CO)_2(SH_2)]$ (VIII) (15), $[(H_2S)Pt(PPh_3)_2]$ (VIII) (16), $[Ru(NH_3)_5(SH_2)]^{2+}$ (17), and $[W(CO)_5(SH_2)]$ (18). Dicarbonylcyclopentadienyl(hydrogen sulfide)manganese (I) (VII), a yellow substance in solution, decomposes to an insoluble green material at room temperature. The $[(H_2S)Pt(PPh_3)_2]$ (VIII) complex is inseparable from its accompanying biproduct, $[(HS)HPt(PPh_3)_2]$, and decomposes in polar solvents. (Hydrogen sulfide)bis(triphenylphosphine)platinum (0) (VIII) reacts with $O_2$ (Equation 1), HCl (Equation 2), and RC(=O)Cl where R = Me, Ph (Equation 3) but is inert to C≡O, HC≡CH, and $H_2C=CH_2$ (19). Protons attached to the

$Cl_4W=S$

I

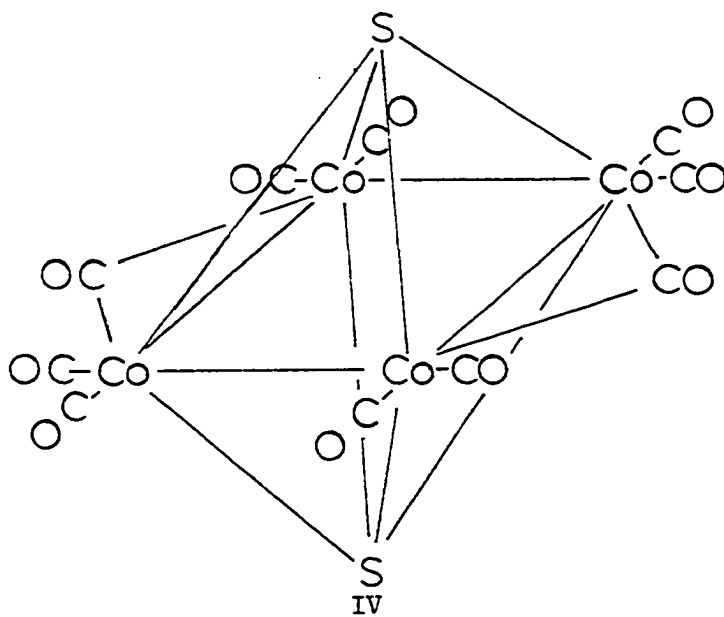

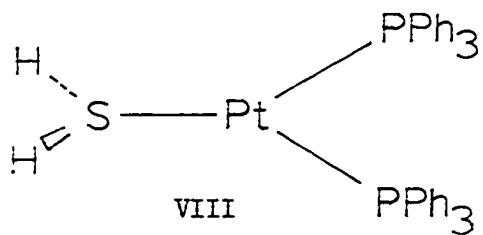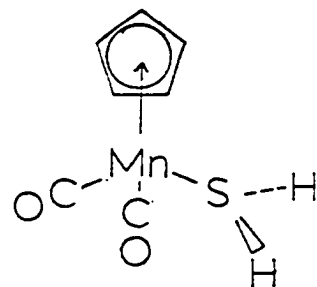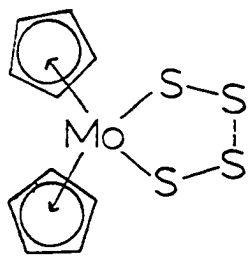II



III



IV

V



VI



VII



VIII

-1- $[(H_2S)Pt(PPh_3)_2] + O_2 \rightarrow [(PPh_3)_2PtS]_2$

-2- $[(H_2S)Pt(PPh_3)_2] + HCl \rightarrow t-[(PPh_3)_2Pt(H)Cl] + H_2S$

-3- $[(H_2S)Pt(PPh_3)_2] + RC(=O)Cl \rightarrow t-[(PPh_3)_2Pt(H)Cl] + RC(=O)SH$
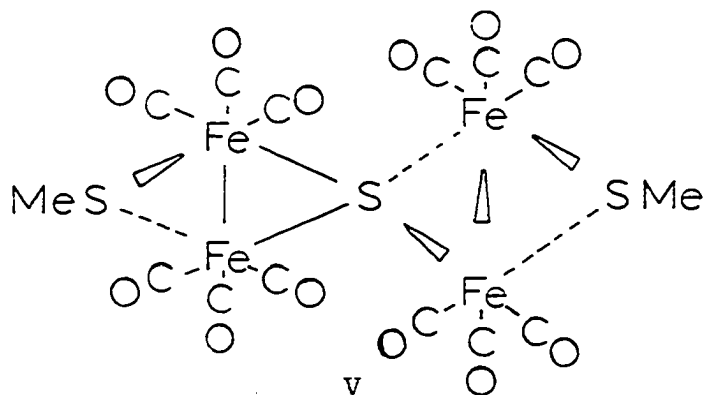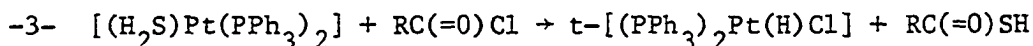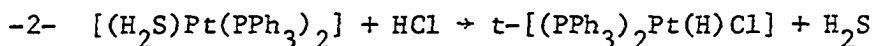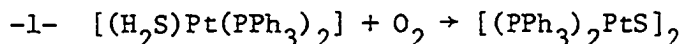
sulfur atom in $[(H_2S)Pt(PPh_3)_2]$ exchange with deuterium in $D_2O$ solution. The value of $pK_1$ for $[Ru(NH_3)_5(SH_2)]^{2+}$ is 4.0 (17) which is considerably higher than the value for the free ligand, $H_2S$ ($pK_1 = 7$) (20). Penta-carbonyl(hydrogen sulfide)tungsten (0), $[W(CO)_5(SH_2)]$, is a green solid (18).

## C. Complexes with Hydrogen Sulfide ($[HS]^-$)

Examples of complexes that contain the mercapto ligand, $[HS]^-$, are

$[(HS)ClIr(CO)(PPh_3)_2H]$ (IX) (21, 22), $[(h^5-C_5H_5)_2Ti(SH)_2]$ (23),

$[(H_2O)_5Cr(SH)]^{2+}$ (24, 25, 26), $t-[(PPh_3)_2Pt(SH)H]$ (16),

$[(CH_2Cl_2)ClRh(SH)(PPh_3)_2H]$ (22), $[Cr(CO)_5(SH)]$ (27), $[NEt_4][\mu-HS[Cr(CO)_5]_2]$

(X) (27), $[Me_3Pt(SH)]_4$ (28), $[Ni(Phen)_3][(CO)_3Mo(Bipy)(SH)]_2$ (29),

$[(h^5-C_5H_5)Ni(PBu_3)(SH)]$ (30), $[Mn(CO)_4(SH)]_2$ (XI) (31, 32),

$[(h^5-C_5H_5)W(CO)_3(SH)]$ (33), $[(NH_3)_5Ru(SH)]^{2+}$ (17), $t-[(PEt_3)_2Pt(SH)H]$ (34),

$[(CO)_4Re(SH)]_2$ (32), $[(CO)_3M(SH)]_4$ (M = Mn, Re) (XII) (32),

$[Rh[C_2(DO)(DOBF_2)](SH)_2]$ (XIII) (35), and $[M(SH)(pp_3)]^+$ (M = Fe, Co, Ni)

(XIV) (36). These complexes with the exception of $t-[(PEt_3)_2Pt(SH)H]$ and $[(NH_3)_5Ru(SH)]^{2+}$ have been isolated in the solid state and characterized

Ph₃P, H, SH, Ir, CO, Cl, PPh₃

**IX**

OC, CO, H, S, CO, CO, Cr, Cr, CO, OC, CO, OC, CO

**X**

O, C, CO, S, H, CO, CO, Mn, Mn, CO, OC, S, H, CO, OC, CO

**XI**

(CO)₃Re, S, H, H, S, Re(CO)₃, S, H, Re(CO)₃, (CO)₃Re, S, H

**XII**

F₂, B, O, S, H, O, N, N, Rh, S, H

**XIII**

Ph₂P, P, Ph₂P, Co, PPh₂, Ph₂P, S, H
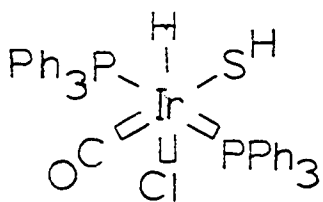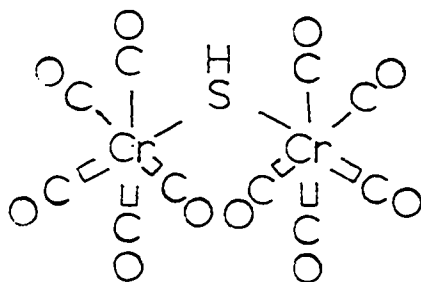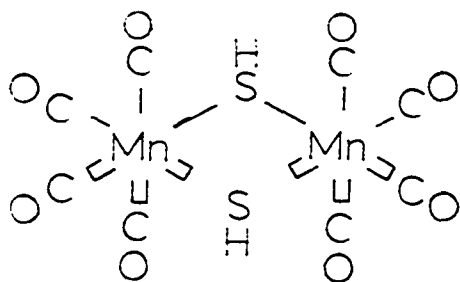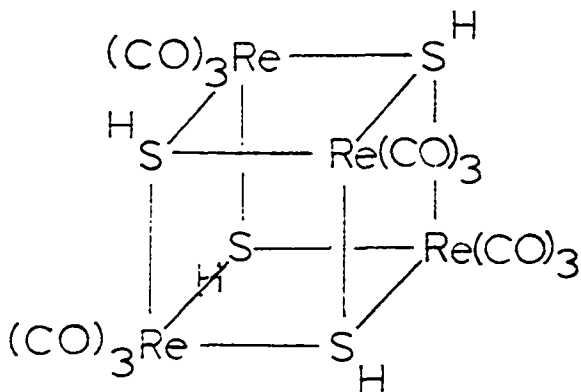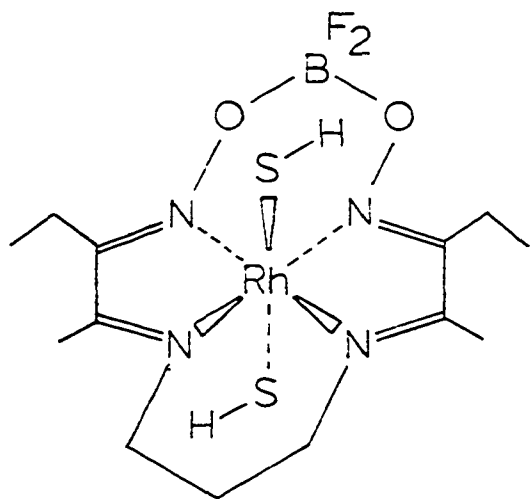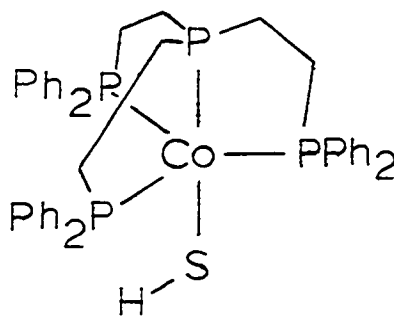
**XIV**

by analytical and spectrophotometric techniques. Typically, the above complexes are prepared by treating a reactive complex (e.g. a complex that is ligand deficient (Equation 4) or a complex containing a relatively labile ligand (Equation 5)) with $H_2S$ or NaSH. Other preparations are illustrated in Equations 6, 7 and 8.

-4- $t-[(PPh_3)_2IrCl(CO)] + H_2S \rightarrow [(HS)ClIr(CO)(PPh_3)_2H]$ (IX)

-5- $[(h^6-C_7H_8)Mo(CO)_3] + Bipy + NaSH \rightarrow [(CO)_3MoBipy(SH)]^- + C_7H_8$

where

Bipy =

-6- $Na_2[Cr_2(CO)_{10}] + ex. SO_2 \xrightarrow{H_2O} [Cr(CO)_5(SH)]$

-7- $[(h^5-C_5H_5)W(CO)_3H] + \overline{SCH_2CMeH} \rightarrow [(h^5-C_5H_5)W(CO)_3(SH)] + H_2C=CMeH$

-8- $[(CO)_4MnSSnMe_3]_2 + HCl \rightarrow [(CO)_4Mn(SH)]_2$ (XI) $+ Me_3SnCl$
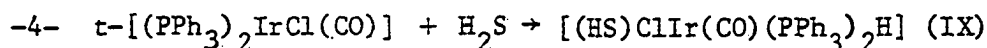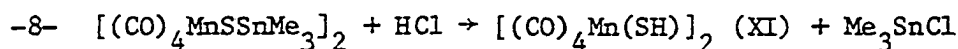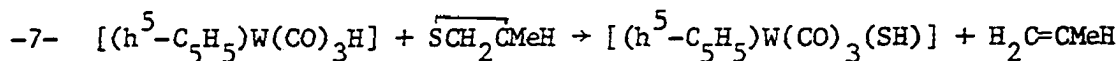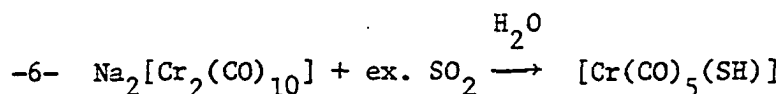
Investigations of the reactivity of complexes which contain the [SH]$^-$ ligand have been reported in the chemical literature by a few groups. Sato et al. reported the insertion of PhC≡CH into the SH bond of $[(h^5-C_5H_5)Ni(PBu_3)(SH)]$ (Equation 9). Reaction between PhC≡CPh and this complex (Equation 10) is complicated (37). Treatment of $[(H_2O)_5Cr(SH)]^{2+}$

-9- $[(h^5-C_5H_5)Ni(PBu_3)(SH)] + PhC≡CH \rightarrow [(h^5-C_5H_5)Ni(PBu_3)(SCPh=CH_2)$

-10- $[(h^5-C_5H_5)Ni(PBu_3)(SH)] + PhC≡CPh \rightarrow [(h^5-C_5H_5)_2Ni_2(PhC≡CPh)]$
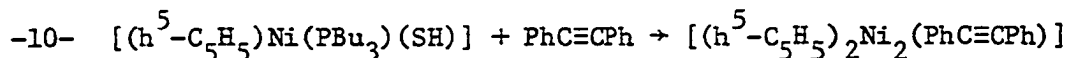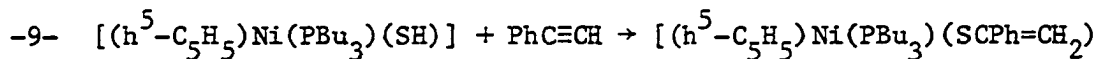
with [NCS]$^-$ gives [(H$_2$O)$_4$Cr(NCS)(SH)]$^+$ (25) and with I$_2$ yields

[(H$_2$O)$_5$CrSSCr(H$_2$O)$_5$]$^{4+}$ (38). With appropriate temperatures and pressures

of C≡O, Kullmer and Vahrenkamp have been able to convert [(CO)$_3$M(SH)]$_4$

(XII) to [(CO)$_4$M(SH)]$_2$ (XI) where M = Mn, Re and [(CO$_4$M(SH)]$_2$ to

[(CO)$_5$M(SH)]. At STP [(CO)$_5$M(SH)] reverts to [(CO)$_4$M(SH)]$_2$ in 30

minutes (39).

<center>D. Metallosulfanes (-S-)</center>

Compared to the number of insoluble binary sulfide compounds,

soluble metal complexes with unsubstituted sulfur as a ligand are rare

(1). Examples of metallosulfanes are [Ag$_3$S]$^+$ (40), [(Et$_3$P)Au]$_2$S (XV)

(41), [[(Ph$_3$P)Au]$_3$S]$^+$ (XVI) (41), [Ni$_2$S(MeC(CH$_2$PPh$_2$)$_3$)$_2$]$^{2+}$ (XVII) (42),

[(h$^5$-C$_5$H$_5$)Mn(CO)$_2$]$_2$S (43), [μ-S[Pt(PPh$_3$)$_2$][Pt(PPh$_3$)(CO)]] (II) (44), and

[μ-S[Pt(PPh$_3$)$_2$]$_2$] (45). All of the above complexes have been isolated

in the solid state and characterized by analytical and spectrophotometric

techniques. A crystal structure determination has been carried out on

II (3). Preparations of these complexes have been effected with Na$_2$S

(Equation 11) and COS (Equation 12). Air easily oxidizes
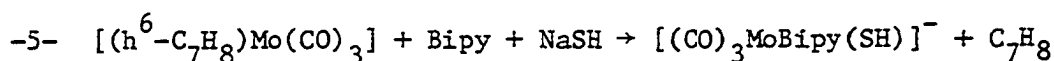
[(h$^5$-C$_5$H$_5$)Mn(CO)$_2$]$_2$S to [(h$^5$-C$_5$H$_5$)Mn(CO)$_2$]SO which may contain a

bridging -S(=O)- ligand (43).

-11-  [BrAu(PEt$_3$)] + Na$_2$S → [(Et$_3$P)Au]$_2$S (XV)

-12-  [Pt(PPh$_3$)$_3$] + COS $\xrightarrow[\text{HCCl}_3]{\text{reflux}}$ [μ-S[Pt(PPh$_3$)$_2$][Pt(PPh$_3$)(CO)]] (II)
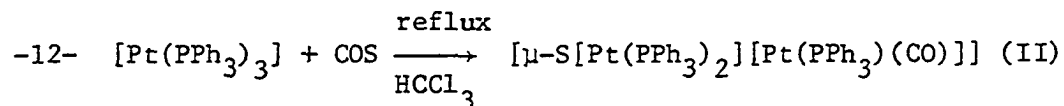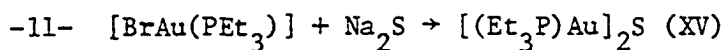
No other reactions have been executed employing these metallosulfanes as a reagent.

$$\begin{array}{c} S \\ Au \quad Au \\ Et_3P \qquad PEt_3 \end{array} \qquad \left[\begin{array}{c} S \\ Au \quad Au \quad Au \\ Ph_3P \qquad PPh_3 \qquad PPh_3 \end{array}\right]^{+}$$

XV                                    XVI

$$Me \begin{array}{c} P \quad P \\ P \\ Ni-S-Ni \\ P \quad P \end{array} Me$$
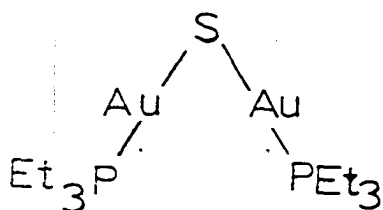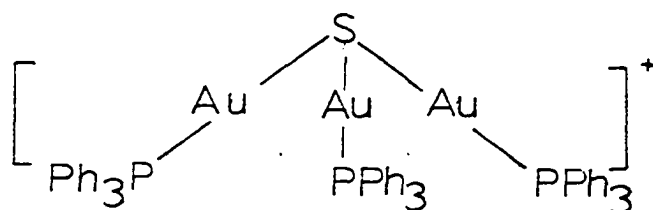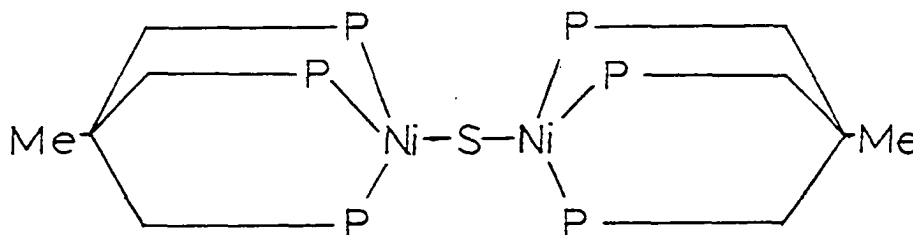
XVII

E.  Intent of the Present Research

Complexes containing mercapto $[HS]^{-}$ or sulfido $[S]^{2-}$ ligands are limited in number as evidenced in the above discussion. The reactivity of these complexes is virtually unknown. In this research our purpose was to examine the possible synthesis of new complexes with these ligands and to investigate their reactivity with organic reagents.

II.  EXPERIMENTAL

A.  Apparatus

1.  Infrared spectra

Solution infrared spectra were obtained using Perkin-Elmer 237, Beckman IR-20A, and Perkin-Elmer 337 spectrophotometers.  A Beckman IR 4250 spectrophotometer was employed to acquire solid phase infrared spectra.  The solution cells, which were matched, had sodium chloride windows and a 0.5 mm path length.  Solid phase spectra were obtained using pressed potassium bromide disks that contained the sample.  Band positions that were obtained on the Perkin-Elmer instruments were calibrated with the 2147 $cm^{-1}$ band of $CO_{(g)}$ and were accurate to within 3 $cm^{-1}$.  Band positions are reported in wavenumbers.

2.  NMR spectra

Varian A-60, Perkin-Elmer R20B, and Varian HA-100 spectrometers were employed to obtain $^1H$ NMR spectra.  An internal standard, tetramethylsilane (TMS), was added to the solutions containing the sample.  Peak positions are reported in $\tau$ units and are accurate to within 0.03 ppm.

Solution $^{13}C$ NMR spectra were acquired with a Bruker HX-90E Fourier Transform Spectrometer that employed proton decoupling.  Deuterated solvents served as the internal lock and peak positions are reported in $\delta$ units relative to TMS.  Tris(acetylacetonate)chromium (III) (25 mg), a paramagnetic substance which shortens the relaxation time ($T_1$) of the

nonprotonated carbons (e.g., M-C≡O), was added to the sample solutions to improve the relative intensities (46, 47).

A Bruker HX-90E Fourier Transform Spectrometer was employed to obtain $^{19}$F NMR spectra. An internal reference, hexafluorobenzene, was added to the solutions that contained the sample. Chemical shifts are reported in δ units relative to trichlorofluoromethane ($CFCl_3$). Peak positions up-field from $CFCl_3$ are assigned positive values.

## 3. Mass spectra

Mass spectra were obtained using an AEI MS 902 spectrometer. Each sample's mass spectrum was recorded with ionizing potentials of 18, 50, and 70 ev. Mass to charge ratios and relative intensities are reported for the observed ions.

## 4. Visible spectra

A Cary 14 spectrophotometer was employed to acquire visible spectra. Solutions of $10^{-4}$ Molar (M) gave suitable spectra. Band positions are reported in nanometers and are accurate to within 3 nm. Molar extinction coefficients are accurate to three significant figures.

## 5. Analyses

Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona; Schwarzkopf Microanalytical Laboratory, Woodside, New York; and Galbraith Laboratories, Inc., Knoxville, Tennessee.

## 6. Melting points

Melting points were observed with a Unitron MK Microscope that was equipped with a Thomas Model 40 micro hot stage attachment. The melting points are uncorrected.

## 7. Conductivity measurements

Conductivity measurements were observed employing an Industrial Instruments Conductivity Bridge Model RC 16B2 and were made at 25.00 $\pm$ 0.05 °C with $10^{-4}$ M solutions containing the sample. Values are reported in $cm^2 ohm^{-1} M^{-1}$ and are accurate to within 5 $cm^2 ohm^{-1} M^{-1}$.

## 8. Gas-solid column chromatography

A qualitative determination for hydrogen, $H_2$, was performed on a Varian Aerograph Series 1700 Instrument. Retention times of the unknown sample and a control sample of $H_2$ were identical, 7 min. 20 sec., with an argon gas flow of 13 cc per minute through a Poropak Q column (5 ft. x 1/4 in. o.d.) with the oven at 105°C.

## 9. Kinetic studies

Half-lives for the reaction of $[(Ph_3P)_2N][W(CO)_5(SH)]$ with MeN=C=O, PhN=C=O, MeN=C=S, or PhN=C=CPh$_2$ were determined by monitoring the disappearance of a suitable stretching frequency on the Perkin-Elmer 337 spectrophotometer. These bands were 2270 $cm^{-1}$ of MeN=C=O, 2240 of PhN=C=O, 2100 of MeN=C=S, and 2052 of $[W(CO)_5(SH)]^-$ in its reaction with PhN=C=CPh$_2$. Runs were performed at room temperature (ca. 23°C) in THF for at least three half-lives with equimolar amounts of the starting

materials ($1.0 \times 10^{-2}$ M).

Reaction rates were determined by monitoring the decrease of the highest wavelength absorption of $[W(CO)_5(SH)]^-$ (450 nm) with a Beckman DB-G spectrophotometer. Temperature was maintained at $26.45 \pm 0.05°C$ by circulating water from a Haake FS-2 constant temperature bath through a constant temperature block that was fitted into the visible spectrophotometer.

In a typical experiment, 3.0 ml of a solution of $[(Ph_3P)_2N][W(CO)_5(SH)]$ in THF or acetone ($7.6 \times 10^{-4}$ M) was added to a quartz cuvette (1 cm$^2$ x 4 cm) which was capped with a septum. The reaction vessel containing the yellow solution was thermostated for 5 minutes in the spectrophotometer. Next, a $\geq 10$ fold molar excess of PhN=C=O which was distilled and stored under an atmosphere of PPN was syringed into the cuvette. The reaction vessel was inverted five times and placed in the spectrophotometer. A decrease in the 450 nm band of the complex, $[W(CO)_5(SH)]^-$, was recorded on a Linear Instruments Corp. 10" flat bed recorder with the change in time.

Pseudo-first-order rate constants, $k_{obsd}$, were determined from slopes of $\ln(A_t-A_\infty)$ vs. t plots where $A_t$ is the absorbance at time t and $A_\infty$ is the constant absorbance at the conclusion of each run. These rate constants were reproducible to within 10% (Table 22).

## 10. Special glassware and techniques

Reactions were carried out in round bottom flasks which were equipped with Standard Tapered 14/20 necks and sidearm stopcocks. Flasks were dried at 110°C for at least 12 hours and flushed with prepurified nitrogen (PPN) immediately before use. Manipulations of reaction mixtures and residues were performed under an atmosphere of PPN.

Partitional crystallization was executed by the following technique. Mixtures containing the metal carbonyl product were filtered with suction through a frit into a 125 ml Erlenmeyer flask which was equipped with a sidearm stopcock. A volume of diethylether that was equal to one-half the volume of the filtrate (X ml) was floated on top of the filtrate. This biphase mixture was placed in the freezer (-40°C). When one phase of liquid was observed above the precipitated materials (normally, the next day), the single phase was decanted from the residue into another Erlenmeyer flask. This procedure was repeated by placing X ml of diethylether on top of the resultant single phase. Next, X ml portions of hydrocarbons were repeatedly floated on top of the consequent single phases until a decanted solution was free of metal carbonyl products. If crystalline solids of the same melting point and solution IR spectrum in the 2300 cm$^{-1}$ to 1600 region were found among the numerous residues, these crystals were combined and characterized. On the other hand, if all the residues were tars, the residues which contained appreciable quantities of metal carbonyl product were combined and the technique repeated with these residues in an alternant solvent system.

## B. Materials

### 1. Solvents

The following solvents were pretreated prior to their use. Diglyme was dried over Drierite for 24 hours, refluxed over copper (I) chloride for 2 hours, and distilled from calcium hydride ($CaH_2$) under an atmosphere of PPN (48). Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored under an atmosphere of PPN. Absolute ethanol (EtOH) was distilled from $CaH_2$ and stored under an atmosphere of PPN. Acetone was dried over Drierite for 24 hours and purged with a stream of PPN. Diethylether and hexanes were stored over activated, type 4a molecular sieves and purged with a stream of PPN. Water was distilled prior to its use. Methylene chloride ($CH_2Cl_2$) and acetonitrile (MeCN) were stored over activated, type 4a molecular sieves.

All other solvents were employed as received.

### 2. Reagents

Preparation of bis(triphenylphosphine)imminium thioacetate ($[(Ph_3P)_2N][SC(=O)Me]$) was effected by the following procedure. To a 100 ml flask were successively added 0.765 g (14.2 mmole) of sodium methoxide (NaOMe), 30 ml of EtOH, and 0.30 ml (4.2 mmole) of thioacetic acid ($HSC(=O)Me$). The resultant pale yellow mixture was stirred for 30 minutes. Next, 2.31 g (4.03 mmole) of bis(triphenylphosphine)imminium chloride, $[(Ph_3P)_2N]Cl$, was added to the mixture. After the mixture was stirred for 18 hours, there resulted a pale yellow mixture containing

white solids. This mixture was diluted with 200 ml of diethylether and filtered with suction through a frit of medium porosity. The pale yellow filtrate was concentrated in vacuo to a yellow oil. Dissolving the oil in acetone and diluting the resultant solution with diethylether gave a white solid (1.13 g, 47% yield). The compound, $[(Ph_3P)_2N][SC(=O)Me]$, was identified by its IR and $^1H$ NMR spectra (respectively, pressed KBr pellet 1545 $cm^{-1}$(s), 1510(s), 1155(w), 1022(w), 942(w), 735(m), 655(m) and $DCCl_3$ 2.50$\tau$(m), 7.70(s) respective relative intensities of 10:1).

Reagents that are included in this paragraph were generated according to published methods and employed in situ. Sodium sulfide, $Na_2S$, resulted from the action of two parts of sodium ethoxide, NaOEt, with one part of $H_2S$ in EtOH (49). Treating tetraethylammonium pentacarbonyl(iodo) chromate (0) or wolframate (0), $NEt_4[M(CO)_5I]$, with an equimolar amount of silver tetrafluoroborate ($Ag[BF_4]$) in acetone gave a yellow suspension of pentacarbonyl(acetone)chromium (0) or tungsten (0), $M(CO)_5$(acetone) (50). One part of methylmercurychloride, MeHgCl, was reacted with one part of silver nitrate, $Ag[NO_3]$, in MeCN or $Ag[BF_4]$ in $CH_2Cl_2$ to yield insoluble silver chloride, AgCl, and respectively $MeHg[NO_3]$ (51) or $MeHg[BF_4]$ (52). An ethereal solution of diazomethane, $CH_2N_2$, was prepared by the procedure of DeBoer and Backer (53). Diphenylketene, $Ph_2C=C=O$, was generated according to the method of Darling and Kidwell and manipulated in n-heptane (54). Following a procedure of Thorn and Ludwig gave an aqueous solution of sodium ethyldithiocarbamate, $Na[S_2CNEtH]$ (55).

Preparation and isolation of the inorganic reagents listed below was effected according to published procedures. Sodium hydrogensulfide, NaSH,

was prepared by the method of Eibeck (56). Dicarbonyl($h^5$-cyclopentadienyl) thiocarbonyliron (+1) hexafluorophosphate, [CpFe(CO)$_2$CS]PF$_6$, was a generous gift of Dr. Thomas Wnuk who made the complex by the procedure of Dombek and Angelici (57). Mr. Michael H. Quick provided dicarbonylchloro-($h^5$-cyclopentadienyl)iron (0), CpFe(CO)$_2$Cl, which he obtained following the method of Dombek and Angelici (58). Pentacarbonyl(bistriphenyl-phosphine) tungsten (0), W(CO)$_5$(PPh$_3$), was prepared according to the procedure of Connor et al. (50). Preparation of NEt$_4$[M(CO)$_5$I] where M = Cr and W was accomplished by the method of Abel et al. (59). Tetraethylammonium iodide (NEt$_4$I) was prepared by Mr. Steven Cook, deceased member of Dr. Angelici's research group, by refluxing ethyl iodide, EtI, with triethyl-amine (NEt$_3$) in EtOH. Bis(triphenylphosphine)imminium ethyldithio-carbamate, [(Ph$_3$P)$_2$N][S$_2$CNEtH], precipitated when an aqueous solution of Na[S$_2$CNEtH] was added to a saturated aqueous solution of [(Ph$_3$P)$_2$N]Cl; it was dried under vacuum (60).

The following organic reagents were prepared and isolated by published methods. Triphenylketenimine, Ph$_2$C=C=NPh, was prepared by the method of Bestmann et al. (61). Preparation of phenylcyanate, PhOC≡N, was carried out by the procedure of Grigat and Putter (62). Clemens et al. provided the method for the formation of ditertiarybutylsulfur-diimine, t-BuN=S=Nt-Bu (63). Schiff bases, t-BuN=CMeH (64) and PhN=CPhH (65), were prepared by the referenced methods. The N-(para-substituted benzylidene) aniline compounds, PhN=C(p-NO$_2$C$_6$H$_4$)H, PhN=C(p-ClC$_6$H$_4$)H, PhN=C(p-OMeC$_6$H$_4$)H, and PhN=C(p-NMe$_2$C$_6$H$_4$)H, were obtained by the procedures of Tabei and Saitou (66).

The reagents which are listed below were stored or handled in special ways before use. Storage and manipulation of Ag[BF$_4$] was effected in an atmosphere of PPN. Reagents which were stored under an atmosphere of PPN at 0°C included HSO$_3$CF$_3$, MeSO$_3$F, EtSO$_3$F, [NO]PF$_6$, and [Et$_3$O]BF$_4$. Cyanamide, H$_2$NC≡N, was kept at -40°C. The following reagents were stored at 0°C: MeN=C=O, MeC(=O)H, $\overline{HNCH_2CH_2}$, and $\overline{SCH_2CH_2}$.

All other reagents were employed as received.

## C.  Procedures

1.  <u>Preparation of bis(triphenylphosphine(imminium)pentacarbonylmercapto group 6A metal (O) complexes [(Ph$_3$P)$_2$N][M(CO)$_5$(SH)] (M = Cr, Mo, and W)</u>

To a 50 ml flask were successively added 0.151 g (2.7 mmole) of NaSH, 10 ml of EtOH, and 1.15 g (2.00 mmole) of [(Ph$_3$P)$_2$N]Cl. The mixture was stirred for 1.5 hours giving a white suspension (NaCl↓). Volatile components of the suspension were removed in vacuo. Next, 20 ml of THF and 2.1 mmole of M(CO)$_6$ where M = Cr, Mo, or W were added to the residue, and the flask was fitted with a reflux condenser, a drying tube that contained Drierite, and a gas displacement apparatus, XVIII. The mixture was refluxed until 45 ml of water had been displaced (1.8 mmole of CO) from the gas displacement apparatus (ca. 1 hour). Successively, filtering the yellow reaction mixture through a frit of medium porosity with suction and partitionally crystallizing the resultant filtrate gave the products. These compounds, [(Ph$_3$P)$_2$N][M(CO)$_5$(SH)], were identified by their spectra which are listed in Tables 4, 8, 12, 16, and 19.
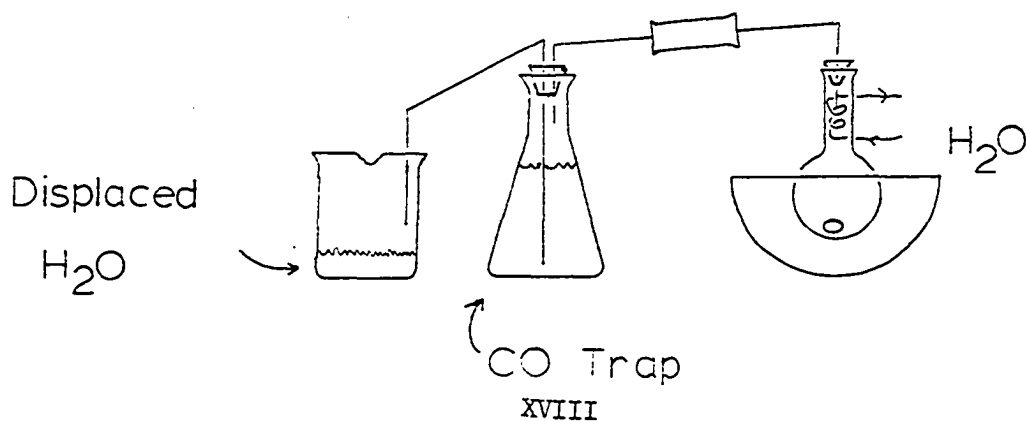
Displaced H₂O

CO Trap

XVIII

Melting points, conductivity measurements, elemental analyses, and percentage yields of the products – except $[(Ph_3P)_2N][(Mo(CO)_5(SH)]$ which could not be isolated in a solid form – are reported in Table 1.

2. **Preparation of tetraethylammonium μ-mercaptobis(pentacarbonyltungsten (0)) (NEt₄[μ-HS[W(CO)₅]₂])**

A white suspension of 0.179 g (3.19 mmole) of NaSH, 2.273 g (6.46 mmole) of $W(CO)_6$, 10 ml of diglyme, and 3 ml of THF in a 50 ml flask which was appended with a reflux condenser, a drying tube that contained Drierite, and a gas displacement apparatus, XVIII, was heated (ca. 120°C) until 150 ml of water had been displaced (6.12 mmole of CO) from the gas displacement apparatus (ca. 2 hours). Stirring the resultant brown mixture with 300 ml of an aqueous solution of NEt₄Br ($2.51 \times 10^{-2}$ M) (7.53 mmole) gave a yellow suspension. Successively, filtering the suspension and repeatedly recrystallizing the precipitate which was

dried under vacuum from hot $HCCl_3$ resulted in transparent yellow needles

of the product. Characteristics of this compound, $NEt_4[\mu-HS[W(CO)_5]_2]$,

are included in Tables 3, 7, 11, 15, 16, and 21.

3. Preparation of bis(triphenylphosphine)imminium pentacarbonyl(2,2-
diphenylthioacetato-S)wolframate (O) ([(Ph$_3$P)$_2$N][W(CO)$_5$(SC(=O)CPh$_2$H)])
and bis(triphenylphosphine)imminium pentacarbonyl(phenylthiocarbamato-
S)wolframate (O) ([(Ph$_3$P)$_2$N][W(CO)$_5$(SC(=O)NPhH)])

In a 25 ml flask a yellow solution that contained 0.448 g (0.500

mmole) of [(Ph$_3$P)$_2$N][W(CO)$_5$(SH)] and 20 ml of THF was treated with 5 ml

of a solution of $Ph_2C=C=O$ in n-heptane (0.10 M) (0.50 mmole) or 40 μl

(0.52 mmole) of $PhN=C=O$. The mixture was stirred for 2 hours and the

resultant yellow suspension was filtered with suction through a frit

which contained Celite. Partitional crystallization of the filtrate

gave tarry residues. Repeating the partitional crystallization on the

resultant metal carbonyl containing residues that were dissolved in

acetone with a diethylether and hexanes system yielded transparent

yellow needles of [(Ph$_3$P)$_2$N][W(CO)$_5$(SC(=O)CPh$_2$H)] or a yellow powder of

[(Ph$_3$P)$_2$N][W(CO)$_5$(SC(=O)NPhH)]. Physical properties and percentage

yields of these compounds are recorded in Tables 1, 4, 8, 12, and 19.

4. Preparation of tetraethylammonium pentacarbonyl(methylthiocarbamato-
S)wolframate (O) (NEt$_4$[W(CO)$_5$(SC(=O)NMeH)] and tetraethylammonium
tetracarbonyl(alkyldithiocarbamato-S,S)wolframate(O)
(NEt$_4$[W(CO)$_4$(S$_2$CNRH)]) (R = Me, Et, and Ph)

A suspension which was composed of 0.166 g (1.00 mmole) of $NEt_4Cl$,

0.084 g (1.5 mmole) of NaSH, and 10 ml of EtOH was stirred for 1 hour.

Volatile components of the resultant mixture were removed under a dynamic

vacuum. Next, 0.352 g (1.00 mmole) of $W(CO)_5$ and 10 ml of acetone were combined with the white powder in the 25 ml reaction flask, and the suspension was refluxed for 2 hours. The consequent yellow mixture of $NEt_4[W(CO)_5(SH)]$, etc. that had cooled to room temperature was treated with 80 μl (1.1 mmole) of MeN=C=O, 1.1 ml of a solution of MeN=C=S in acetone (0.95 M) (1.0 mmole), 87 μl (1.0 mmole) of EtN=C=S, or 0.12 ml (1.0 mmole) of PhN=C=S. This mixture was refluxed for 2 hours. Successively, filtering the resultant brown suspension through a frit containing Celite with suction and partitionally crystallizing the yellow filtrate resulted in yellow plates of $NEt_4[W(CO)_5(SC(=O)NMeH)]$, yellow needles of $NEt_4[W(CO)_4(S_2CNMeH)]$, or yellow oils of $NEt_4[W(CO)_4(S_2CNEtH)]$ and $NEt_4[W(CO)_4(S_2CNPhH)]$. These products were identified by their spectra which are reported in Tables 4, 5, 8, 9, 12, 13, 16, and 19. Melting points, conductivity measurements, elemental analyses, and percentage yields of $NEt_4[W(CO)_5(SC(=O)NMeH)]$ and $NEt_4[W(CO)_4(S_2CNMeH)]$ are listed in Table 1.

5. <u>Preparation of bis(triphenylphosphine)imminium tetracarbonyl-</u>
<u>(phenyldithiocarbamato-S,S)wolframate (O) ($[(Ph_3P)_2N][W(CO)_4(S_2CNPhH)]$)</u>
<u>and bis(triphenylphosphineimminium tetracarbonyl(N-phenyl, 2,2-diphenyl-</u>
<u>thioimidato-S,N)wolframate (O) ($[(Ph_3P)_2N][W(CO)_4(S(NPh)CCPh_2H)]$)</u>

To a 50 ml flask were consecutively added 0.448 g (0.500 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$, 15 ml of THF, and 62 μl (0.52 mmole) of PhN=C=S or 0.138 g (0.511 mmole) of PhN=C=CPh_2. The yellow combination was stirred for 18 hours at room temperature. Successively, filtering the resultant suspension through a frit that contained Celite with suction and

partitionally crystallizing the consequent yellow filtrate gave tarry

residues. Repeating the partitional crystallization on the resulting

oils containing metal carbonyl products that were dissolved in acetone

with a diethylether and hexanes system gave transparent yellow crystals

of $[(Ph_3P)_2N][W(CO)_4(S_2CNPhH)] \cdot 0.61Me_2C=0 \cdot 0.47Et_2O$ or another oil of

$[(Ph_3P)_2N][W(CO)_4(S(NPh)CCPh_2H)]$. Spectrophotometric properties of these

compounds are recorded in Tables 5, 9, 13, 16, and 19. In Table 1

are listed the elemental analyses, melting point, conductivity measure-

ment, and percentage yield of $[(Ph_3P)_2N][W(CO)_4(S_2CNPhH)]$.

6. Preparation of pentacarbonyl(2,2-diphenylthioacetanilide)tungsten
(0) $(W(CO)_5(S=C(NPhH)CPh_2H))$

To a 25 ml flask were successively added 0.185 g (0.207 mmole) of

$[(Ph_3P)_2N][W(CO)_5(SH)]$, 10 ml of THF, 0.0782 g (0.291 mmole) of PhN=C=

$CPh_2$, and 20 $\mu$l (0.23 mmole) of $HSO_3CF_3$. This mixture was stirred for

4.5 hours. Volatile components of the consequent dark red suspension

were removed under a dynamic vacuum. Liquid-solid column (35 cm x 10 mm)

chromatography of the 20% $CH_2Cl_2$/hexanes (V/V) soluble portion of the

resultant brown residue over Silica-gel (60-200 mesh) of Brockman

Activity Grade II (67) gave a yellow eluate which was concentrated to a

yellow powder. Washing the powder with 2.5 ml of hexanes which were cooled

to -78°C gave the product, yellow crystals of $W(CO)_5(S=C(NPhH)CPh_2H)$, in

26% yield. Characteristics of the product are included in Tables 2, 6,

10, 14, 18, and 20.

7. Preparation of pentacarbonyl(2-thio-1,3-diisopropylurea)tungsten (0)
   $(W(CO)_5(S=C(Ni-PrH)_2)$

A yellow mixture which was made up of 0.451 g (0.504 mmole) of

$[(Ph_3P)_2N][W(CO)_5(SH)]$, 10 ml of THF, and 1.2 ml of a solution of

i-PrN=C=Ni-Pr in THF (0.421 M) (0.505 mmole) was treated with 49 µl

(0.55 mmole) of $HSO_3CF_3$ in a 25 ml flask. The resultant brown mixture was

stirred for 18 hours. Volatile components of the reaction mixture were

removed under a dynamic vacuum, and the 50% $HCCl_3$/hexanes (V/V) soluble

portion of the residue was eluted over a column (35 cm x 15 mm) of Silica-

gel (60-200 mesh) of Brockman Activity Grade II (67). Collection of the

yellow eluate, concentration in vacuo, and washing the consequent yellow

solids twice with 5 ml of hexanes resulted in the product,

$W(CO)_5(S=C(Ni-PrH)_2)$. In Tables 2, 6, 10, 14, 18, and 20 are listed the

physical properties and percentage yield of the product.

8. Preparation of bis(triphenylphosphine)imminium pentacarbonyl(thio-
   acetato-S)wolframate (0) $([(Ph_3P)_2N][W(CO)_5(SC(=O)Me)]$

In apparatus similar to that employed for the $[(Ph_3P)_2N][M(CO)_5(SH)]$

preparation, equimolar amounts of $[(Ph_3P)_2N][SC(=O)Me]$ and $W(CO)_6$ were

refluxed in THF for 3 hours. Work up of the products was accomplished in

a manner analogous to that employed for $[(Ph_3P)_2N][M(CO)_5(SH)]$.

Characteristics of this compound, $[(Ph_3P)_2N][W(CO)_5(SC(=O)Me)]$, are

included in Tables 1, 4, 8, 12, 16, and 19.

9. **Preparation of tetraethylammonium pentacarbonyl(1,1,1,3,3-pentafluoro-propan-2-one-3mercaptido)wolframate (O)** ($NEt_4[W(CO)_5(SCF_2C(=O)CF_3)]$)

In a 50 ml flask a suspension of 0.245 g (1.50 mmole) of $NEt_4Cl$, 0.158 g (2.80 mmole) of NaSH, and 10 ml of EtOH was stirred for 2 hours. Volatile components of the reaction mixture were removed in vacuo. Adding 0.522 g (1.50 mmole) of $W(CO)_6$ and 20 ml of acetone to the resultant residue and refluxing this suspension for 2.5 hours yielded a brown mixture which was cooled to $-72°C$ in a i-PrOH/Dry Ice bath. Next, an excess of $(CF_3)_2C=O$ was condensed into the cold reaction flask for 10 minutes. The mixture was returned to room temperature in the cold bath (ca. 2 hours) and stirred for an additional 16 hours. Filtering the consequent brown suspension with suction through a frit that contained Celite and partitionally crystallizing the yellow filtrate gave yellow needles of the product, $NEt_4[W(CO)_5(SCF_2C(=O)CF_3)]$. Spectrophotometric properties of the product are listed in Tables 4, 8, 12, 17, and 19. In Table 1 are reported the melting point, conductivity measurement, elemental analysis, and percentage yield of the product.

10. **Preparation of pentacarbonylpara-alkylthiobenzaldehyde tungsten (O)** ($W(CO)_5(S=C(p-RC_6H_4)H)$) (R=$-NMe_2$, $-OMe$, and Me)

A yellow solution that contained 0.448 g (0.500 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$, 10 ml of THF, and 0.0760 g (0.510 mmole) of $O=C(p-NMe_2C_6H_4)H$, 64 µl (0.52 mmole) of $O=C(p-OMeC_6H_4)H$, or 59 µl (0.50 mmole) of $O=C(p-MeC_6H_4)H$ was treated with 44 µl (0.50 mmole) of $HSO_3CF_3$ in a 25 ml flask yielding a purple-black mixture immediately.

Volatile components of the mixture were removed under a dynamic vacuum.

Successively, elution of the 20% $CH_2Cl_2$/hexanes soluble portion of the

black residue over a column (30 cm x 20 mm) of Florisil (60-100 mesh),

collection of the deep purple eluate, and concentration of the eluate

under a stream of nitrogen gave lustrous yellow plates of

$W(CO)_5(S=C(p-NMe_2C_6H_4)H$, transparent purple needles of

$W(CO)_5(S=C(p-OMeC_6H_4)H$, or a purple powder of $W(CO)_5(S=C(p-MeC_6H_4)H$.

Characteristics of these products are recorded in Tables 2, 6, 10, 14,

and 20.


11.  Preparation of pentacarbonyl(cyanamide)tungsten (0) $(W(CO)_5(N\equiv CHN_2))$
and pentacarbonyl(thiourea)tungsten (0) $(W(CO)_5(S=C(NH_2)_2)$

A yellow combination of 0.581 g (1.00 mmole) of $NEt_4[W(CO)_5I]$ and

10 ml of acetone in a 25 ml flask was cooled in an ice bath (0°C) for 10

minutes.  Dropwise addition of a solution of 1 ml of $Ag[BF_4]$ in acetone

(1.0 M) (1.0 mmole) to the yellow solution resulted in an immediate

precipitation of yellow AgI.  The suspension was stirred for 1 hour in the

ice bath.  Next, 0.0420 g (1.00 mmole) of $N\equiv CNH_2$ or 0.152 g (2.00 mmole)

of $S=C(NH_2)_2$ were added to the yellow suspension, and it was stirred for an

additional 1.5 hours at room temperature.  Volatile components of the

reaction mixture were removed under a dynamic vacuum.  Consecutively,

elution of the $HCCl_3$ soluble portion of the residue over a column (30 cm x

15 mm) of Florisil (60-100 mesh), collection of the yellow eluate, and

slow concentration in vacuo gave yellow powders of the products,

$W(CO)_5(N\equiv CNH_2)$ and $W(CO)_5(S=C(NH_2)_2)$ in respectively 72% and 73% yields.

Physical properties of these compounds are included in Tables 2, 6, 10, 14, and 20.

12. Preparation of bis(triphenylphosphine)imminium pentacarbonyl-(2,3,3,4, 4,5,5,6,6-nonafluoro-1-ene-mercaptido)wolframate (0)

$[(Ph_3P)_2N][W(CO)_5(S\overline{C=CF(CF_2)_3CF_2})]$
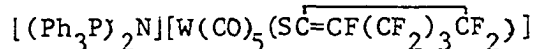
To a 25 ml flask were successively added 0.448 g (0.500 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$, 10 ml of THF, and 0.10 ml (0.50 mmole) of $\overline{CF=CF(CF_2)_3CF_2}$. The mixture was stirred for 3 hours. Partitional crystallization of the resultant black green reaction solution gave yellow crystals of the product, $[(Ph_3P)_2N][W(CO)_5(S\overline{C=CF(CF_2)_3CF_2})]$. In Tables 4, 8, 12, 17, and 19 are listed the spectrophotometric properties of the compound. The melting point, percentage yield, conductivity measurement, and elemental analyses of $[(Ph_3P)_2N][W(CO)_5(S\overline{C=CF(CF_2)_3CF_2})]$ are contained in Table 1.

13. Preparation of tetraethylammonium μ-thioacetatobis(pentacarbonyl-tungsten (0)) $(NEt_4[\mu-MeC(=O)S[W(CO)_5]_2])$, tetraethylammonium μ-trimethyltinmercaptidobis(pentacarbonyltungsten (0)) $(NEt_4[\mu-Me_3SnS[W(CO)_5]_2]$, tetraethylammonium μ-methylmercury-mercaptidobis(pentacarbonyltungsten (0)) $(NEt_4[\mu-MeHgS[W(CO)_5]_2]$, tetraethylammonium μ-benzylmercaptidobis(pentacarbonyltungsten (0))· $(NEt_4[\mu-PhCH_2S[W(CO)_5]_2])$, tetramethylammonium μ-phenylmercaptido-bis(pentacarbonyltungsten (0)) $(NEt_4[\mu-PhS[W(CO)_5]_2])$, and tetraethyl-ammonium μ-diphenylphosphinemercaptidobis(pentacarbonyltungsten (0)) $(NEt_4[\mu-Ph_2PS[W(CO)_5]_2])$

To a yellow solution that was composed of 0.406 g (0.500 mmole) of $NEt_4[\mu-HS[W(CO)_5]_2]$ and 10 ml of THF was added 0.0243 g (0.577 mmole) of NaH (57% oil dispersion). Immediately, the reaction mixture turned green

with the release of 12 ml of $H_2$ $(g)$ (0.49 mmole). Next, 41 μl (0.58

mmole) of MeC(=O)Cl, 0.115 g (0.577 mmole) of $Me_3SnCl$, 0.145 g (0.577

mmole) of MeHgCl, 66 μl (0.58 mmole) of $PhCH_2Cl$, 74 μl (0.58 mmole) of

$PhSO_2Cl$, or 0.10 ml (0.58 mmole) of $Ph_2PCl$ was added to the 25 ml

reaction flask; the consequent mixture was stirred for 2 hours.

Volatile components of the resultant brown mixture were removed under a

dynamic vacuum. The acetone soluble portion of this residue was washed

into 50 ml of an aqueous solution of $NEt_4Br$ (0.27 M) (13.5 mmole). The

mixture was stirred for 1 hour. Successively, filtering the resultant

yellow-brown suspension through a frit containing Celite with suction,

filtering the acetone soluble portion of these crude solids through the

frit that was employed above, and drying the acetone soluble filtrate

under a dynamic vacuum gave a yellow powder of the product. Repeated

recrystallization of the powder from hot $HCCl_3$ or mixtures of $HCCl_3$ and

hexanes resulted in transparent yellow needles of $NEt_4[\mu-MeC(=O)S[W(CO)_5]_2]$,

$NEt_4[\mu-Me_3SnS[W(CO)_5]_2]$, $NEt_4[\mu-MeHgS[W(CO)_5]_2]$, $NEt_4[\mu-PhCH_2S[W(CO)_5]_2]$,

$NEt_4[\mu-PhS[W(CO)_5]_2]$, or $NEt_4[\mu-Ph_2PS[W(CO)_5]_2]$. Characteristics of

these compounds are reported in Tables 3, 7, 11, 15, and 21.

## 14. Preparation of bis(triphenylphosphine)imminium μ-thioacetatobis-(pentacarbonyltungsten (0)) ($[(Ph_3P)_2N][\mu-MeC(=O)S[W(CO)_5]_2]$)
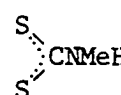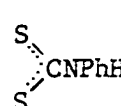
A yellow solution of 0.581 g (0.500 mmole) of $NEt_4[W(CO)_5I]$ and

10 ml of acetone in a 25 ml flask was cooled in an ice bath (0°C) for

10 minutes. Dropwise addition of 0.5 ml of a solution of $Ag[BF_4]$ in

acetone (1.0 M) (0.50 mmole) to the yellow mixture gave an immediate

precipitation of yellow AgI. The yellow suspension was stirred for

0.5 hour in the ice bath. Next, 0.469 g (0.500 mmole) of

$[(Ph_3P)_2N][W(CO)_5(SC(=O)Me)]$ was added to the reaction flask, and the

mixture was stirred for 1 hour. Consecutively diluting the resultant

suspension with 60 ml of diethyl ether, filtering the resulting suspension

through a frit of medium porosity with suction, diluting the yellow

filtrate with hexanes, and cooling the resultant mixture to -40°C gave

transparent yellow plates of the product, $[(Ph_3P)_2N][\mu-MeC(=O)S[W(CO)_5]_2]$,

in 78% yield. In Tables 3, 7, 11, 15, 16, and 21 are listed the physical

properties of the compound.

15. Preparation of tetraethylammonium μ-(methylthiocarbamato-S)bis(penta-
carbonyltungsten (0)) ($NEt_4[\mu-HMeNC(=O)S[W(CO)_5]_2]$)

This compound was prepared and isolated in a manner similar to that

employed for $NEt_4[\mu-Me_3SnS[W(CO)_5]_2]$ with the following modifications.

After the green mixture was treated with 43 μl (0.58 mmole) of MeN=C=O

which was substituted for $Me_3SnCl$, the mixture was stirred for 3 hours.

To the resultant brown-black suspension was added 12.3 ml (0.502 mmole)

of $HCl_{(g)}$ giving a brown-yellow mixture. The product,

$NEt_4[\mu-HMeNC(=O)S[W(CO)_5]_2]$, was identified by its elemental analysis and

spectra which are reported in Tables 3, 7, 11, 15, and 21.

Table 1. Physical[a] and analytical data for the $[(Ph_3P)_2N][LM(CO)_5]$ and $[(Ph_3P)_2N][LW(CO)_4]$ complexes

| L | M | $\Lambda$[b] | M.p. (°C) | Yield % | Analyses[c] %C | %H | %S |
|---|---|---|---|---|---|---|---|
| [SH] | W | 114 | 116–9 | 93 | 54.50(54.99) | 3.87(3.49) | 3.47(3.58) |
| [SH] | Cr | 119 | 133–6 | 73 | 64.29(64.48) | 4.30(4.09) | |
| [SC(=O)Me] | W | 126 | 145–9 | 82 | 54.90(55.09) | 3.66(3.55) | |
| [SC(=O)CPh_2H] | W | 105 | 116–9 | 66 | 60.84(60.62) | 4.02(3.79) | |
| [SC(=O)NMeH][d] | W | 155 | 105–8 | 17 | 32.89(33.10) | 4.17(4.44) | 6.12(5.89) |
| [SC(=O)NPhH] | W | 125 | 99–101 | 28 | not determined | | |
| [SCF_2C(=O)CF_3][d] | W | 151 | 96–8 | 8 | 30.92(30.35) | 3.38(3.18) | |
| [SC̅=̅C̅F̅(̅C̅F̅_2̅)̅_3̅C̅F̅_2] | W | 121 | 98–100 | 46 | 50.06(49.62) | 2.64(2.66) | |
| $\overset{S}{\underset{S}{\diagdown}}$ CNMeH[d] | W | | 99–101[e] | 78 | 30.28(31.59) | 4.49(4.55) | |
| $\overset{S}{\underset{S}{\diagdown}}$ CNPhH[f,g] | W | 126 | 80–2 | 26 | 55.29(56.76) | 4.21(4.17) | 6.03(5.98) |

[a]Color: yellow.

[b]Conductivity measurement ($\sim 10^{-4}$ M in MeCN) units $= cm^2 ohm^{-1} M^{-1}$.

[c]Found (calculated).

[d]$[NEt_4]^+$ (counter cation).

[e]Decomposed.

[f]Contained 0.61 $Me_2C=O$ and 0.47 $Et_2O$ (determined from relative integrated intensities by ^{1}H NMR).

[g]Nitrogen analysis: 2.60(2.61).

Table 2. Physical and analytical data for the $[LW(CO)_5]$ complexes

| L | Color[a] | M.p. (°C) | Yield % | Analyses[b] %C | %H | %N |
|---|---|---|---|---|---|---|
| S=C(p-NMe$_2$C$_6$H$_4$)H | P | 144–6[c] | 52 | 34.62(34.37) | 2.36(2.26) | 2.76(2.86) |
| S=C(p-OMeC$_6$H$_4$)H | P | 108–10[c] | 32 | 32.94(32.80) | 1.69(1.76) | |
| S=C(p-MeC$_6$H$_4$)H | P | 72–4[c] | 50 | not determined | | |
| S=C(NPhH)CPh$_2$H | Y | 42–4 | 26 | 48.07(47.87) | 2.76(2.73) | |
| S=C(NH$_2$)$_2$ | Y | 136–9[c] | 73 | 18.20(18.02) | 1.07(1.01) | |
| S=C(Ni-PrH)$_2$ | Y | 131–4 | 60 | 29.87(29.77) | 3.36(3.33) | |
| N≡CNH$_2$ | Y | 105–7 | 72 | 19.85(19.69) | 0.57(0.55) | |

[a]Abbreviations used: P(purple), Y(yellow).

[b]Found (calculated).

[c]Decomposed.

Table 3. Physical[a] and analytical data for the $NEt_4[\mu-RS[W(CO)_5]_2]$ complexes

| R | $\wedge$[b] | M.p. (°C) | Yield % | Analyses[c] %C | %H | %S |
|---|---|---|---|---|---|---|
| H- | 142 | 110-3[d] | 84 | 26.48(26.55) | 2.64(2.61) | 4.40(3.95) |
| MeC(=O)- | 154 | 94-6 | 45 | not determined | | |
| MeC(=O)-[e] | 142 | 130-3 | 78 | 45.02(45.73) | 2.78(2.64) | 2.73(2.54) |
| $Me_3Sn-$ | 88[f] | 103-5[d] | 51 | 25.84(25.90) | 3.01(3.00) | |
| HMeNC(=O)- | 158 | 120-2[d] | 38 | 27.69(27.67) | 2.87(2.79) | |
| $Ph_2P-$ | 135 | 130-2 | 37 | 36.07(36.20) | 3.07(3.04) | |
| MeHg- | 97[f] | 101-3 | 57 | 22.34(22.25) | 2.31(2.26) | |
| $PhCH_2-$ | 139 | 96-8 | 34 | 32.85(33.32) | 2.61(3.02) | |
| Ph- | 147 | 110-2[d] | 7 | 32.53(32.50) | 2.82(2.84) | |

[a]Color: yellow.

[b]Conductivity measurement ($\sim 10^{-4}$ M in MeCN) units = $cm^2 ohm^{-1} M^{-1}$.

[c]Found (calculated).

[d]Decomposed.

[e]$[(Ph_3P)_2N]^+$ (counter cation).

[f]In $MeNO_2$.
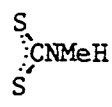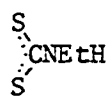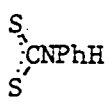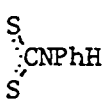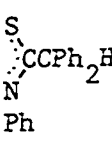
Table 4. CO stretching frequencies ($cm^{-1}$) for the $[(Ph_3P)_2N][LM(CO)_5]$ complexes

| L | M | Solvent | cm$^{-1a}$ | | | |
|---|---|---|---|---|---|---|
| | | | $A_1$ | $B_1$ | E | $A_1$ |
| [SH] | W | $CH_2Cl_2$ | 2056 | – | 1912 | 1843 |
| [SH] | W | THF | 2049 | – | 1911 | 1847 |
| [SH] | Mo | THF | 2037 | 1967 | 1913 | 1846 |
| [SH] | Cr | $CH_2Cl_2$ | 2044 | – | 1914 | 1849 |
| [SC(=O)Me] | W | $CH_2Cl_2$ | 2060 | 1968 | 1917 | 1854 |
| [SC(=O)CPh$_2$H] | W | $CH_2Cl_2$ | 2060 | 1968 | 1916 | 1853 |
| [SC(=O)NMeH] | W | $CH_2Cl_2$ | 2061 | 1966 | 1915 | 1850 |
| [SC(=O)NMeH][b] | W | $CH_2Cl_2$ | 2062 | 1968 | 1916 | 1858 |
| [SC(=O)NPhH] | W | $CH_2Cl_2$ | 2061 | 1968 | 1917 | 1856 |
| [SCF$_2$C(=O)CF$_3$][b] | W | $CH_2Cl_2$ | 2063 | – | 1924 | 1865 |
| [SC=CF(CF$_2$)$_3$CF$_2$] | W | $CH_2Cl_2$ | 2066 | 1971 | 1925 | 1862 |

[a]Relative band intensities (respectively): $A_1$ weak, $B_1$ shoulder, E very strong, and $A_1$ moderate.

[b][NEt$_4$]$^+$ (counter cation).

Table 5. CO stretching frequencies (cm$^{-1}$) for the $[LW(CO)_4]^-$ complexes in $CH_2Cl_2$

| L | cation | cm$^{-1}$ [a] | | | |
|---|---|---|---|---|---|
| | | $A_1$ | $B_1$ | $A_1$ | $B_1$ |
| S<br>$\overset{\cdot\cdot}{\underset{\cdot\cdot}{\vdots}}$CNMeH<br>S | NEt$_4$ | 2000 | 1874 | 1841 | 1796 |
| S<br>$\vdots$CNEtH<br>S | NEt$_4$ | 1999 | 1873 | 1841 | 1795 |
| S<br>$\vdots$CNPhH<br>S | NEt$_4$ | 1999 | 1876 | 1843 | 1800 |
| S<br>$\vdots$CNPhH<br>S | (Ph$_3$P)$_2$N | 2000 | 1874 | 1848 | 1804 |
| S<br>$\vdots$CCPh$_2$H<br>N<br>Ph | (Ph$_3$P)$_2$N | 1995 | 1868 | 1843 | 1801 |

[a]Relative band intensities (respectively): $A_1$ moderate, $B_1$ very strong, $A_1$ strong, and $B_2$ strong.

Table 6. CO stretching frequencies ($cm^{-1}$) for the [LW(CO)$_5$] complexes

| L | Solvent | $cm^{-1}$[a] | | | |
| | | $A_1$ | $B_1$ | E | $A_1$ |
|---|---|---|---|---|---|
| S=CMe$_2$ | hexanes | 2075(m) | 1987(w) | 1953(vs) | 1943(sh) |
| S=C(p-NMe$_2$C$_6$H$_4$)H | hexanes | 2068(m) | – | 1947(vs), 1938(vs) | 1925(s) |
| S=C(p-OMeC$_6$H$_4$)H | hexanes | 2070(m) | – | 1956(vs), 1946(vs) | 1937(s) |
| S=C(p-MeC$_6$H$_4$)H | hexanes | 2071(m) | – | 1957(s), 1948(vs) | 1940(vs) |
| S=C(NPhH)CPh$_2$H | hexanes | 2073(m) | 1988(w) | 1945(vs), 1934(s) | 1923(m) |
| S=C(NH$_2$)$_2$ | CH$_2$Cl$_2$ | 2072(w) | 1980(w) | 1933(vs) | 1901(sh) |
| S=C(Ni-PrH)$_2$ | CH$_2$Cl$_2$ | 2071(w) | 1979(w) | 1930(vs) | 1895(sh) |
| N≡CNH$_2$ | CH$_2$Cl$_2$ | 2077(w) | 1975(w) | 1935(vs) | 1894(m) |

[a]Abbreviation for relative band intensities: w (weak), m (moderate), s (strong), vs (very strong), and sh (shoulder).

Table 7. CO stretching frequencies ($cm^{-1}$) for the $NEt_4[\mu\text{-}RS[W(CO)_5]_2]$ complexes in $CH_2Cl_2$

| R | cation | $cm^{-1}$[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| H– | $NEt_4$ | 2068 | 2056 | 1969 | 1933 | 1908 | 1859 |
| H–[b] | $NEt_4$ | 2068 | 2056 | – | 1933 | 1906 | 1871 |
| MeC(=O)– | $NEt_4$ | 2072 | 2062 | 1972 | 1938 | 1912 | 1869 |
| MeC(=O)– | $(Ph_3P)_2N$ | 2073 | 2064 | 1976 | 1941 | 1914 | 1872 |
| HMeNC(=O)– | $NEt_4$ | 2072 | 2060 | 1974 | 1936 | 1909 | 1866 |
| $Me_3Sn$– | $NEt_4$ | 2067 | 2055 | 1967 | 1931 | 1897 | 1856 |
| MeHg– | $NEt_4$ | 2065 | 2052 | 1970 | 1929 | 1902 | 1856 |
| $Ph_2P$– | $NEt_4$ | 2067 | 2057 | 1976 | 1930 | 1910 | 1860 |
| $PhCH_2$– | $NEt_4$ | 2067 | 2055 | 1966 | 1932 | 1901 | 1860 |
| Ph– | $NEt_4$ | 2068 | 2057 | 1970 | 1935 | 1908 | 1861 |

[a] Relative band intensities (respectively): 1 shoulder, 2 weak, 3 shoulder, 4 very strong, 5 shoulder, and 6 moderate.

[b] In THF.

Table 8. Infrared bands $(cm^{-1})$ in addition to CO stretching frequencies for the $[(Ph_3P)_2N][LM(CO)_5]^a$ complexes in pressed disks of KBr

| L | M | $cm^{-1}$ [b] |
|---|---|---|
| [SH] | W | 599(w), 590(sh), 490(w), 446(vw) |
| [SH] | Cr | 660(w), 489(w), 458(sh), 450(vw) |
| [SC(=O)Me] | W | 1604(w)[c], 969(vw), 946(vw), 806(vw), 658(vw), 601(w), 590(w), 471(vw), 450(vw), 440(vw) |
| [SC(=O)CPh$_2$H] | W | 1605(w)[c], 1490(w), 1450(w), 997(w), 980(w), 910(vw), 841(vw), 627(vw), 618(vw), 597(w), 580(w), 442(vw,br) |
| [SC(=O)NMeH][d] | W | 3440(w)[e], 1590(w)[c], 1192(w), 1008(w), 816(w), 603(sh), 596(w), 554(vw), 433(vw) |
| [SC(=O)NPhH] | W | 3240(br,vw)[e], 1620(w)[c], 1595(w), 1510(w), 1495(w), 969(vw), 896(vw), 815(w), 619(vw), 598(w), 590(w), 447(vw) |
| [SCF$_2$C(=O)CF$_3$][d] | W | 1680(w)[c], 1350(w), 1256(w), 1226(sh), 1223(w), 1200(sh), 1190(w), 1103(w), 1075(vw), 868(vw), 724(vw), 700(vw), 675(vw), 604(vw), 591(sh), 584(w), 553(vw), 478(vw) |
| [SC=CF(CF$_2$)$_3$CF$_2$][f] | W | 1230(w), 1200(w), 1190(sh), 1160(w), 1099(w), 1025(w), 958(w), 845(w), 590(w), 375(vw) |

[a] Omitted bands of $[(Ph_3P)_2N]Cl$.

[b] Abbreviations for relative band intensities: w (weak), vw (very weak), sh (shoulder) and br (broad).

[c] $\nu(C=O)$.

[d] $[NEt_4]^+$ (counter cation), omitted bands of $[NEt_4]Br$.

[e] $\nu(N-H)$.

[f] An IR spectrum of a concentrated solution of this compound in $CH_2Cl_2$ has a band at 1639 (vw) $(\nu C=C)$.

Table 9. Infrared bands ($cm^{-1}$) in addition to CO stretching frequencies
for the $[(Ph_3P)_2N][LM(CO)_4]$[a] complexes in pressed disks of KBr

| L | $cm^{-1}$[b] |
|---|---|
| S<br>⫶CNMeH[c]<br>S | 3350(w)[d], 3200(sh)[d], 3180(w)[d], 1500(vw,br)[e], 1335(w), 1015(vw), 958(w), 951(sh), 622(w), 588(w), 569(w), 465(vw) |
| S<br>⫶CNPhH<br>S | 3190(vw,br)[d], 1525(vw)[e], 1495(vw), 1325(w), 970(vw), 619(sh), 616(vw), 598(vw), 580(vw), 568(vw) |
| S<br>⫶CCPh₂H<br>N<br>Ph | 1585(vw), 1515(sh), 1500(w)[e], 630(vw), 620(vw), 590(vw), 382(vw) |

[a] Omitted bands of $[(Ph_3P)_2N]Cl$.

[b] Abbreviations of relative band intensities: w (weak), vw (very weak), sh (shoulder), and br (broad).

[c] $[NEt_4]^+$ (counter cation), omitted bands of $[NEt_4]Br$.

[d] $\nu$ (N-H).

[e] $\nu$ (C-N).

Table 10.  Infrared bands (cm$^{-1}$) in addition to CO stretching frequencies
for the [LW(CO)$_5$] complexes in pressed disks of KBr

| L | cm$^{-1}$[a] |
|---|---|
| S=C(p-NMe$_2$C$_6$H$_4$)H | 2915(vw), 1616(w), 1598(w), 1480(vw), 1383(w), 1343(w), 1321(w)[b], 1226(vw), 1170(w), 988(vw), 967(w), 935(w), 884(vw), 803(w), 707(vw), 591(w), 573(w), 535(vw), 502(vw), 413(vw), 368(w) |
| S=C(p-OMeC$_6$H$_4$)H | 2923(vw), 2855(vw), 1596(w), 1565(vw), 1512(vw), 1464(vw), 1441(vw), 1373(vw), 1318(vw), 1305(vw), 1269(w)[b], 1219(vw), 1189(vw), 1171(w), 1119(vw), 1023(vw), 1006(vw), 996(vw), 933(vw), 879(vw), 839(vw), 812(vw), 745(vw), 631(vw), 592(vw), 573(vw), 520(vw), 444(vw), 374(vw) |
| S=C(p-MeC$_6$H$_4$)H | 2940(vw), 2910(vw), 2840(vw), 1595(w), 1355(vw), 1305(vw), 1290(vw), 1210(vw), 1175(w), 1120(vw), 1003(vw), 925(vw), 870(w), 808(w), 740(vw), 700(vw), 585(w), 567(w), 489(w), 364(w) |
| S=C(NPhH)CPh$_2$H | 3275(vw)[c], 3215(vw)[c], 3040(vw), 2990(vw), 2925(vw), 1502(w), 1495(sh), 1457(vw), 1400(vw), 1148(vw), 1113(vw), 1095(vw), 1070(vw), 1023(vw), 998(vw), 843(vw), 764(w), 748(sh), 733(vw), 700(w), 635(vw), 603(w), 586(w), 566(vw) |

[a]Abbreviations for relative band intensities: w (weak), vw (very weak), sh (shoulder), and br (broad).

[b]$\nu$ (C=S).

[c]$\nu$ (N-H).

Table 10 (Continued)

| L | cm$^{-1}$ [a] |
|---|---|
| S=C(NH$_2$)$_2$ | 3470[c], 3450(sh)[c], 3365(w)[c], 3340(w)[c], 3200(vw)[c], 1620(w), 1610(w), 1475(w), 1430(w), 1390(w), 715(vw), 601(w), 593(sh), 584(w), 556(w,br), 528(w,br), 481(w), 441(w,br) |
| S=C(Ni-PrH)$_2$ | 3345(w)[c], 3330(w)[c], 2950(vw), 1555(sh), 1550(w), 1495(w), 1455(vw), 1440(sh), 1410(vw), 1380(vw), 1360(vw), 1340(vw), 1240(w), 1155(w), 1117(w), 968(vw), 945(vw), 875(vw), 846(vw), 749(w), 645(w), 603(w), 595(w), 592(w), 553(vw), 449(vw,br) |
| N≡CNH$_2$ | 3430(sh)[c], 3400(w)[c], 3290(w)[c], 3190(sh)[c], 2315(sh)[d], 2270(w)[d], 1620(w), 1580(w), 1490(w), 1440(w), 1410(w), 1152(vw,br), 583(w,br), 552(vw) |

[d] $\nu$ (C≡N).

Table 11. Infrared bands (cm$^{-1}$) in addition to CO stretching frequencies for NEt$_4$[$\mu$-RS[W(CO)$_5$]$_2$][a] complexes in pressed disks of KBr

| R | cm$^{-1}$ [b] |
|---|---|
| H- | 590(w), 545(vw), 371(w) |
| MeC(=O)- | 1643(w)[c], 1147(vw), 1112(vw), 943(vw), 649(vw), 637(vw), 585(w), 545(vw), 425(vw), 370(w) |
| MeC(=O)[d]- | 1640(w)[c], 936(vw), 853(vw), 638(vw), 602(w), 592(w) |
| Me$_3$Sn- | 1179(vw), 591(w), 578(w), 544(vw), 524(vw), 515(vw), 408(vw), 369(w) |
| MeHg- | 585(w), 543(vw), 365(w) |
| Ph$_2$P- | 3005(vw), 2995(vw), 1307(vw), 1158(vw), 848(vw), 745(w), 698(w), 598(w), 585(w), 551(w), 512(w), 457(vw), 421(vw), 405(vw), 378(w) |
| HMeNC(=O)- | 3342(w)[e], 1664(w)[c], 1212(w), 810(vw), 710(vw), 590(w), 555(vw), 433(vw), 375(w) |
| PhCH$_2$- | 1598(vw), 1580(vw), 1231(vw), 912(vw), 842(vw), 761(vw), 697(w), 595(sh), 583(w), 550(vw), 468(vw), 382(w), 369(w) |
| Ph- | 1576(vw), 1063(vw), 1019(vw), 750(vw), 692(vw), 587(w), 545(vw), 486(vw), 368(w) |

[a] Omitted bands of [NEt$_4$]Br.

[b] Abbreviations for relative band intensities: w (weak) and vw (very weak).

[c] $\nu$(C=O).

[d] [(Ph$_3$P)$_2$N]$^+$ (counter cation), omitted bands of [(Ph$_3$P)$_2$N]Cl.

[e] $\nu$ (N-H).

Table 12. $^1$H chemical shifts for the $[(Ph_3P)_2N][M(CO)_5L]$ complexes

| L | M | Solvent | $\tau^{a,b}$ |
|---|---|---------|----------|
| [SH] | W | DCCl$_3$ | 2.50(m)(30)[PPN]$^{+c}$, 12.93(s)(1) S$\underline{H}$ |
| [SH] | Mo | DCCl$_3$ | 2.50(m)(-)[PPN]$^+$, 13.38(s)(-) S$\underline{H}$ |
| [SH] | Cr | $(CD_3)_2C=O^d$ | 2.35(m)(30)[PPN]$^+$, 14.67(s)(1) S$\underline{H}$ |
| [SC(=O)Me] | W | DCCl$_3$ | 2.50(m)(10)[PPN]$^+$, 7.55(s)(1) C$\underline{H}_3$ |
| [SC(=O)CPh$_2$H] | W | DCCl$_3$ | 2.64(m)(40)[PPN]$^+$ and Ph's $\underline{H}$, 4.24(s)(1) C$\underline{H}$ |
| [SC(=O)NMeH]$^e$ | W | CD$_3$CN$^d$ | 6.85(q)(8) [N(C$\underline{H}_2$CH$_3$)$_4$]$^+$, 7.41(s)(3) C$\underline{H}_3$, 8.77(t)(12)[N(CH$_2$C$\underline{H}_3$)$_4$]$^+$ |
| [SCF$_2$C(=O)CF$_3$]$^e$ | W | CD$_3$CN$^d$ | 6.81(q)(8) [N(C$\underline{H}_2$CH$_3$)$_4$]$^+$, 8.81(t)(12) [N(CH$_2$C$\underline{H}_3$)$_4$] |
| [S$\overline{C=CF(CF_2)_3C}$F$_2$] | W | DCCl$_3$ | 2.50(m)(-) [PPN]$^+$ |

$^a$Chemical shifts (splittings)(relative intensities) assignment.

$^b$Abbreviations for splitting: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

$^c$[PPN]$^+$ = [(Ph$_3$P)$_2$N]$^+$.

$^d$Contained H$_2$O impurity.

$^e$[NEt$_4$]$^+$ (counter cation).

Table 13. $^1$H chemical shifts for the $[(Ph_3P)_2N][LW(CO)_4]$ complexes

| L | Solvent | $\tau$[a,b] |
|---|---|---|
| S⟍⟋;CNMeH[c] S⟋ | $CD_3CN$[d] | 6.85(q) $[N(C\underline{H}_2CH_3)_4]^+$ and 7.14(s) $C\underline{H}_3$ combined relative relative integrated intensities (11), 8.80 (t)(12) $[N(CH_2C\underline{H}_3)_4]^+$ |
| S⟍⟋;CNPhH[e] S⟋ | $DCCl_3$ | 2.02(m)(-) $N\underline{H}$, 2.58(m)(-) $[PPN]^+$[f] and Ph's $\underline{H}$ |
| S⟍⟋;CCPh_2H N⟋ Ph | $DCCl_3$ | 2.60(m)(-) $[PPN]^+$[f] and Ph's $\underline{H}$, 4.83(s)(-) $C\underline{H}$ |

[a]Chemical shifts (splittings) (relative intensities) assignment.

[b]Abbreviations for splitting: s(singlet), t(triplet), q(quartet), and m(multiplet).

[c]$[NEt_4]^+$ (counter cation).

[d]Contained $H_2O$ impurity.

[e]Contained 0.47 $Et_2O$ (6.50(q)(2) and 8.78(t)(3)) and 0.61 $Me_2C=O$ (7.82(s)).

[f]$[PPN]^+ = [(Ph_3P)_2N]^+$.

Table 14. $^1H$ chemical shifts for the $[LW(CO)_5]$ complexes

| L | Solvent | $\tau^{a,b}$ |
|---|---------|------|
| $S=C(p-NMe_2C_6H_4)H$ | $DCCl_3$ | -0.58(s)(1) $\underline{C}H$, 2.80(d of d)(4) Ph's $\underline{H}$, 6.82(s)(6) $N(C\underline{H}_3)_2$ |
| $S=C(p-OMeC_6H_4)H$ | $DCCl_3$ | -1.10(s)(1) $C\underline{H}$, 2.60(d of d)(4) Ph's $\underline{H}$, 6.07(s)(3) $OC\underline{H}_3$ |
| $S=C(p-Me(C_6H_4)H$ | $DCCl_3$ | -1.11(s)(1) $C\underline{H}$, 2.52(d of d)(4) Ph's $\underline{H}$, 7.65(s)(3) $C\underline{H}_3$ |
| $S=C(NPhH)CPh_2H$ | $DCCl_3$ | 2.82(m)(16) Ph's $\underline{H}$ and $N\underline{H}$, 4.49(s)(1) $C\underline{H}$ |
| $S=C(NH_2)_2$ | $(CD_3)_2C=O^c$ | 2.55(m)(-) $N\underline{H}_2$ |
| $S=C(Ni-PrH)_2$ | $DCCl_3$ | 4.22(m)(-) $N\underline{H}$, 5.98(m)(1) $C\underline{H}$, 8.67(d)(6) $C\underline{H}_3$ |
| $N\equiv CNH_2$ | $CD_3CN^c$ | 4.62(m)(-) $N\underline{H}_2$ |

[a] Chemical shifts (splittings) (relative intensities) assignment.

[b] Abbreviations for splitting: s(singlet), d(doublet, and m(multiplet).

[c] Contained $H_2O$ impurity.

Table 15. $^1$H chemical shifts for the $NEt_4[\mu\text{-RS}[W(CO)_5]_2]$ complexes

| R | Solvent | $\tau^{a,b}$ |
|---|---------|--------------|
| H– | $DCCl_3$ | 6.72(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 8.58(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$, 11.70(s)(1) $S\underline{H}$ |
| MeC(=O)– | $DCCl_3$ | 6.77(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 7.40(s)(3) $C\underline{H}_3$, 8.62(t) $[N(CH_2C\underline{H}_3)_4]^+$ |
| MeC(=O)–$^c$ | $DCCl_3$ | 2.50(m)(10) $[PPN]^+$, 7.39(s)(1) $C\underline{H}_3$ |
| $Me_3Sn$– | $DCCl_3$ | 6.74(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 8.60(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$, 9.51(s)(9) $C\underline{H}_3$ |
| MeHg– | $(CD_3)_2C=O^d$ | 6.45(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 8.58(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$, 9.23(s)(3) $C\underline{H}_3$ |
| $Ph_2P$– | $(CD_3)_2C=O^d$ | 2.38(m)(10) Ph's $\underline{H}$, 6.50(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 8.58(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$ |
| HMeNC(=O)– | $(CD_3)_2C=O^d$ | 3.45(br)(–) $N\underline{H}$, 6.48(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 7.25$^{d,e}$(e) $C\underline{H}_3$, 8.58(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$ |
| $PhCH_2$– | $(CD_3)_2C=O^d$ | 2.70(m)(5) Ph's $\underline{H}$, 5.96(s)(2) $PhC\underline{H}_2$–, 6.48(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 8.58(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$ |
| Ph– | $(CD_3)_2C=O^d$ | 2.67(m)(5) Ph's $\underline{H}$, 6.50(q)(8) $[N(C\underline{H}_2CH_3)_4]^+$, 8.58(t)(12) $[N(CH_2C\underline{H}_3)_4]^+$ |

$^a$Chemical shifts (splittings) (relative intensities) assignments.

$^b$Abbreviations for splitting: s(singlet), d(doublet), t(triplet), q(quartet), m(multiplet), br(broad).

$^c[(Ph_3P)_2N]$ (counter cation).

$^d$Contained $H_2O$ impurity.

$^eJ_{\underline{H}_3CN\underline{H}} = 5$ Hz.

Table 16. $^{13}$C chemical shifts for the $[(Ph_3P)_2N][LM(CO)_5]$, $[(Ph_3P)_2N][(CO)_4W(S_2CNPhH)]$, and $NEt_4[\mu-RS[W(CO)_5]_2]$ complexes in DCCl$_3$

| Compound | $\delta^{a,b}$ |
|---|---|
| PPN[W(CO)$_5$(SH)] | -203.4(s)trans$\underline{C}$O, -199.8(s)cis$\underline{C}$O, -130.5(m)[PPN]$^+$ |
| PPN[Cr(CO)$_5$(SH)]$^c$ | -224.3(s)trans$\underline{C}$O, -219.4(s)cis$\underline{C}$O, -127.5(m)[PPN]$^+$ |
| PPN[W(CO)$_5$(SC(=O)Me)] | -206.2(s)S$\underline{C}$(=O), -204.9(s)trans$\underline{C}$O, -199.5(s) cis$\underline{C}$O, -126.7(m)[PPN]$^+$, -34.4(s)$\underline{C}$H$_3$ |
| NEt$_4$[W(CO)$_5$SC(=O)NMeH]$^d$ | -204.1(s)trans$\underline{C}$O, -199.6(s)cis$\underline{C}$O, -199.2(s) S$\underline{C}$(=O), -51.8(s)[N($\underline{C}$H$_2$CH$_3$)$_4$]$^+$, -25.8(s)$\underline{C}$H$_3$, -6.5(s) [N(CH$_2$$\underline{C}$H$_3$)$_4$]$^+$ |
| PPN[(CO)$_4$W(S₂CNPhH)] with S̈CNPhH | -199.9(s)S$_2$$\underline{C}$N, -197.7(s)$\underline{C}$O$^e$, -188.8(s)$\underline{C}$O$^e$, -131.4 through -116.0(m)[PPN]$^+$ and Ph's $\underline{C}$ |
| NEt$_4$[$\mu$-HS[W(CO)$_5$]$_2$]$^d$ | -201.2(s)trans$\underline{C}$O, -199.3(s)cis$\underline{C}$O, -51.8(s) [N($\underline{C}$H$_2$CH$_3$)$_4$]$^+$, -6.4(s)[N(CH$_2$$\underline{C}$H$_3$)$_4$]$^+$ |
| PPN[$\mu$-MeC(=O)S[W(CO)$_5$]$_2$] | -203.3(s)S$\underline{C}$(=O), -203.1(s)trans$\underline{C}$O, -199.1(s) cis$\underline{C}$O$^f$, -130.5(m)[PPN]$^+$, -30.8(s)$\underline{C}$H$_3$ |

$^a$Chemical shifts (splittings) assignment.

$^b$Abbreviations for splitting: s(singlet) and m(multiplet).

$^c$In (CD$_3$)C=O.

$^d$In CD$_3$CN.

$^e$Not assigned.

$^f$J$_{183_W-^{13}C}$ = 128.0 Hz.

Table 17. $^{19}$F chemical shifts for the $[LW(CO)_5]^-$ complexes in solutions of $DCCl_3$

| L | $\delta^{a,b}$ |
|---|---|
| $[SCF_2C(=O)CF_3]^{c,d}$ | 68.5(s)(3)C$\underline{F}_3$, 78.5(s)(2)C$\underline{F}_2$ |
| $[S\overline{C=CF(CF_2)_3C}F_2]^e$ | 109.4(m)(2)3C$\underline{F}_2$, 117.4(m)(2)6C$\underline{F}_2$, 126.1(m)(1) 2C$\underline{F}$, 134.8(m)(2)5C$\underline{F}_2$, 135.6(m)(2)4C$\underline{F}_2$ |

$^a$Referenced to $CCl_3F$ ($\delta=0$).

$^b$Chemical shifts (splittings) (relative intensities) assignment.

$^c[NEt_4]^+$ (counter cation).

$^d$Contained trace impurity (83.4(s)).

$^e[(Ph_3P)_2N]^+$ (counter cation).

Table 18. Mass spectra of the $LW(CO)_5$ complexes

| L | $m/e^{-a}$ |
|---|---|
| $S=C(NPhH)CPh_2H^{b,c}$ | $629-625(-)W(CO)_5(S=C(NPhH)CPh_2H)^+(A)$, $545-541(-)$ $A-C_3O_3$, $489-485(-)A-C_5O_5$, $303(-)A-C_5O_5W$, $271(-)$ $A-C_5O_5SW$, $150(-)A-C_{12}H_5O_5SW$, $93)-)A-C_{18}H_{10}O_5SW$, $77(-)A-C_{18}H_{12}NO_5SW$ |
| $S=C(Ni-PrH)_2^d$ | $486-482(66)W(CO)_5(S=C(Ni-PrH_2)^+(B)$, $85(11)$ $B-C_7H_3NO_5SW$, $69(35)B-C_8H_7NO_5SW$, $58(100)$ $B-C_{10}H_{10}N_2O_5SW$ |

[a] Mass to charge ratio (relative intensity) fragment.

[b] Ionization potential 70 ev at 140°C.

[c] Peaks not sufficiently intense for measurement.

[d] Ionization potential 50 ev with vacuum lock.

Table 19. Visible[a] spectra of the $[(Ph_3P)_2N][LM(CO)_5]$ complexes and $[(Ph_3P)_2N][(CO)_4W(S_2CNPhH)]$ in MeCN

| L | M | $nm(mole^{-1}cm^{-1})$[b] |
|---|---|---|
| [SH] | W | 447(506), 385(1280) |
| [SH] | Cr | 380(401), 370(481), 362(552) |
| [SC(=O)Me] | W | 418(921), 377(1550) |
| $[SC(=O)CPh_2H]$ | W | 410(sh), 378(1510) |
| $[SC(=O)NMeH]$[c] | W | 424(1065), 377(1126) |
| [SC(=O)NPhH] | W | 417(775), 376(1300) |
| $[SCF_2C(=O)CF_3]$[c] | W | 446(408), 380(844) |
| $[S\overline{C=CF(CF_2)_3CF_2}]$ | W | 443(537), 376(1480) |
| $\begin{matrix} S \\ \diagdown \\ \quad CNPhH \\ \diagup \\ S \end{matrix}$ | W | 394(991) |

[a]Recorded from 600 nm to 350.

[b]Extinction coefficient.

[c]$[NEt_4]^+$ (counter cation).

Table 20. Visible[a] spectra of the $LW(CO)_5$ complexes

| L | Solvent | $nm(mole^{-1}cm^{-1})$[b] | |
|---|---|---|---|
| $S=C(p-NMe_2C_6H_4)H$ | $C_6H_6$ | 570(47,800) | 408(20,600) |
| $S=C(p-OMeC_6H_4)H$ | $C_6H_6$ | 544(16,900) | 359(18,100) |
| $S=C(p-MeC_6H_4)H$ | $C_6H_6$ | 543(11,200) | 368(sh) |
| $S=C(NPhH)CPh_2H$ | hexanes | 400(4570) | 374(4470) |
| $S=C(NH_2)_2$ | MeCN | 413(1040) | 376(1950) |
| $S=C(Ni-PrH)_2$ | MeCN | 416(869) | 376(1650) |
| $N\equiv CNH_2$ | MeCN | 412(sh) | 384(2620) |

[a]Recorded from 600 nm to 350.

[b]Extinction coefficient.

Table 21. Visible[a] spectra of the $NEt_4[\mu-RS[W(CO)_5]_2]$ complexes in MeCN

| R | $nm(mole^{-1}cm^{-1})$[b] | | |
|---|---|---|---|
| H- | 448(929) | 377(2760) | |
| MeC(=O)- | 439(1380) | 369(3260) | |
| MeC(=O)-[c] | 444(1770) | 374(3640) | |
| $Me_3Sn-$ | 474(776) | 383(sh) | 356(sh) |
| $Ph_2P-$ | 428(810) | 372(sh) | |
| HMeNC(=O)- | 444(1520) | 375(2960) | |
| MeHg- | 450(sh) | 381(sh) | |
| $PhCH_2-$ | 449(847) | 374(sh) | |
| Ph- | 455(1620) | 371(sh) | |

[a] Recorded from 600 nm to 350.

[b] Extinction coefficient.

[c] $[(Ph_3P)_2N]^+$ (counter cation).

Table 22. Rate constants for the reaction of PhN=C=O with $[(Ph_3P)_2N][W(CO)_5(SH)]$ at $26.45 \pm 0.05°C$

| Solvent | PhN=C=O $(10^{-3}$ M) | $k_{obsd}$ $(10^{-4}$ sec$^{-1})$ |
|---------|------------------------|------------------------------------|
| acetone | 8.01 | 10.8 |
| | 23.2 | 24.0 |
| | 23.2 | 22.7 |
| | 40.0 | 30.3 |
| | 54.2 | 38.0 |
| | 83.7 | 47.6 |
| | 102 | 47.0 |
| | 102 | 50.5 |
| | 198 | 70.0 |
| | 430 | 170 |
| THF | 7.74 | 3.67 |
| | 24.5 | 9.65 |
| | 38.7 | 14.0 |
| | 77.4 | 20.8 |
| | 77.4[a] | 27.8 |
| | 110 | 25.5 |

[a]Added $NEt_3$ $(8.36 \times 10^{-3}$ M).
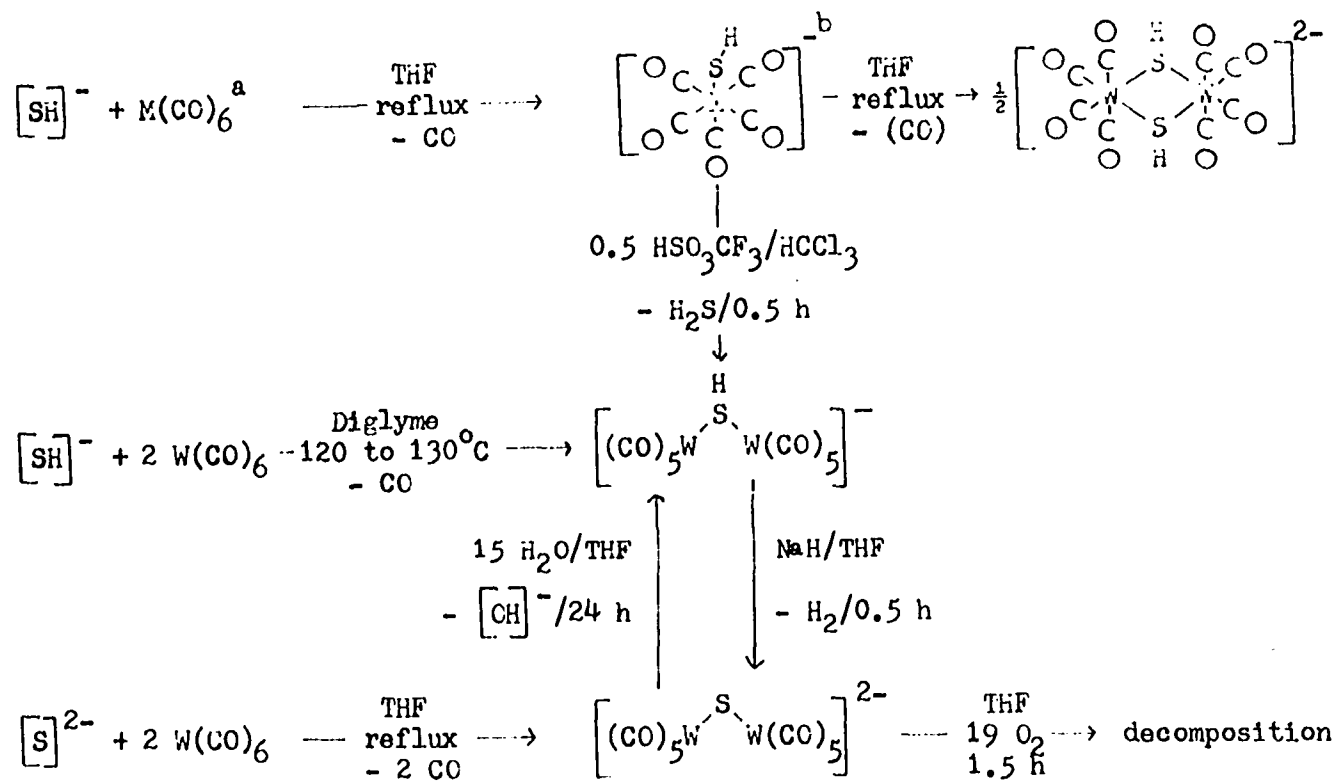
## III. RESULTS AND DISCUSSION

### A. Preparation of the Mercapto and Sulfido Complexes
### (Figure 1)

#### 1. Mercapto complexes

Preparation of $[M(CO)_5(SH)]^-$ was accomplished according to Scheme I.

Scheme I:

$$-13- \quad NaSH + [(Ph_3P)_2N]Cl \xrightarrow[r.t.]{EtOH} [(Ph_3P)_2N]SH + NaCl\downarrow$$

$$-14- \quad [(Ph_3P)_2N]SH + M(CO)_6 \xrightarrow[reflux]{THF} [(Ph_3P)_2N][M(CO)_5(SH)] + CO\uparrow$$

Bis(triphenylphosphine)imminium hydrogen sulfide was prepared by the method of Cotton (Equation 13) (68). This product, $[(Ph_3P)_2N]SH$, which was sensitive to air was not separated from the insoluble NaCl. A slight excess of $[M(CO)_6]$ was added to the reaction mixture to insure complete reaction of the ionic reactant. Progress of the reaction was monitored by the amount of CO evolved. Washing the ionic products, $[(Ph_3P)_2N][M(CO)_5(SH)]$, with hexanes guaranteed that they were free of $M(CO)_6$.

Alternate preparations of $[W(CO)_5(SH)]^-$ were inferior to the above procedure. Refluxing NaSH or a mixture of $[NH_4]SH$ and NaCl (Equation 13) with $W(CO)_6$ in THF did not give products. Mixtures of either $[NEt_4]SH$ and NaCl (Equation 13) or $[BzNEt_3]SH$ and NaCl were refluxed with $W(CO)_6$ in THF to yield small amounts of $NEt_4[W(CO)_5(SH)]$ (yellow crystals) or
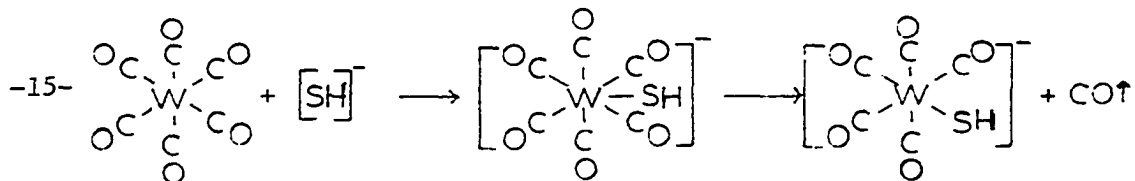
$$\left[\text{SH}\right]^- + \text{M(CO)}_6{}^a \quad \xrightarrow[\text{- CO}]{\text{THF} \atop \text{reflux}} \quad \left[\begin{array}{c} \text{O}_{\text{C}} \quad \overset{\overset{\text{H}}{|}}{\text{S}} \quad _{\text{C}}\text{O} \\ \text{O}^{\text{C}} \quad _{\text{C}}^{\text{C}} \quad ^{\text{C}}\text{O} \\ \text{O} \end{array}\right]^{-b} \quad \xrightarrow[\text{- (CO)}]{\text{THF} \atop \text{reflux}} \quad \tfrac{1}{2}\left[\begin{array}{c} \text{O}_{\text{C}}\overset{\text{O}}{\underset{\text{C}}{\parallel}}\text{S}\quad\overset{\text{O}}{\underset{\text{C}}{\parallel}}{}_{\text{C}}\text{O} \\ \text{O}^{\text{C}}{}_{\text{C}}\text{W}\quad\text{S}\quad\text{W}{}_{\text{C}}{}^{\text{C}}\text{O} \\ \text{O} \quad \text{H} \quad \text{O} \end{array}\right]^{2-}$$

$$\Big| \quad 0.5 \text{ HSO}_3\text{CF}_3/\text{HCCl}_3$$

$$- \text{H}_2\text{S}/0.5 \text{ h}$$

$$\downarrow$$

$$\left[\text{SH}\right]^- + 2 \text{ W(CO)}_6 \xrightarrow[\text{- CO}]{\text{Diglyme} \atop \text{120 to 130}^\circ\text{C}} \left[(\text{CO})_5\text{W}\overset{\overset{\text{H}}{|}}{\underset{}{\text{S}}}\text{W(CO)}_5\right]^-$$

$$\begin{array}{cc} 15 \text{ H}_2\text{O/THF} \uparrow & \downarrow \text{NaH/THF} \\ - \left[\text{OH}\right]^-/24 \text{ h} & - \text{H}_2/0.5 \text{ h} \end{array}$$

$$\left[\text{S}\right]^{2-} + 2 \text{ W(CO)}_6 \xrightarrow[\text{- 2 CO}]{\text{THF} \atop \text{reflux}} \left[(\text{CO})_5\text{W}\overset{\text{S}}{\underset{}{}}\text{W(CO)}_5\right]^{2-} \xrightarrow[\text{1.5 h}]{\text{THF} \atop 19 \text{ O}_2} \text{decomposition}$$

---

[a] Cr, Mo and W.

[b] No reaction with NaH in THF or 10 NaOH in THF.

Figure 1. Preparation of carbonyl group 6A metal mercapto and sulfido complexes

BzNEt$_3$[W(CO)$_5$(SH)] (yellow oil), respectively. Solution IR spectra of

NEt$_4$[W(CO)$_5$(SH)], BzNEt$_3$[W(CO)$_5$(SH)], and [(Ph$_3$P)$_2$N][W(CO)$_5$(SH)] in CH$_2$Cl$_2$

(Table 4) were identical.

Occasionally, trace amounts of [W(CO)$_4$(SH)]$_2^{2-}$ and [$\mu$-HS[W(CO)$_5$]$_2$]$^-$

were found among partitions (Chapter II, Section A.10) of the product

mixture. Initial partitions from diethylether and THF mixtures gave

0-5% yields of impure [(Ph$_3$P)$_2$N]$_2$[[W(CO)$_4$(SH)]$_2$]. This product, which was

also prepared by refluxing [(Ph$_3$P)$_2$N][W(CO)$_5$(SH)] in THF for 2

hours, was characterized by its solution IR spectrum in CH$_2$Cl$_2$ (1999

cm$^{-1}$(m), 1880(vs), 1830(s), 1779(s)) and $^1$H NMR spectrum in DCCl$_3$

(2.50 $\tau$(m)(-) [(Ph$_3$P)$_2$N]$^+$, 11.16(s)(-) S$\underline{H}$). These spectrophotometric

properties were in good qualitative agreement with those of [Mn(CO)$_4$(SH)]$_2$,

XI, (solution IR spectrum in CCl$_4$ 2077 cm$^{-1}$(m), 2018(vs), 2004(s), 1972(s)

and $^1$H NMR spectrum in CCl$_4$ 10.54 $\tau$(s)) (32). Oils of

[(Ph$_3$P)$_2$N][$\mu$-HS[W(CO)$_5$]$_2$] were obtained by concentrating the final

partition of the product mixture in vacuo. Solution IR spectra of this

minor product, [(Ph$_3$P)$_2$N][$\mu$-HS[W(CO)$_5$]$_2$], and of NEt$_4$[$\mu$-HS(W(CO)$_5$]$_2$]

(Table 7) were the same. Preparation of NEt$_4$[$\mu$-HS[W(CO)$_5$]$_2$ (see below)

was also accomplished by a thermal procedure involving [SH]$^-$ and W(CO)$_6$.

Preparation of [W(CO)$_5$(SH)]$^-$ (Equation 14) appeared to take place

by an associative mechanism involving nucleophilic attack by [SH]$^-$ at the

metal (Equation 15). Evidence for this is that no reaction occurred

between equimolar amounts of W(CO)$_6$ and PPh$_3$(2.0 mmole) in reluxing THF

$$-15- \quad \text{(structure)} + [SH]^- \longrightarrow \left[ \text{(structure)} \right]^- \longrightarrow \left[ \text{(structure)} \right]^- + CO\uparrow$$

over a 3 hour period; $W(CO)_6$ with a molar equivalent of $[(Ph_3P)_2N]SH$

(13 mmole) was converted in good yield to $[(Ph_3P)_2N][W(CO)_5(SH)]$ and CO by

refluxing the mixture for 1 hour. If a dissociative mechanism (Equation

16) was operable under these mild conditions (THF b.p. 67°C), $PPh_3$

$$-16- \quad W(CO)_6 \underset{+CO}{\overset{-CO}{\rightleftarrows}} [W(CO)_5 \text{ (solvent)}] \overset{+L}{\rightleftarrows} W(CO)_5L$$

would trap the reactive intermediate, $[W(CO)_5(\text{solvent})]$, to give

$W(CO)_5(PPh_3)$. Similar substitution reactions under mild thermal

conditions have been shown to contain a ligand-dependent term in their

rate law (69, 70). Froelich and Darensbourg reported the preparation of

$HMn(CO)_4(PPh_3)$ from equimolar amounts of $[(PPh_3)Mn(CO)_5][PF_6]$ and NaSH

in MeCN at room temperature. This product appeared to result from

$[SH]^-$ attack at a carbonyl carbon followed by elimination of COS

(Equation 17) (71). As no carbonyl(hydrido)tungsten complexes were

$$-17- \quad [M(CO)_5L]^+ + [SH]^- \rightarrow [M(CO)_4(L)\overset{O}{\overset{\|}{C}}-SH] \rightarrow cis - HM(CO)_4L + COS\uparrow$$

observed in the product mixtures of $[W(CO)_5(SH)]^-$, $[W(CO)_5(SH)]^-$

apparently resulted from attack of $[SH]^-$ at the metal (Equation 15).

Attempts to prepare more highly substituted carbonyl (mercapto)

tungsten complexes (e.g. $[W(CO)_4(PR_3)(SH)]^-$) were unsuccessful.

Stirring $[(Ph_3P)_2N][W(CO)_5(SH)]$ with a molar equivalent of $PPh_3$ for 48

hours at room temperature resulted in $W(CO)_5(PPh_3)$ (25% yield); no other

soluble metal carbonyl containing products were present in the resultant

reaction mixture. Solution IR spectra of this product and of an

authentic sample of $W(CO)_5(PPh_3)$ (Chapter II, Section B) were identical.

Conversely, refluxing equimolar amounts of $W(CO)_5(PPh_3)$ and

$[(Ph_3P)_2N]SH$ (Equation 13) in THF for 24 hours gave $[W(CO)_5(SH)]^-$ in

24% yield and $W(CO)_5(PPh_3)$ (75% recovered). A 50-fold molar excess

of $P(n-Bu)_3$ was stirred with $[(Ph_3P)_2N][(W(CO)_5(SH)]$ in THF for 1 hour

to give a $[L_2W(CO)_4]^-$ complex which was characterized by its solution

IR spectrum in THF ($1992$ $cm^{-1}$(m), $1868$(vs), $1792$(s)). This product which

decomposed during isolation procedures was not identified.

Preparation of $[\mu-HS[W(CO)_5]_2]^-$ was accomplished in accordance with

Equation 18. A slight excess of $W(CO)_6$ was employed in the reaction,

$$-18- \quad NaSH + 2 W(CO)_6 \xrightarrow[\text{120-130°C}]{\text{diglyme/THF}} Na[\mu-HS[W(CO)_5]_2] + 2 CO\uparrow$$

and its progress was monitored by the amount of CO evolved. Trouble-

some sublimation of $W(CO)_6$ onto the cooler parts of the reaction flask

during the reaction period in diglyme was eliminated by addition of a

small amount of THF to the reaction mixture; this resulted in a refluxing

reaction mixture. No attempt was made to isolate the product as its

sodium salt. Addition of the warm reaction mixture to a concentrated

aqueous solution of $[NEt_4]Br$ immediately precipitated a yellow powder.

Transparent yellow needles of $NEt_4[\mu-HS(W(CO)_5]_2]$ were obtained by

cooling a hot saturated $CHCl_3$ solution of the yellow powder to $-40°C$.

Reaction stoichiometry was not dictating the type of product formed in the above reaction (Equation 18). Heating equimolar amounts of NaSH and $W(CO)_6$ in a diglyme and THF mixture at $120-130°C$ for 45 minutes gave $[\mu-HS[W(CO)_5]_2]^-$ exclusively. The mechanism which led to selective formation of this product was not elucidated.
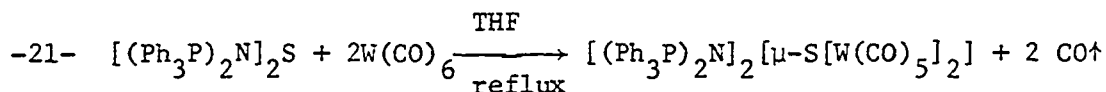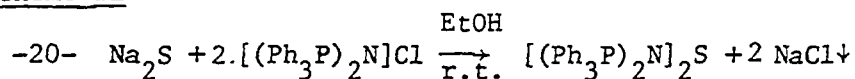
## 2. Sulfido complexes

Treatment of a yellow solution of $NEt_4[\mu-HS[W(CO)_5]_2$ and THF at room temperature with an equivalent amount of NaH (57% oil dispersion) gave a green mixture which was believed to contain predominantly $Na[NEt_4][\mu-S[W(CO)_5]_2]$ (Equation 19). Reaction took place quickly

-19- $NEt_4[\mu-HS[W(CO)_5]_2] + NaH \xrightarrow{THF} Na[NEt_4][\mu-S[W(CO)_5]_2] + H_2\uparrow$

(e.g. ca 10 minutes for 0.5 mmole of reactants). An equimolar amount of gas was evolved from the reaction mixture; 14 ml of $H_2O$ were displaced from a gas displacement apparatus (XVIII) when 5 ml of THF was added to a flask containing 0.314 g (0.387 mmole) of $NEt_4[\mu-HS[W(CO)_5]_2]$ and 0.0191 g (0.453 mmole) of NaH (57% oil dispersion). This gas was shown to be $H_2$ by GC analysis (Chapter 2, Section A.8) of the atmosphere above the resultant green mixture. The air sensitive product, $Na[NEt_4][\mu-S[W(CO)_5]_2]$, whose solution IR spectrum in THF was 2051 $cm^{-1}$(vw), 2038(w), 1930(sh), 1908(vs), 1852(m) was neither isolated in the solid state nor characterized thoroughly.

An alternate preparation of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ appeared successful, but the product could not be isolated as a solid. Preparation of $[(Ph_3P)_2N]_2[\mu\text{-}S[W(CO)_5]_2]$ was effected according to Scheme II. Air

Scheme II:

-20- $\quad Na_2S + 2.[(Ph_3P)_2N]Cl \xrightarrow[\text{r.t.}]{\text{EtOH}} [(Ph_3P)_2N]_2S + 2 NaCl\downarrow$

-21- $\quad [(Ph_3P)_2N]_2S + 2W(CO)_6 \xrightarrow[\text{reflux}]{\text{THF}} [(Ph_3P)_2N]_2[\mu\text{-}S[W(CO)_5]_2] + 2 CO\uparrow$

sensitive $[(Ph_3P)_2N]_2S$ was not separated from insoluble NaCl after the volatile components of the reaction mixture, Equation 20, were removed in vacuo. A slight excess of $W(CO)_6$ was used to guarantee complete reaction of the ionic reactant; progress of the reaction, Equation 21, was followed by the amount of CO evolved. Partitional crystallization of the resultant green suspension (Equation 21) gave green oils initially and yellow oils. These oils were destroyed without further characterization (the green color of $[(Ph_3P)_2N]_2[\mu\text{-}S[W(CO)_5]_2]$ was identical to the color of $Na[NEt_4][\mu\text{-}S[W(CO)_5]_2]$ (above)).

Preparation of $[W(CO)_5S]^{2-}$ by Equations 22 and 23 failed. Gas

-22- $\quad [W(CO)_5(SH)]^- + NaH \xrightarrow[\text{r.t.}]{\text{THF}} Na[W(CO)_5S]^- + H_2\uparrow$

-23- $\quad [W(CO)_5(SH)]^- + MeLi \xrightarrow[\text{r.t.}]{\text{THF}} Li[W(CO)_5S]^- + CH_4\uparrow$

evolution from the mixtures was not observed during the reaction period (18 hours and 1 hour respectively). Solution IR spectra of the resultant

reaction mixtures demonstrated that $[W(CO)_5(SH)]^-$ was the only metal carbonyl containing component present (Table 4). At the conclusion of the reaction period, gas evolution (presumedly $H_2$ or $CH_4$) was observed upon the addition of $H_2O$ to the reaction mixture.

As discussed below, the value of pka for $[\mu\text{-HS}[W(CO)_5]_2]^-$ was determined to be between 15 and 18 which was similar to the value of pka = 17 for $[HS]^-$ (20). Treatment of a yellow solution of $NEt_4[\mu\text{-HS}[W(CO)_5]_2]$ and HOMe (pka = 16 in ethereal solvents (72)) with a molar equivalent of NaOMe at room temperature gave no reaction; however, a green mixture of $Na(NEt_4)[\mu\text{-S}[W(CO)_5]_2]$ was obtained by treating a yellow solution of $NEt_4[\mu\text{-HS}[W(CO)_5]_2]$ and HOEt (pka = 18 in ethereal solvents (72)) with an equimolar amount of NaOEt.

Hydrogen bound to sulfur in $[W(CO)_5(SH)]^-$ was less acidic than the proton of $[\mu\text{-HS}[W(CO)_5]_2]^-$. A tenfold molar excess of NaOEt in THF quickly (ca. 5 minutes) and quantitatively deprotonated $[\mu\text{-HS}[W(CO)_5]_2]^-$ to give a green solution of $Na[NEt_4][\mu\text{-S}[W(CO)_5]_2]$. This product was identified by its solution IR spectrum in THF (see above) and its reaction with a tenfold molar excess of MeC(=O)Cl to give $NEt_4[\mu\text{-MeC}(=O)S[W(CO)_5]_2]$ whose $CH_2Cl_2$ solution IR and $DCCl_3$ solution $^1H$ NMR spectra were the same as those of an authentic sample (Tables 7 and 15, respectively). On the other hand, no reaction took place when $[(Ph_3P)_2N][W(CO)_5(SH)]$ was treated with a tenfold molar excess of NaOEt in THF. Removal of electron density from the mercapto ligand should increase the acidity of its proton; the proton of

$[\mu\text{-HS}[W(CO)_5]_2]^-$ that had two $W(CO)_5$ groups coordinated to sulfur was more acidic than the hydrogen of $[W(CO)_5(SH)]^-$.

### B.  Chemical Properties of the Mercapto and Sulfido Complexes

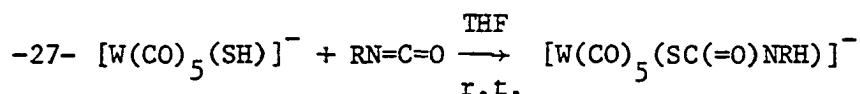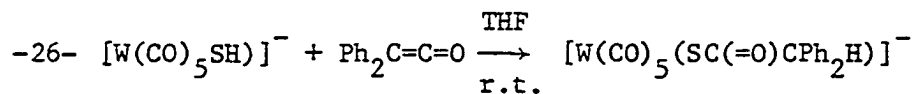1. Reactions of organic carbonyl containing reagents with $[W(CO)_5(SH)]^-$, $[\mu\text{-HS}[W(CO)_5]_2]^-$, and $[\mu\text{-S}[W(CO)_5]_2]^{2-}$

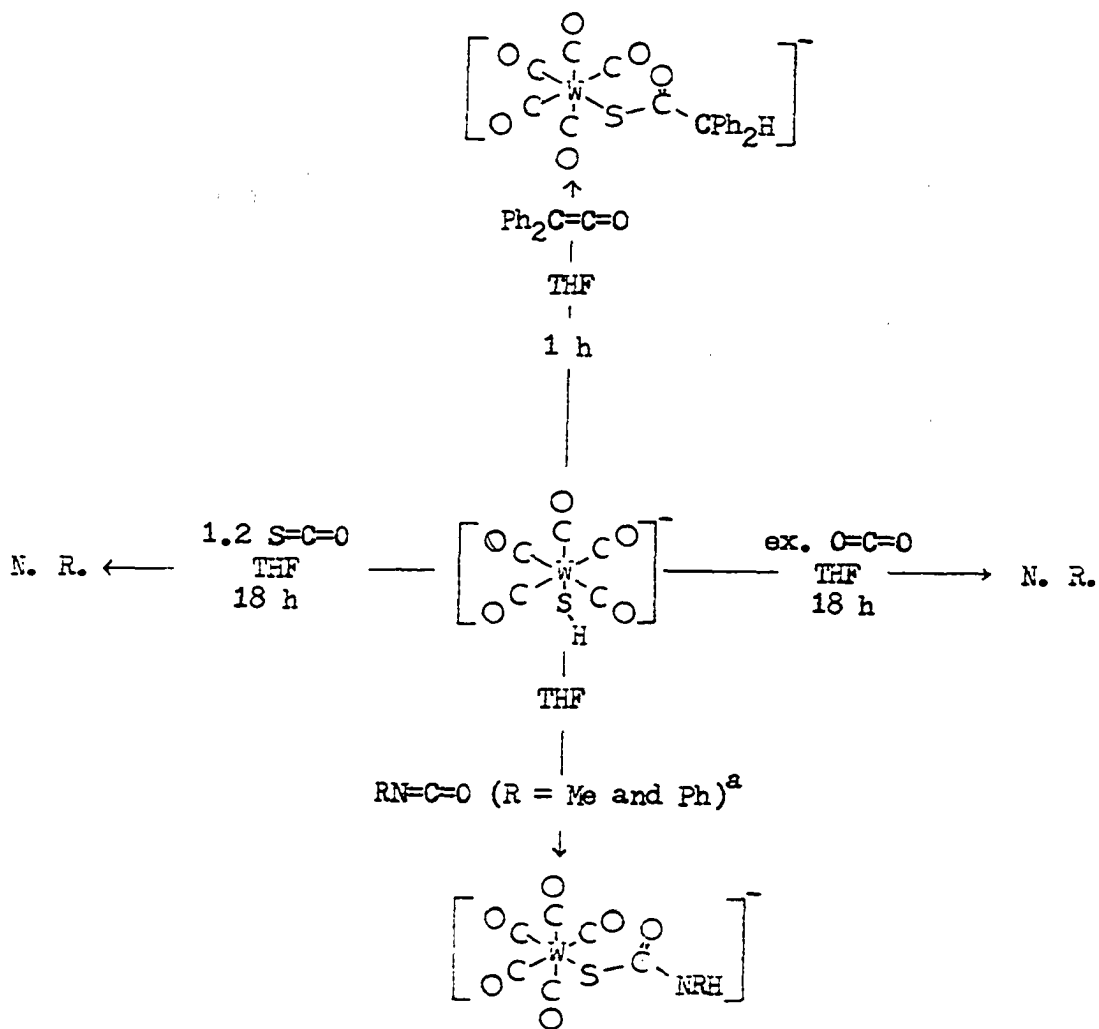a.  Addition reactions with $[W(CO)_5(SH)]^-$ (heterocumulenes) (Figure 2)

Preparations and reactions of isocyanates, RN=C=O, (73, 74) and ketenes, $R_2C=C=O$, (73, 75), have been reviewed. Isocyanates, Equation 24, and ketenes, Equation 25, which have reactivities lying between those of the

-24-   $PhN=C=O + n\text{-BuSH} \rightarrow HPhNC(=O)SBu$ (76)

-25-   $Me_2C=C=O + EtSH \rightarrow HMe_2CC(=O)SEt$ (77)

corresponding acylhalides and anhydrides (78), add to the C=N and C=C bonds in reactions with ROH, RSH, $R_2NH$, and HX (73). Reactions of $[W(CO)_5(SH)]^-$ with RN=C=O and $Ph_2C=C=O$ (below) were analogous to the reaction of RSH with these reagents.

Preparation of $[W(CO)_5(SC(=O)CPh_2H)]^-$ and $[W(CO)_5(SC(=O)NRH)]^-$ where R = Ph, Me was carried out according to Equations 26 and 27, respectively.

-26-   $[W(CO)_5SH)]^- + Ph_2C=C=O \xrightarrow[\text{r.t.}]{\text{THF}} [W(CO)_5(SC(=O)CPh_2H)]^-$

-27-   $[W(CO)_5(SH)]^- + RN=C=O \xrightarrow[\text{r.t.}]{\text{THF}} [W(CO)_5(SC(=O)NRH)]^-$

$^{a}$R = Me, $t_{1/2}$ = 1.0 h and R = Ph, $t_{1/2}$ = 5 min.
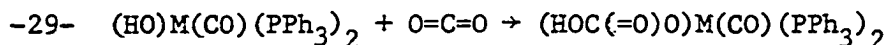
Figure 2. Reactivity of heterocumulenes which contain the carbonyl, C=O, group with $[W(CO)_5(SH)]^-$
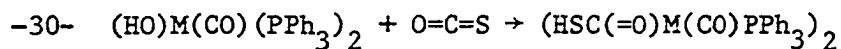
Reactions were performed with a slight excess of the organic reagent to insure complete conversion of the ionic reactant to the product. An instantaneous reaction took place between $Ph_2C=C=O$ and $[W(CO)_5(SH)]^-$; half-lives for the reaction of $MeN=C=O$ and $PhN=C=O$ with $[W(CO)_5(SH)]^-$ were 1.0 hr. and 5 min., respectively (Chapter 2, Section A.9). Isolation of $[(Ph_3P)_2N][W(CO)_5(SC(=O)NMeH)]$ as a solid was not possible, but its solution IR $(CH_2Cl_2)$ and visible (MeCN) spectra were identical to the spectra of $NEt_4[W(CO)_5(SC(=O)NMeH)]$ (Tables 4 and 19) which was prepared in accordance with Equation 28. A suspension of $NEt_4[W(CO)_5(SH)]$

$$-28-\quad NEt_4[W(CO)_5(SH)] + MeN=C=O \xrightarrow[\text{reflux}]{\text{acetone}} NEt_4[W(CO)_5(SC(=O)NMeH)]$$

in acetone was obtained by following Scheme I. Acetone was substituted for THF solvent in Equation 14. A slight excess of $MeN=C=O$ was added to the resultant suspension (Equation 14) that had been refluxed (acetone b.p. 56°C) for 2 hours, and this mixture was refluxed for an additional 2 hours. Partitional crystallization of the ionic products $([(Ph_3P)_2N][W(CO)_5(SC(=O)CPh_2H)]$, $[(Ph_3P)_2N][W(CO)_5(SC(=O)NPhH)]$, and $NEt_4[W(CO)_5(SC(=O)NMeH)])$ from acetone, diethylether, and hexanes mixtures afforded yellow crystalline solids.

Reactions of $O=C=O$ with transition metal compounds have been reviewed by Volpin and Kolomnikov (79). Addition of either $O=C=O$, Equation 29, or $O=C=S$, Equation 30, to $(HO)M(CO)(PPh_3)_2$ where M = Rh, Ir has been

$$-29-\quad (HO)M(CO)(PPh_3)_2 + O=C=O \rightarrow (HOC(=O)O)M(CO)(PPh_3)_2$$
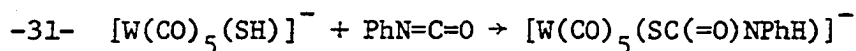
-30-  $(HO)M(CO)(PPh_3)_2 + O=C=S \rightarrow (HSC(=O)M(CO)PPh_3)_2$

observed by Flynn and Vaska (80). The chemistry of H-S-W system of

$[W(CO)_5(SH)]^-$ did not parallel the reactivity of the H-O-M systems above.

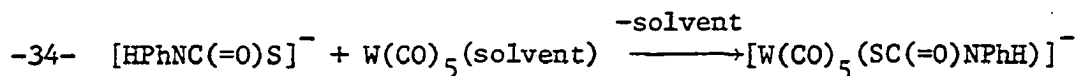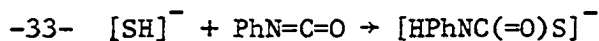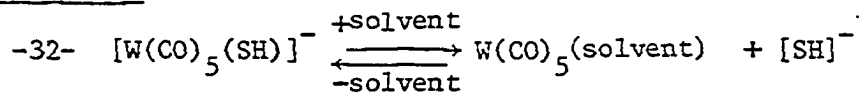No reaction appeared to occur between $[W(CO)_5(SH)]^-$ and an excess

amount of O=C=O or an equimolar amount of O=C=S in THF at room tempera-

ture over an 18 hour period. Apparently, neither the S-M (81) nor the

S-H bonds of $[W(CO)_5(SH)]^-$ were sufficiently activated to add to the

O=C or S=C bonds of O=C=O or S=C=O.

To determine whether coordinated SH (Equation 31) or dissociated

$[SH]^-$ (Scheme III) was the reactive species in Equation 27, reaction

rate determinations and trapping experiments were conducted. If

-31-  $[W(CO)_5(SH)]^- + PhN=C=O \rightarrow [W(CO)_5(SC(=O)NPhH)]^-$

Equations 31 or 32 were rate determining steps, reaction by coordinated

SH or dissociated $[SH]^-$ would be second order or first order, respectively.

Scheme III:

-32-  $[W(CO)_5(SH)]^- \xrightleftharpoons[-solvent]{+solvent} W(CO)_5(solvent) + [SH]^-$

-33-  $[SH]^- + PhN=C=O \rightarrow [HPhNC(=O)S]^-$

-34-  $[HPhNC(=O)S]^- + W(CO)_5(solvent) \xrightarrow{-solvent} [W(CO)_5(SC(=O)NPhH)]^-$

Furthermore, if reaction occurred by Scheme III, addition of a ligand

(L), which substituted for solvent in $W(CO)_5(solvent)$ (Equation 32),

would give W(CO)$_5$L as a product.

Mechanisms for the addition of ROH, RSH, R$_2$NH, and HX to isocyanates (RN=C=O) and ketenes (R$_2$C=C=O) have been reviewed by Satchell and Satchell (82). Reaction of thiols, RSH, with isocyanates at room temperature in the absence of catalyst was slow (76). In the presence of tri-alkylamines (NR$_3$), a catalyst, the reaction of RN=C=O with RSH was first order with respect to RN=C=O, RSH, and NR$_3$ (83). Reaction was smoothest in strongly ionizing solvents; Dyer and Glenn reported that the uncatalyzed reaction of PhN=C=O with n-BuSH in DMSO or DMF was too fast for kinetic studies (84).

A kinetic study of the reaction of PhN=C=O with [W(CO)$_5$(SH)]$^-$ was undertaken to gain information about the mechanism of this process. Reactions were carried out at 26.45 $\pm$ 0.05°C in acetone or THF using at least a tenfold molar excess of PhN=C=O. Following the course of this reaction by repeatedly scanning the M-C≡O stretching region with the IR spectrophotometer (2200 cm$^{-1}$ - 1700) showed that the product, [W(CO)$_5$(SC(=O)NPhH)]$^-$, was formed quantitatively with no observable intermediates. Problems in obtaining solids of the product resulted in low isolated yields. The reaction was found to be first-order in [W(CO)$_5$(SH)]$^-$ and complex with respect to PhN=C=O. Data for the reaction are shown in Table 22. A plot of k$_{obsd.}$ vs. [PhN=C=O] gave a curved line which tended to first-order with a zero intercept at low concentrations and to zero-order at higher concentrations. Plotting ln k$_{obsd.}$ vs. ln[PhN=C=O] gave a straight line of fractional slope
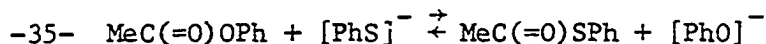
(0.6 and 0.8 in acetone and THF, respectively). This reaction was complex; neither Equation 31 nor Equation 32 were rate determining steps.

Rates for the reaction of PhN=C=O with $[W(CO)_5(SH)]^-$ or RSH were affected in the same way in the absence or presence of catalyst and in more strongly ionizing solvents. Addition of $NEt_3$, a catalyst for the reaction of RSH with RN=C=O (see above), accelerated the reaction of $[W(CO)_5(SH)]^-$ with PhN=C=O (Table 22). Reaction between $[W(CO)_5(SH)]^-$ and PhN=C=O was faster in acetone, a more ionizing solvent, than in THF (e.g., acetone, 21.4 (dielectric constant) and THF, 8.2 (85)).

Attempts to trap a reactive intermediate $(W(CO)_5(solvent)$, Scheme III) by adding a 50-fold molar excess of $PPh_3$ or CO to a solution of $[W(CO)_5(SH)]^-$ in THF at room temperature failed. Repeatedly scanning the 2200 $cm^{-1}$ to 1700 region with the IR spectrophotometer for 2 hours demonstrated that no $W(CO)_6$ (1983 $cm^{-1}$) or $W(CO)_5(PPh_3)$ (1946 $cm^{-1}$) was formed in the reaction mixture. Both $W(CO)_6$ and $W(CO)_5(PPh_3)$ were shown to be virtually inert to $[SH]^-$ under these conditions (this chapter, Section A.1).
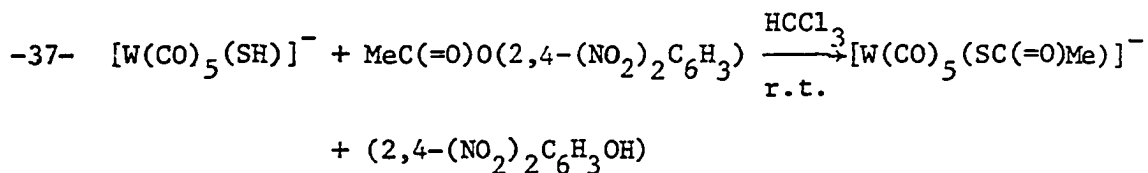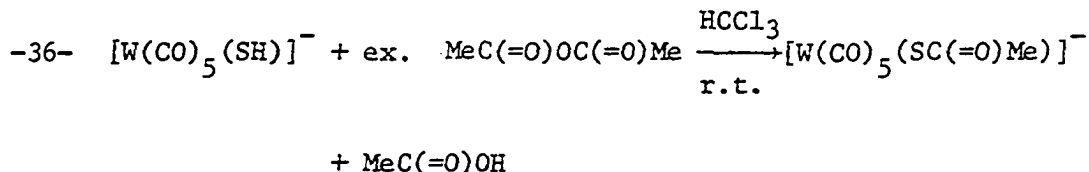
Although a suitable mechanism for the reaction of $[W(CO)_5(SH)]^-$ with PhN=C=O was not determined from kinetic studies, trapping experiments (above) suggested that reaction occurred between coordinated SH and PhN=C=O. Qualitative similarities were observed by kinetic studies between the reaction of $[W(CO)_5(SH)]^-$ or RSH and RN=C=O.

b. **Substitution reactions with** $[W(CO)_5(SH)]^-$ **(Figure 3)**    Acyl

transfers between sulfur and oxygen nucleophiles, Equation 35, have

$$-35-\quad MeC(=O)OPh + [PhS]^- \rightleftarrows MeC(=O)SPh + [PhO]^-$$

been investigated by numerous chemists and biochemists (86). Similarly,

$[W(CO)_5(SH)]^-$ reacted with $MeC(=O)OC(=O)Me$ and $MeC(=O)O(2,4-(NO_2)_2C_6H_3)$

to give an acylated product.

Preparation of $[W(CO)_5(SC(=O)Me)]^-$ was accomplished according to

Equations 36 and 37.  Adding a drop of $MeC(=O)OC(=O)Me$ (ca. 0.5 mmole)

$$-36-\quad [W(CO)_5(SH)]^- + ex.\ MeC(=O)OC(=O)Me \xrightarrow[\text{r.t.}]{HCCl_3} [W(CO)_5(SC(=O)Me)]^-$$

$$+ MeC(=O)OH$$

$$-37-\quad [W(CO)_5(SH)]^- + MeC(=O)O(2,4-(NO_2)_2C_6H_3) \xrightarrow[\text{r.t.}]{HCCl_3} [W(CO)_5(SC(=O)Me)]^-$$

$$+ (2,4-(NO_2)_2C_6H_3OH)$$

to a solution of $[(Ph_3P)_2N][W(CO)_5(SH)]$ (ca. 0.03 mmole) and $DCCl_3$

(0.6 ml) in a $^1H$ NMR tube (Equation 36) and obtaining a spectrum of the

resultant solution after 30 minutes demonstrated that

$[(Ph_3P)_2N][W(CO)_5(SC(=O)Me)]$ (7.55 $\tau$ (s); 68% by relative integrated

intensities), $MeC(=O)OH$ (7.93 $\tau$ (s); 103% by relative integrated

intensities), and $MeC(=O)OC(=O)Me$ (7.78 $\tau$ (s)) were present.  This

mixture was concentrated to a residue under a stream of PPN; its solution

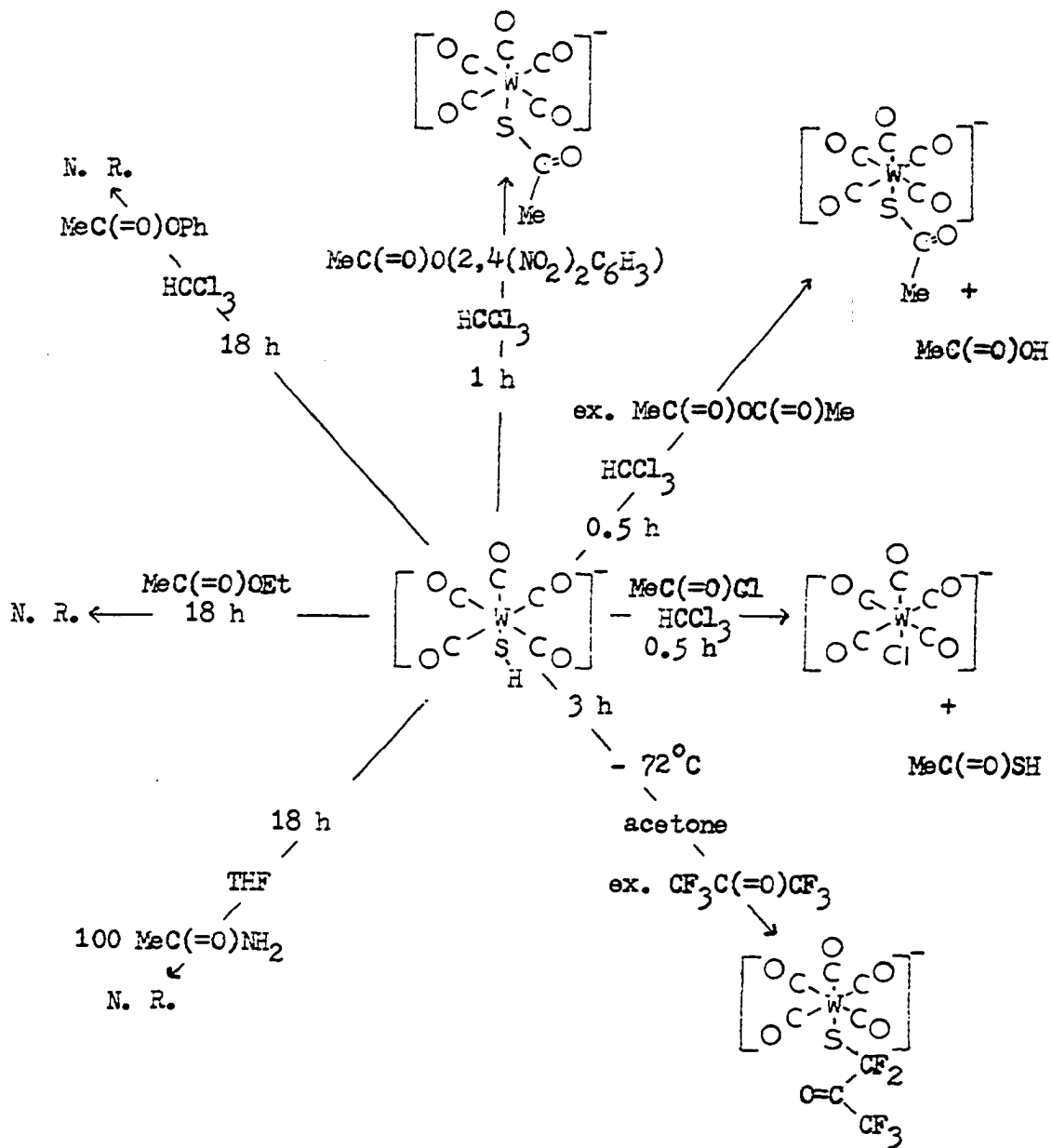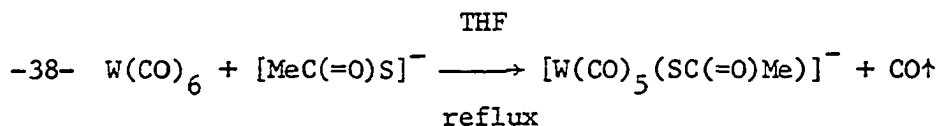IR spectrum in $CH_2Cl_2$ confirmed the presence of $[W(CO)_5(SC(=O)Me)]^-$

Figure 3. Reactivity of carbonyl, C=O, containing reagents with
[W(CO)$_5$(SH)]$^-$ (substitutions)

(Tables 4 and 12). Similarly, treatment of a solution of

$[(Ph_3P)_2N][W(CO)_5(SH)]$ (0.051 g, 0.056 mmole) and $DCCl_3$ (0.6 ml) in a

$^1H$ NMR tube with $MeC(=O)O(2,4-(NO_2)_2C_6H_3)$ (0.013g, 0.058 mmole), Equation

37, for 1 hour gave $[(Ph_3P)_2N][W(CO)_5(SC(=O)Me)]$ (42% yield by relative

integrated intensities). The final solution IR spectrum in $CH_2Cl_2$

established the identity of $[W(CO)_5(SC(=O)Me)]^-$ as a reaction product.

No reaction appeared to take place between equimolar amounts of

$[(Ph_3P)_2N][W(CO)_5(SH)]$ and $MeC(=O)OPh$, $MeC(=O)OEt$, or $MeC(=O)NH_2$ in THF

over an 18 hour period. Treating a solution of $[(PPh_3)_2N][W(CO)_5(SH)]$

and $DCCl_3$ with an excess of $MeC(=O)Cl$ quantitatively gave

$[(Ph_3P)_2N][W(CO)_5Cl]$ whose solution IR spectrum in $CH_2Cl_2$ and visible

spectrum in MeCN were the same as those of an authentic sample ((87)

substituting refluxing THF for hot diglyme).

An authentic sample of $[W(CO)_5(SC(=O)Me)]^-$ was prepared by re-

fluxing $W(CO)_6$ and $[MeC(=O)S]^-$ in THF (Equation 38). A slight excess of

$$-38-\quad W(CO)_6 + [MeC(=O)S]^- \xrightarrow[\text{reflux}]{\text{THF}} [W(CO)_5(SC(=O)Me)]^- + CO\uparrow$$
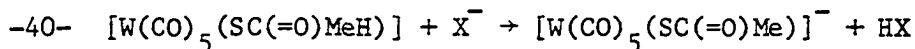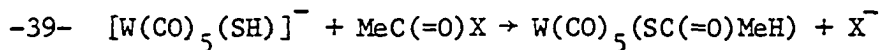
$W(CO)_6$ was employed to guarantee complete conversion of the ionic

reactant to products; progress of the reaction was monitored by the

amount of CO evolved.

An unusual feature of the acyl transfer reactions between

$[W(CO)_5(SH)]^-$ and $MeC(=O)OC(=O)Me$ (equation 36), or

$MeC(=O)O(2,4-(NO_2)_2C_6H_3)$ (Equation 37) was the transfer of the H on S to

the leaving groups (X = $[MeC(=O)O]^-$ and $[2,4-(NO_2)_2C_6H_3O]^-$, respectively)

(Scheme IV). Movement of the proton to the leaving groups, suggests an

Scheme IV:

-39- $[W(CO)_5(SH)]^- + MeC(=O)X \rightarrow W(CO)_5(SC(=O)MeH) + X^-$

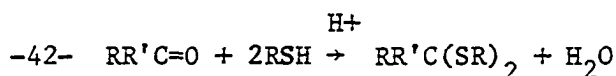-40- $[W(CO)_5(SC(=O)MeH)] + X^- \rightarrow [W(CO)_5(SC(=O)Me)]^- + HX$

enhanced acidity of the coordinated MeC(=O)SH ligand (pka of

MeC(=O)OH=4.75, 2,4-$(NO_2)_2C_6H_3OH$, 3.96; and MeC(=O)SH, 3.33 (88)).

Coordination of $H_2S$ in $[Ru(NH_3)SH_2]^{2+}$ lowered its pka value by three

units (17) (Chapter I, Section B).

c. Fragmentation reactions with $[W(CO_5(SH)]^-$ (Figures 4 and 5)

Thiols, RSH, react with ketones or aldehydes in the presence of an

acid (a catalyst) to give a hemithioacetal (Equation 41) or thioacetal

(Equation 42) (89).

$$\text{-41-} \quad RR'C=O + RSH \xrightarrow{H+} RR'C(OH)SR$$

$$\text{-42-} \quad RR'C=O + 2RSH \xrightarrow{H+} RR'C(SR)_2 + H_2O$$

A mixture of $CF_3C(=O)CF_3$ and $H_2S$ in a bomb at 80°C gave a hemithioacetal,

$(CF_3)_2C(OH)SH$ (90). Paralleling the apparent inertness of ketones and

aldehydes to RSH at room temperature under neutral conditions,

$[W(CO)_5(SH)]^-$ did not appear to react with the carbonyl C of ketones

and aldehydes.

Stirring equimolar amounts of MeC(=O)Me or HC(=O)$(p-Me_2NC_6H_4)$ with
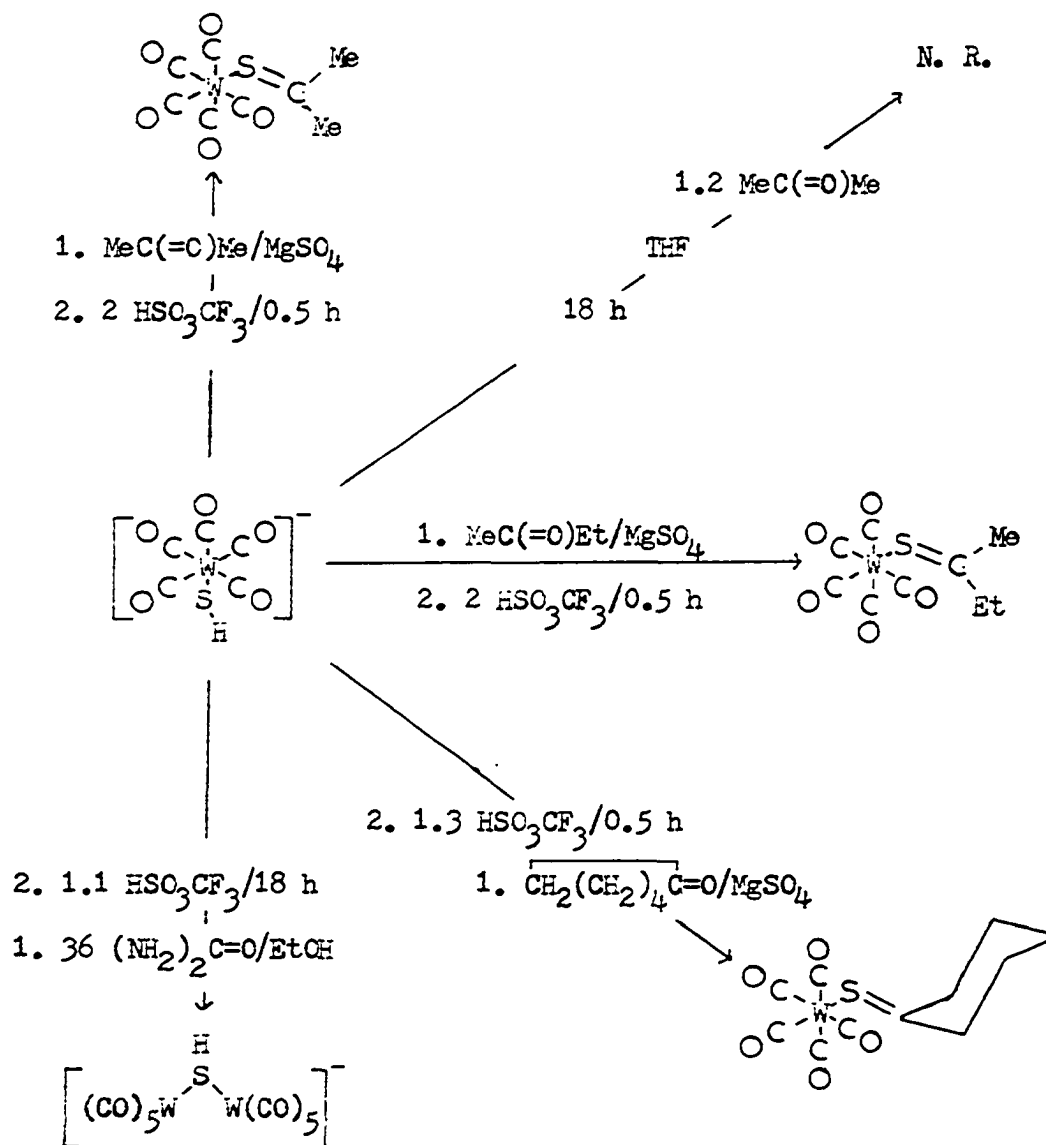
$[W(CO)_5(SH)]^-$ in THF at room temperature and obtaining solution IR

Figure 4.   Reactivity of carbonyl, C=O, containing reagents with
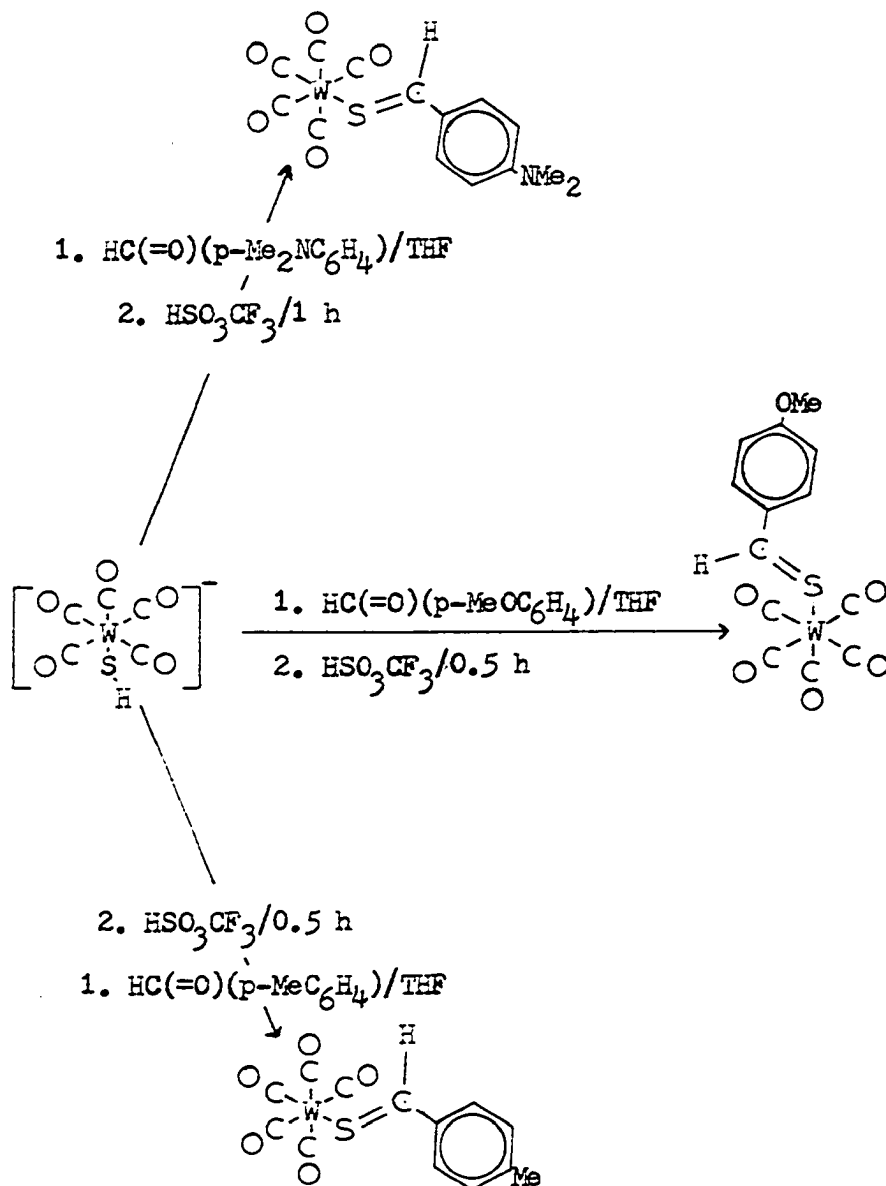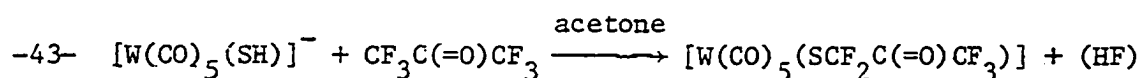[W(CO)$_5$(SH)]$^-$ (fragmentations)

Figure 5. Reactivity of reagents that contain the carbonyl group, C=O, with $[W(CO)_5(SH)]^-$ (fragmentations)
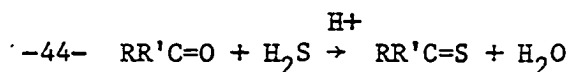
spectra of the reaction mixtures after 18 hours demonstrated that no

reaction had taken place with $[W(CO)_5(SH)]^-$. Condensing an excess of

$CF_3C(=O)CF_3$ into a mixture of $NEt_4[W(CO)_5(SH)]$ and acetone at $-72°C$

and stirring the resultant mixture for 2 hours at $-72°C$ and an additional

16 hours at room temperature gave $NEt_4[W(CO)_5(SCF_2C(=O)CF_3)]$ (Equation

43). A suspension of $NEt_4[W(CO)_5(SH)]$ and acetone was procured according

$$-43-\quad [W(CO)_5(SH)]^- + CF_3C(=O)CF_3 \xrightarrow{\text{acetone}} [W(CO)_5(SCF_2C(=O)CF_3)] + (HF)$$
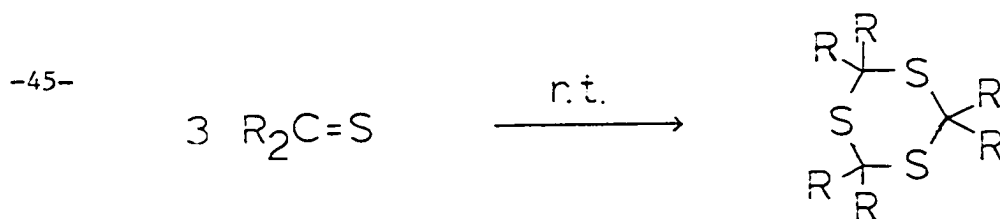
to Scheme I. Acetone was substituted for THF solvent in Equation 14, and

an excess of $CF_3C(=O)CF_3$ was employed to insure complete reaction of the

ionic reactant.

Reaction of $CF_3C(=O)CF_3$ with $[W(CO)_5-(SH)]^-$ (Equation 43) did not

parallel the analogous reaction of $CF_3C(=O)CF_3$ with $H_2S$ (above). Typically,

the carbonyl carbon of $CF_3C(=O)CF_3$ is attacked by nucleophiles to give

addition products (91); however, substitution for $F^-$ by a nucleophile is

commonly observed as fluorocarbons have increased susceptibility to

nucleophilic attack owing to withdrawal of electron density onto the

fluorine atoms (92). This substitution reaction (Equation 43) is in-

cluded in Figure 3.

Preparations and reactions of thioketones and thioaldehydes have

been independently reviewed by Campaigne (93) and Mayer (94). Thio-

ketones are prepared by the reaction of a ketone with $H_2S$ in the presence

of an acid (Equation 44); the success of this procedure is dependent on

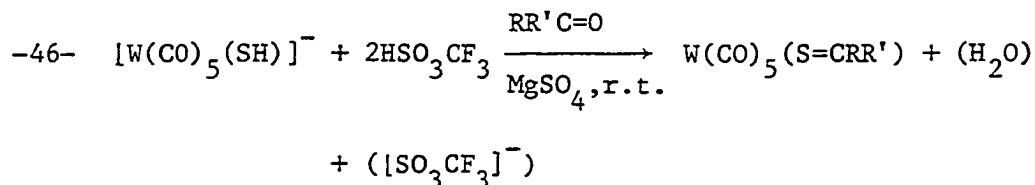$$-44-\quad RR'C=O + H_2S \xrightarrow{H+} RR'C=S + H_2O$$

the temperature of the reaction mixture. In the temperature range -80°C

to -40°C thioketones are predominantly produced, but from -25°C to room

temperature gemdithiols, $R_2C(SH)_2$ (Equation 42), are preferentially

formed. Aliphatic thioketones and both aliphatic and aromatic

thioaldehydes are intensely colored substances that decompose to trithianes,

Equation 45, at room temperature (except $t-Bu_2C=S$ (95)). A number of

$\alpha,\beta$-unsaturated thioaldehydes, the first examples of stable thioaldehyde

-45-

$$3 \ R_2C=S \quad \xrightarrow{r.t.}$$
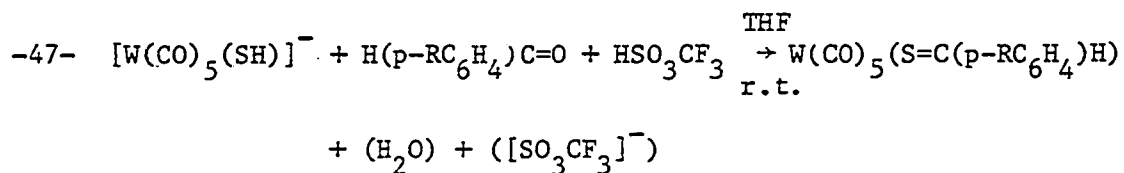


monomers at room temperature, have been isolated recently (96). Reaction

of $[W(CO)_5(SH)]^-$ with ketones and aldehydes in the presence of acid are

similar to the low temperature reaction of $H_2S$ with ketones and alde-

hydes (Equation 44).

Fragmentation of the oxygen atom, O, from aliphatic ketones by

acidifying mixtures of $\lfloor W(CO)_5(SH)\rfloor^-$ and ketones resulted in

$W(CO)_5(S=CR'R)$ where $R=R'=Me$; $R=Me$, $R'=Et$; $R'=R=\overline{CH_2C(=S)(CH_2)_3CH_2}$ (Equation

46). Treating a suspension of 0.498 g (0.556 mmole) of

-46- $\lfloor W(CO)_5(SH)\rfloor^- + 2HSO_3CF_3 \xrightarrow[\text{MgSO}_4,\text{r.t.}]{RR'C=O} W(CO)_5(S=CRR') + (H_2O)$

$+ (\lfloor SO_3CF_3\rfloor^-)$

[(Ph$_3$P)$_2$N][W(CO)$_5$(SH)], excess MgSO$_4$, and 15 ml of acetone at room temperature with 80 µl (1.2 mmole) of HSO$_3$CF$_3$ gave W(CO)$_5$(S=CMe$_2$). Isolation was effected by concentrating the resultant reaction mixture to a residue in vacuo and subliming red crystals of the product in 24% yield from the residue. Solution IR (hexanes) and $^1$H NMR (DCCl$_3$) spectra of this product were the same as those of an authentic sample of W(CO)$_5$(S=CMe$_2$) (97). Similarly, W(CO)$_5$(S=CEtMe) and W(CO)$_5$(S=$\overline{C(CH_2)_4CH_2}$) were prepared in low yield (ca. 10%) without isolation and identified by their solution IR spectra in hexanes (e.g. 2067 cm$^{-1}$(w), 1976(w), 1948 (vs), 1936(m) (97) and 2069 cm$^{-1}$(w), 1980(w), 1946(vs), 1936(m), respectively). Reactions were fast; MgSO$_4$, a desiccant, was added to the reaction mixture to remove H$_2$O which presumably was generated as a reaction product. Using two parts of HSO$_3$CF$_3$ in Equation 46 gave the highest yield (24%) of W(CO)$_5$(S=CMe$_2$); with one part of HSO$_3$CF$_3$ the yield of this product was 14%. Performing the reaction in a ketone solvent was necessary; no evidence for W(CO)$_5$(S=CMe$_2$) was found in the hexanes soluble portion of the residues which resulted from consecutively treating equimolar amounts of [W(CO)$_5$(SH)]$^-$ and acetone in THF with one part of HSO$_3$CF$_3$ and concentrating the reaction mixture in vacuo.
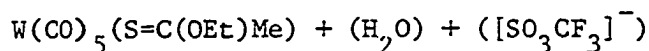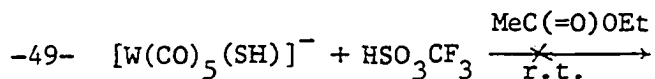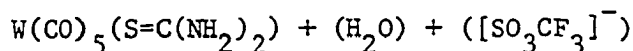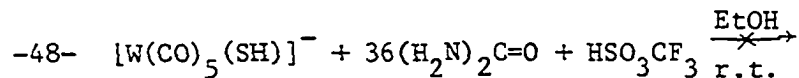
Thioaldehyde complexes (W(CO)$_5$(S=C(p-RC$_6$H$_4$)H) where R = Me$_2$N, MeO, Me) were prepared according to Equation 47. Yellow reaction mixtures of [W(CO)$_5$(SH)]$^-$, H(p-RC$_6$H$_4$)C=O, and THF rapidly turned purple,

$$-47- \quad [W(CO)_5(SH)]^- + H(p\text{-}RC_6H_4)C=O + HSO_3CF_3 \xrightarrow[\text{r.t.}]{\text{THF}} W(CO)_5(S=C(p\text{-}RC_6H_4)H)$$
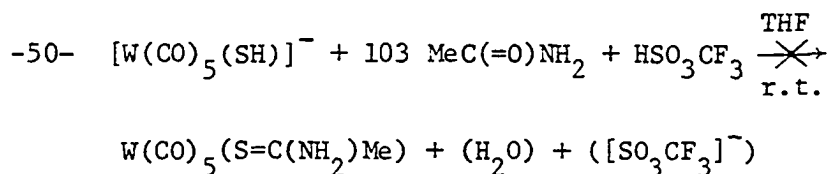
$$+ (H_2O) + ([SO_3CF_3]^-)$$

the color of the thioaldehyde complexes in solution, with the addition of

$HSO_3CF_3$ at room temperature. Addition of a desiccant ($MgSO_4$ above)

was unnecessary; it may not be needed in Equation 46. Yellow plates of

$W(CO)_5(S=C(p-Me_2NC_6H_4)H)$ were metallic in appearance;

$W(CO)_5(S=C(p-RC_6H_4)H)$ where R = MeO, Me were isolated as purple-black

needles.

Whereas preparation of aliphatic thioketone complexes by Equation 46

seemed to be general (e.g. $MeC(=O)Me$, $MeC(=O)Et$, and $\overline{CH_2(CH_2)_4C=O}$ reacted

to give some product), arylthioaldehyde complexes (Equation 47) were

obtained only when electron-releasing groups ($Me_2N-$, MeO-, and Me- (98))

were bonded to the para position of the aryl ring. Thioaldehyde complexes

were not obtained by executing the procedures of Equation 47 with

$HMeC=O$, $HPhC=O$, $H(p-ClC_6H_4)C=O$, $H(p-O_2NC_6H_4)C=O$, $H(m-O_2NC_6H_4)C=O$, and

$H(CH_2=CH)C=O$ which were substituted for $H(p-RC_6H_4)C=O$.

Attempts to prepare pentacarbonyltungsten complexes of thiourea

(Equation 48), ethylthioacetate (Equation 49), and thioacetamide (Equation

50) were unsuccessful. A mixture of 0.180g (0.201 mmole) of

$$-48- \quad [W(CO)_5(SH)]^- + 36(H_2N)_2C=O + HSO_3CF_3 \xrightarrow[\text{r.t.}]{\text{EtOH}}\!\!\!\!\!\times$$

$$W(CO)_5(S=C(NH_2)_2) + (H_2O) + ([SO_3CF_3]^-)$$

$$-49- \quad [W(CO)_5(SH)]^- + HSO_3CF_3 \xrightarrow[\text{r.t.}]{\text{MeC(=O)OEt}}\!\!\!\!\!\times$$

$$W(CO)_5(S=C(OEt)Me) + (H_2O) + ([SO_3CF_3]^-)$$

$$-50-\quad [W(CO)_5(SH)]^- + 103\ MeC(=O)NH_2 + HSO_3CF_3 \xrightarrow[\text{r.t.}]{\text{THF}}$$

$$W(CO)_5(S=C(NH_2)Me) + (H_2O) + ([SO_3CF_3]^-)$$

$[(PH_3P)_2N][W(CO)_5(SH)]$, 0.432 g (7.20 mmole) of $(H_2N)_2C=O$, and

10 ml of EtOH was treated with 20 µl (0.23 mmole) of $HSO_3CF_3$; this mixture

was stirred for 18 hours. Consecutively, reducing the resultant yellow

reaction mixture to a residue in vacuo, extracting the diethylether

soluble portion of the residue, and concentrating the extracts to a foam

in vacuum gave $[(Ph_3P)_2N][\mu-HS(W(CO)_5)_2]$ in 84% yield (based on

$[(Ph_2P)_2N][W(CO)_5(SH)]$) (Figure 4). Solution IR $(CH_2Cl_2)$ and $^1H$ NMR

$(DCCl_3)$ spectra of this product and of $NEt_4[\mu-HS(W(CO)_5)_2]$ (Tables 7 and

15) were identical (e.g. $^1H$ NMR of $[(Ph_3P)_2N][\mu-HS(W(CO)_5)_2]$ in $DCCl_3$

2.50 τ (m) $[(Ph_3P)_2N]^+$ and 11.68 τ (s) S$\underline{H}$ with relative integrated

intensities of 30 to 1, respectively). Similarly, acidifying a mixture of

$[W(CO)_5(SH)]^-$ and either $MeC(=O)OEt$ or a 103 molar excess of $MeC(=O)NH_2$

in THF gave the same product, $[\mu-HS[W(CO)_5]_2]^-$, which was identified

by its solution IR spectrum in $CH_2Cl_2$.

    d. <u>Reactions with $[\mu-HS[W(CO)_5]_2]^-$ (Figure 6)</u>    Organic carbonyl

containing reagents appeared inert to $[\mu-HS[W(CO)_5]_2]^-$. A solution of

$[\mu-HS(W(CO)_5]_2]^-$ and acetone was treated with 2 parts of $Ph_2C=C=O$ or 1

part of $MeN=C=O$; the resultant mixtures were stirred for 18 hours at

room temperature without reaction. No reaction occurred between equimolar

amounts of $[\mu-HS[W(CO)_5]_2]^-$ and $MeC(=O)O(2,4-(O_2N)_2C_6H_3)$ in MeCN at room

temperature over a 4 hour period. Coordination of the mercapto ligand of

N. R.

↑
|

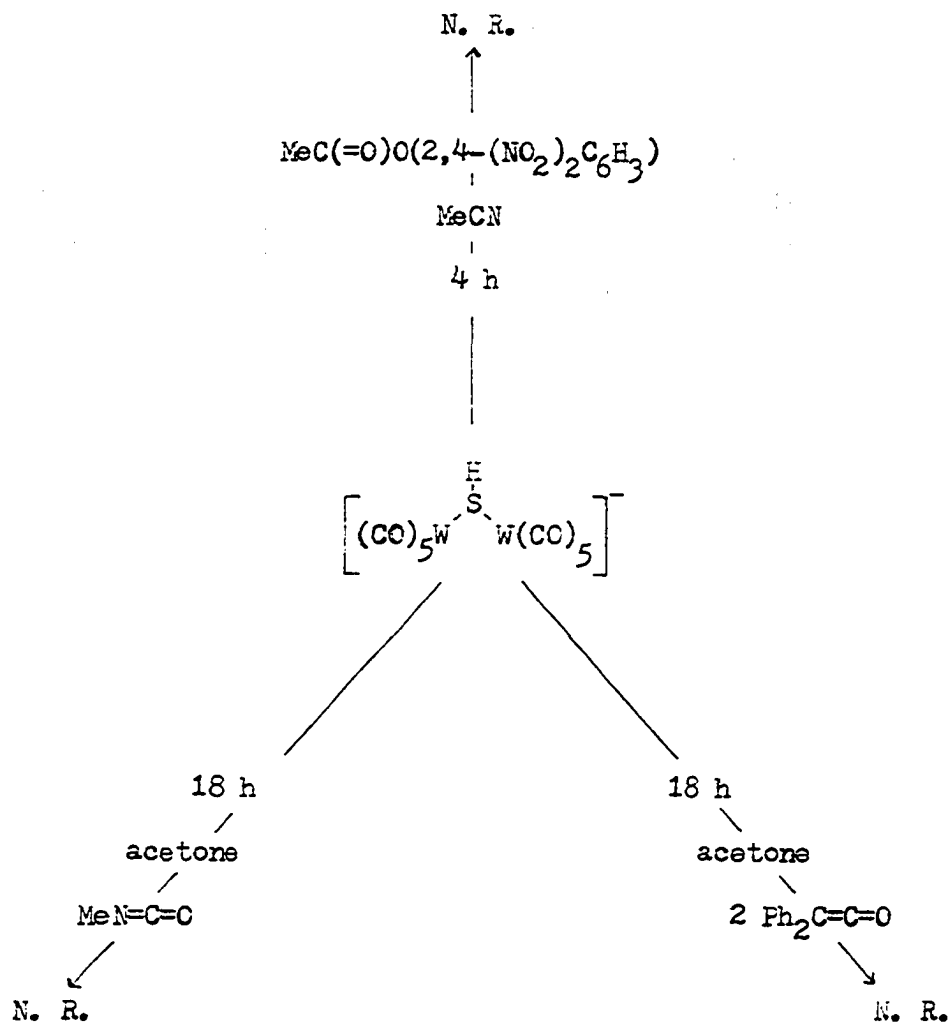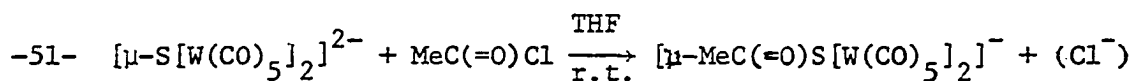MeC(=O)O(2,4-(NO$_2$)$_2$C$_6$H$_3$)
|

MeCN
|

4 h
|
|
|
|

$$\left[(CO)_5\overset{\overset{\displaystyle H}{\mid}}{W}\overset{S}{\diagdown}W(CO)_5\right]^-$$

18 h                                    18 h
/                                          \
acetone                              acetone
/                                          \
MeN=C=O                          2 Ph$_2$C=C=O
/                                          \
↙                                          ↘
N. R.                                    N. R.

Figure 6.   Reactivity of [μ-HS[(W(CO)$_5$]$_2$]$^-$ with reagents which contain the carbonyl, C=O, functionality

$[W(CO)_5(SH)]^-$ to another $W(CO)_5$ group, which increased the acidity of the hydrogen (this chapter, Section A.2), lowered the reactivity of the coordinated ligand to organic carbonyl containing reagents.
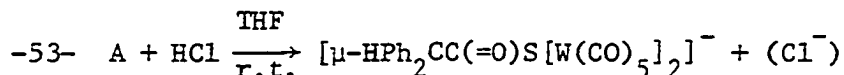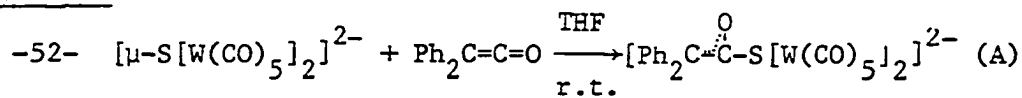
    e. Reactions with $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ (Figure 7)    Preparation of $[\mu\text{-}MeC(=O)S[W(CO)_5]_2]^-$ was accomplished in accordance with Equation 51.

-51-  $[\mu\text{-}S[W(CO)_5]_2]^{2-} + MeC(=O)Cl \xrightarrow[\text{r.t.}]{\text{THF}} [\mu\text{-}MeC(=O)S[W(CO)_5]_2]^- + (Cl^-)$

A green suspension of the binuclear dianion, $[\mu\text{-}S[W(CO)_5]_2]^{2-}$, was prepared following Equation 19 and was employed in situ. A slight molar excess of $MeC(=O)Cl$ was used to guarantee complete conversion of the binuclear dianion to the ionic product. Reaction was rapid; the reaction mixture turned yellow-brown with the addition of $MeC(=O)Cl$. The product, $NEt_4[\mu\text{-}MeC(=O)S[W(CO)_5]_2]^-$, was precipitated from a concentrated aqueous solution of $[NEt_4]Br$ to effect replacement of trace amounts of $Na^+$ counter cation with $[NEt_4]^+$.

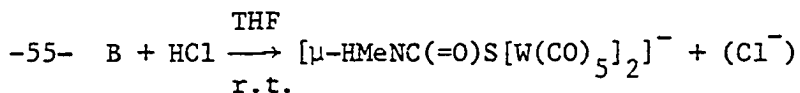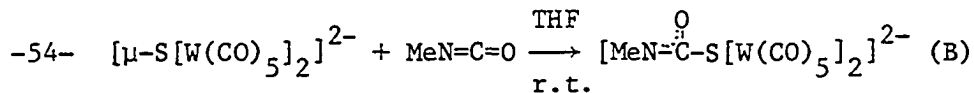    Treating a yellow suspension of $NEt_4Na[\mu\text{-}Ph_2CC(=O)S[W(CO)_5]_2]$ (A) or $NEt_4Na[\mu\text{-}MeNC(=O)S[W(CO)_5]_2]$ (B) with HCl (g) gave $NEt_4[\mu\text{-}HPh_2CC(=O)S[W(CO)_5]_2]$ (Scheme V) and $NEt_4[\mu\text{-}HMeNC(=O)S[W(CO)_5]_2]$

Scheme V:

-52-  $[\mu\text{-}S[W(CO)_5]_2]^{2-} + Ph_2C=C=O \xrightarrow[\text{r.t.}]{\text{THF}} [Ph_2C\overset{O}{\overset{\|}{\text{-}}}C\text{-}S[W(CO)_5]_2]^{2-}$ (A)

-53-  $A + HCl \xrightarrow[\text{r.t.}]{\text{THF}} [\mu\text{-}HPh_2CC(=O)S[W(CO)_5]_2]^- + (Cl^-)$

(Scheme VI), respectively. A green suspension of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ was

Scheme VI:

-54-   $[\mu\text{-}S[W(CO)_5]_2]^{2-} + MeN=C=O \xrightarrow[\text{r.t.}]{\text{THF}} [MeN=\overset{O}{\overset{\|}{C}}\text{-}S[W(CO)_5]_2]^{2-}$ (B)

-55-   B + HCl $\xrightarrow[\text{r.t.}]{\text{THF}} [\mu\text{-}HMeNC(=O)S[W(CO)_5]_2]^- + (Cl^-)$

prepared according to Equation 19 and was treated with a slight excess of

$Ph_2C=C=O$ or $MeN=C=O$. Reaction took place quickly giving a yellow-brown

mixture. Products, A and B, were not isolated or characterized; the color

change, green to yellow, was indicative of their formation in Equations 52

and 54. After the resultant mixtures had stirred for 2 hours, an equi-

valent amount of HCl was added to the reaction mixture. Products,

$NEt_4[\mu\text{-}HPh_2CC(=O)S[W(CO)_5]_2]$ and $NEt_4[\mu\text{-}HMeNC(=O)S[W(CO)_5]_2]$, were

precipitated from a concentrated aqueous solution of $[NEt_4]Br$ to insure

that $[NEt_4]^+$ was the only countercation present. Unlike

$NEt_4[\mu\text{-}HMeNC(=O)S[W(CO)_5]_2]$ which was prepared cleanly,

$NEt_4[\mu\text{-}HPh_2CC(=O)S[W(CO)_5]_2]$ was obtained with $NEt_4[W(CO)_5(SC(=O)CPh_2H)]$

(ca. 15%). Repeated attempts to fractionally crystallize the desired

product, $NEt_4[\mu\text{-}HPh_2CC(=O)S[W(CO)5]_2]$, from the mononuclear impurity

failed. Solution $(CH_2Cl_2)$ and solid phase (KBr) IR spectral features

(e.g. 2072 $cm^{-1}$(vw), 2061(w), 1973(sh), 1937(vs), 1913(s), 1870(m) and

1680 $cm^{-1}$(vw) $\nu(C=O)$) demonstrated that $NEt_4[\mu\text{-}HPh_2CC(=O)S[W(CO)_5]_2]$ was

present as the major component of the mixture.

No reaction occurred between $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ and

$H(p\text{-}Me_2NC_6H_4)C=O$ in THF over an 18 hour period at room temperature;

treating the resultant green suspension with 2 parts of $HSO_3CF_3$ gave

$W(CO)_5(S=C(p-Me_2NC_6H_4)H)$ (Equation 56) in 19% yield. Reaction took

-56- $[\mu-S[W(CO)_5]_2]^{2-}$ + $H(p-Me_2NC_6H_4)C=O$ + 2 $HSO_3CF_3$ $\xrightarrow[\text{r.t.}]{\text{THF}}$

$W(CO)_5(S=C(p-Me_2NC_6H_4)H)$ + $(H_2O)$ + $(2[SO_3CF_3]^-)+(W(CO)_5(THF))$

place quickly. Consecutively, concentrating the resultant purple

reaction mixture to a residue in vacuum, eluting the 40% (V/V) $CH_2Cl_2/$

hexanes soluble portion over Florisil, and concentrating the purple

eluate under a stream of PPN gave lustrous, golden plates of the

product. A solution IR spectrum in hexanes and melting point of this

product were the same as those of $W(CO)_5(S=C(p-Me_2NC_6H_4)H$ (Tables 2 and

6).
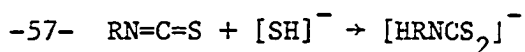
The order of reactivity of the compounds with organic carbonyl con-

taining reagents followed the sequence (most reactive to least):

$[\mu-S[W(CO)_5]_2]^{2-}$ ≃ $\lfloor W(CO)_5(SH)]^-$ >>> $[\mu-HS[W(CO)_5]_2]^-$. Both

$\lfloor\mu-S[W(CO)_5]_2]^{2-}$ and $[W(CO)_5(SH)]^-$ underwent addition (e.g. $Ph_2C=C=O$ and

$MeN=C=O$), acyl transfer (e.g. $MeC(=O)Cl$ or $MeC(=O)OC(=O)Me$, respectively),

and fragmentation (e.g. $H(p-Me_2NC_6H_4)C=O$) reactions with the reagents; both

of them failed to react with $H(p-Me_2NC_6H_4)C=O$ in the absence of acid.

Organic carbonyl containing reagents (e.g. $Ph_2C=C=O$, $MeN=C=O$, and

$MeC(=O)O(2,4-(NO_2)_2C_6H_3))$ were inert to $[\mu-HS\lfloor W(CO)_5]_2]^-$. Exchanging a

proton for a $W(CO)_5$ group on a coordinated sulfur atom did not significant-

ly affect the reactivity of the ligand (e.g. $\lfloor W(CO)_5(SH)]^-$ and

$[\mu-S[W(CO)_5]_2]^{2-}$ have similar reactivities with organic carbonyl containing

reagents).

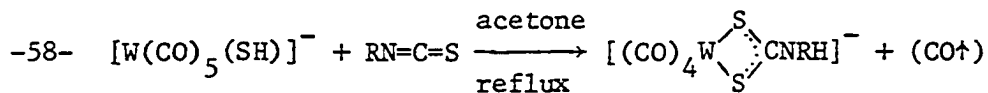2. Reactions of imide containing reagents with [W(CO)$_5$(SH)]$^-$ and [μ-HS[W(CO)$_5$]$_2$]$^-$

    a. Addition reactions with [W(CO)$_5$(SH)]$^-$ and [μ-HS[W(CO)$_5$]$_2$]$^-$ (heterocumulenes) (Figure 8)    Ulrich (99) and Assony (100) have independently reviewed the preparations and reactions of alkylisothiocyanates. Sodium hydrogensulfide, NaSH, reacts with RN=C=S where R=Bz, Ph to give alkyldithiocarbamates (Equation 57) (101).

$$-57-\quad RN{=}C{=}S + [SH]^- \rightarrow [HRNCS_2]^-$$

This reaction, an addition of [SH]$^-$ to the C=N bond, is similar to the reaction of [W(CO)$_5$(SH)]$^-$ with RN=C=S.

Preparation of [W(CO)$_4$(S$_2$CNRH)]$^-$ where R = Me, Et, Ph was effected according to Equation 58. A suspension of NEt$_4$[W(CO)$_5$(SH)] and acetone

$$-58-\quad [W(CO)_5(SH)]^- + RN{=}C{=}S \xrightarrow[\text{reflux}]{\text{acetone}} [(CO)_4W{\overset{S}{\underset{S}{\diagup\!\diagdown}}}CNRH]^- + (CO\uparrow)$$

(Scheme I) was treated with a slight excess of RN=C=S; the resultant mixture was refluxed (acetone b.p. 56°C) for 2 hours. Partitional crystalliaation of the ionic products from acetone, diethylether, and hexanes gave yellow crystals of NEt$_4$[W(CO)$_4$(S$_2$CNMeH)] and brown tars of NEt$_4$[W(CO)$_4$(S$_2$CNRH)] where R = Et, Ph. Solution IR spectra of these tars in CH$_2$Cl$_2$ (e.g. R = Et, 1999 cm$^{-1}$(m), 1873(vs), 1841(s), 1795(s) and R = Ph, 1999 cm$^{-1}$(m), 1876(vs), 1843(s), 1800(s)) and samples of these products which were prepared by alternate methods, Equation 59 and 60, were
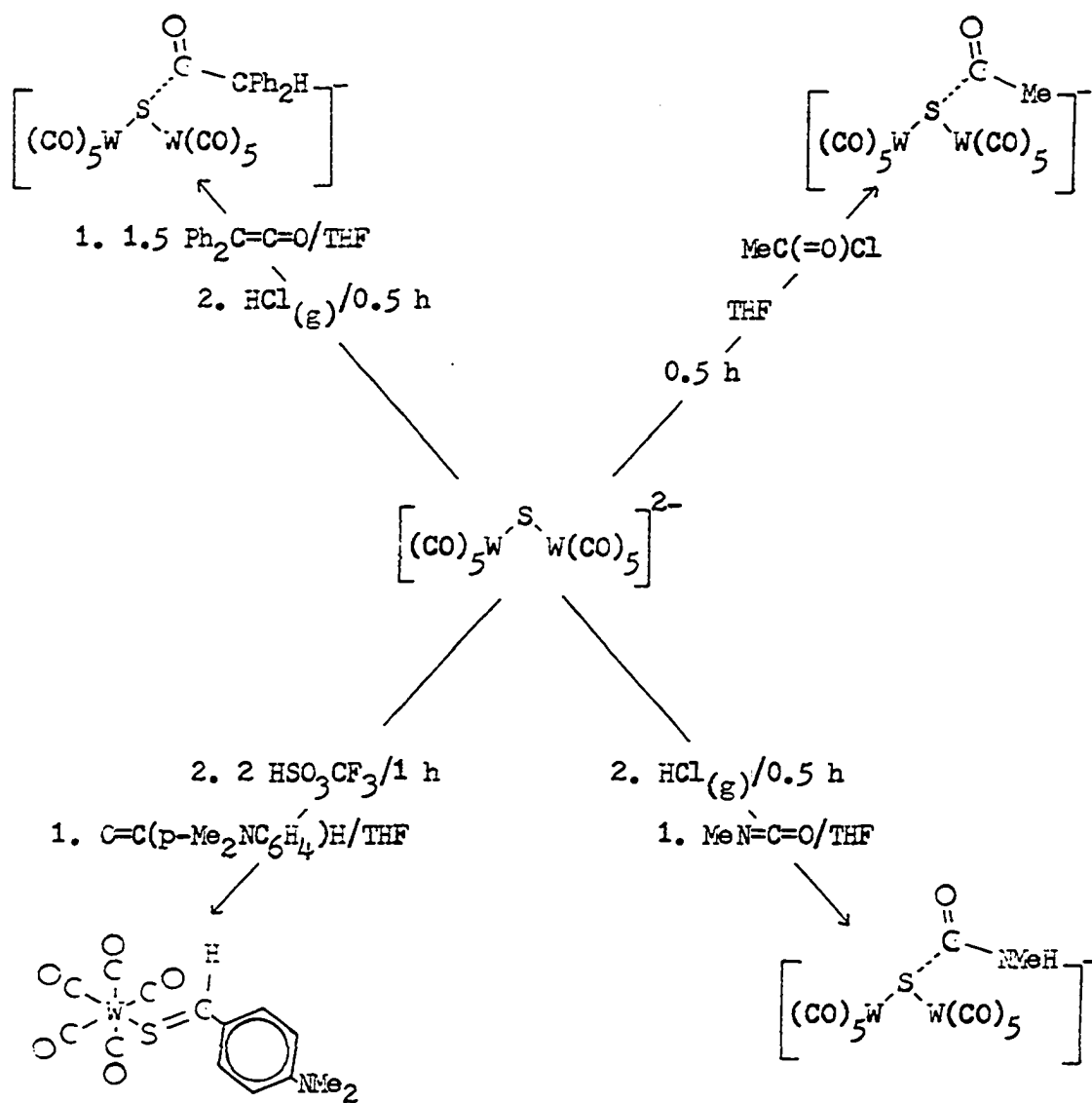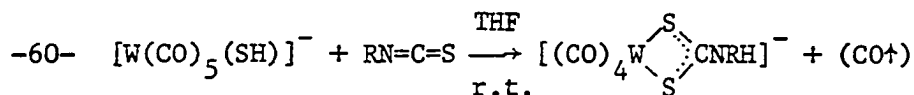
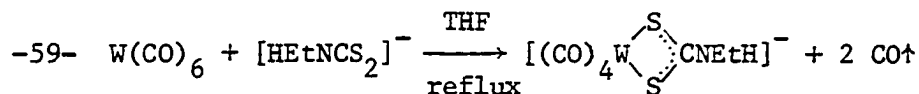Figure 7. Reactivity of carbonyl, C=O, containing reagents with $[\mu$-S$[W(CO)_5]_2]^{2-}$

$^a$R = Me, $t_{1/2}$ = 11.3 h.

$^b t_{1/2}$ = 2.0 h.

Figure 8. Reactivity of heterocumulenes that contain the imide, C=N, group with [W(CO)$_5$(SH)]$^-$ and [$\mu$-HS[W(CO)$_5$]$_2$]$^-$

-59- $W(CO)_6 + [HEtNCS_2]^- \xrightarrow[\text{reflux}]{\text{THF}} [(CO)_4W\overset{S}{\underset{S}{\diagdown}}CNEtH]^- + 2\ CO\uparrow$

-60- $[W(CO)_5(SH)]^- + RN{=}C{=}S \xrightarrow[\text{r.t.}]{\text{THF}} [(CO)_4W\overset{S}{\underset{S}{\diagdown}}CNRH]^- + (CO\uparrow)$

identical. Procedures employed for the preparation and isolation of

$[(Ph_2P)_2N][W(CO)_4(S_2CNEtH)]$ (foams) via Equation 59 were similar to those

used to obtain $[(Ph_3P)_2N][W(CO)_5(SH)]$ (this chapter, Section A.1). For

example, a slight excess of $W(CO)_6$ was employed and progress of the

reaction was monitored by the amount of CO evolved. In Equation 60 a

slight excess of RN=C=S where R = Me, Et, Ph was used; reaction was

slow at room temperature (e.g. $t_{1/2}$ for MeN=C=S = 11.3 hours (Chapter II,

Section A.9)). Partitional crystallization of the ionic products from

acetone, diethylether, and hexanes systems gave orange crystals of

$[(Ph_3P)_2N][W(CO)_4(S_2CNPhH)]\cdot 0.61\ MeC({=}O)Me\cdot 0.47\ Et_2O$ and tars of

$[(Ph_3P)_2N][W(CO)_4(S_2CNRH)]$ where R = Me, Et.

Attempts to convert $[(Ph_3P)_2N][W(CO)_4(S_2CNEtH)]$, which was tenta-

tively identified by its solution IR spectrum in $CH_2Cl_2$ (above), to an

isolable crystalline complex containing the $[HEtNCS_2]^-$ ligand were un-

successful. No reaction occurred when an excess amount of $PPh_3$ was stirred

with $[W(CO)_4(S_2CNEtH)]^-$ at room temperature in THF for 18 hours.

Stirring $[W(CO)_4(S_2CNEtH)]^-$ with an excess amount of MeI in THF at room

temperature for 18 hours gave $[(Ph_3P)_2N][W(CO)_5I]$ (28% yield). This

product was identified by its solution IR and visible spectra which

were the same as the spectra obtained from an authentic sample of

$NEt_4[W(CO)_5I]$ (Chapter II, Section B.2).

Reaction of isothiocyanates with $[W(CO)_5(SH)]^-$ (Equation 60) occurred

in two steps (Scheme VII). Precedence for both monodentate and bidentate

<u>Scheme VII</u>:

-61-  $[W(CO)_5(SH)]^- + RN=C=S \rightarrow [W(CO)_5(SC(=S)NRH)]^-$

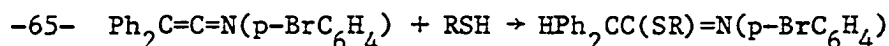-62-  $[W(CO)_5(SC(=S)NRH)]^- \rightarrow [(CO)_4W\overset{S}{\underset{S}{<}}CNRH]^- + (CO\uparrow)$

coordination by dithiocarbamates has been established by the isola-

tion of $CpFe(CO)(S_2CNMe_2)$ (Equation 63) (102) and $CpFe(CO)_2(SC(=S)NMe_2)$

(Equation 64) (103). By repeatedly scanning the 2200 $cm^{-1}$ to 1700 region

-63-  $[CpFe(CO)_2]_2 + Me_2NC(=S)SSC(=S)NMe_2 \xrightarrow[18h, r.t.]{C_6H_{12}}$

$Cp(CO)Fe\overset{S}{\underset{S}{<}}CNMe_2$

-64-  $CpFe(CO)_2Cl + NaS_2CNMe_2 \xrightarrow[r.t.]{acetone} CpFe(CO)_2SC(=S)NMe_2$

with the IR spectrophotometer during the course of the reaction of

$MeN=C=S$ with $[(Ph_3P)_2N][W(CO)_5(SH)]$ in THF, a shoulder, which was not

present at the conclusion of the reaction, on the $A^1$ band (2049 $cm^{-1}$)

of $[W(CO)_5(SH)]^-$ suggested that $[W(CO)_5(SC(=S)NRH]^-$ was an intermediate in

the reaction (Equation 61). Furthermore, performing an analogous experi-

ment in $HCCl_3$ gave a greater yield of this intermediate. After equimolar

amounts of $[W(CO)_5(SH)]^-$ and $MeN=C=S$ in $HCCl_3$ were kept at room temperature

for 18 hours, volatile components of the mixture were removed under a

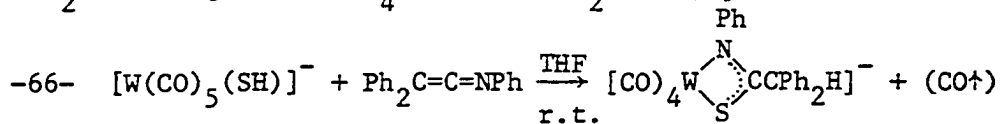stream of PPN. A solution IR spectrum of a portion of the resultant tars

in $CH_2Cl_2$ suggested that $[W(CO)_5(SC(=S)NMeH)]^-$ had been formed almost

quantitatively (e.g. $[W(CO)_5(SC(=S)NMeH)]^-$ 2061 $cm^{-1}$(w), 1966(sh),

1916(vs), 1869(s,br) and $[W(CO)_4(S_2CNMeH)]^-$ 2000 $cm^{-1}$(vw), 1869 (s,br),

1796(w)). Ten days later another solution IR spectrum of a portion

of these tars, which had been stored in an atmosphere of PPN, in $CH_2Cl_2$

showed only $[W(CO)_4(S_2CNMeH)]^-$. Apparently, $[W(CO)_5(SC(=S)NMeH)]^-$ was

converted to $[W(CO)_4(S_2CNMeH)]^-$ with the loss of CO in the absence

of solvent; no additional attempts were made to isolate

$[W(CO)_5(SC(=S)NMeH)]^-$ whose solution IR spectrum in $CH_2Cl_2$ was

virtually identical to the spectrum of $[(Ph_3P)_2N][W(CO)_5(SC(=O)NMeH)]^-$

(Table 4).

Preparations and reactions of ketenimines have been reviewed by

Krow (104). Thiols, RSH where R = Et, n-Pr, Ph, and mercaptides, $[SPh]^-$,

add to the C=C bond of ketenimines, $R_2C=C=NR$, giving thioimidates

(Equation 65) (105). Addition of $[W(CO)_5(SH)]^-$ to ketenimines is prece-

-65-  $Ph_2C=C=N(p-BrC_6H_4) + RSH \rightarrow HPh_2CC(SR)=N(p-BrC_6H_4)$

dented by an organic reaction (Equation 65).

Treating a mixture of $[W(CO)_5(SH)]^-$ and THF with an equimolar amount

of $Ph_2C=C=NPh$ gave $[W(CO)_4(SC(=NPh)CPh_2H)]^-$ (Equation 66). A slight

-66-  $[W(CO)_5(SH)]^- + Ph_2C=C=NPh \xrightarrow[\text{r.t.}]{\text{THF}} [CO]_4W\begin{smallmatrix}Ph\\N\\ \\S\end{smallmatrix}CCPh_2H]^- + (CO\uparrow)$

excess of $Ph_2C=C=NPh$ was employed to guarantee complete conversion of the

ionic reactant to the product; the half-life for the reaction was

2.0 hours (Chapter II, Section A.9). Addition of coordinated SH to the

C=C of $Ph_2C=C=NPh$ to give $[W(CO)_5SC(=NPh)CPh_2H]^-$ (like the reaction of

$Ph_2C=C=O$ with $[W(CO)_5(SH)]^-$ (Equation 26)) presumably preceded the loss

of CO and coordination of N giving the product, $[W(CO)_4(SC(=NPh)CPh_2H)]^-$.

Acidifying a mixture of $[W(CO)_4(SC(=NPh)CPh_2H)]^-$ and THF under an

atmosphere of CO gave a thioacetamide complex (Equation 67). Consecu-

-67-  $[(CO)_4W\overset{\displaystyle N}{\underset{\displaystyle S}{\diagup}}CCPh_2H]^- + HSO_3CF_3 \xrightarrow[CO,r.t.]{THF}$

$W(CO)_5(S=C(NPhH)CPh_2H) + ([SO_3CF_3]^-)$

tively, stirring the resultant mixture for 30 minutes, concentrating

this mixture to a residue in vacuum, extracting the yellow 50/50 (V/V)

hexanes and diethylether soluble portion of the residue, and removing

the volatile components of the extracts under a stream of PPN gave a

yellow amorphous residue of the product in 36% yield. Solution IR

spectra of $W(CO)_5(S=C(NPhH)CPh_2H)$, the product, and an authentic sample

(Chapter II, Section C.6), in hexanes (Table 6) were identical.

Preparation of this product via Equation 67 and the spectrophotometric

data that were obtained from tars of the product in Equation 66 (Tables

5, 9, and 13) confirmed the formulation of $[(PH_3P)_2N][W(CO)_4(SC(=NPh)CPh_2H)]$

as the product in reaction 66.

Phenylmercaptan, PhSH, adds to the C=N bond of $t-BuN=C=Nt-Bu$ in

refluxing benzene to give $t-BuN=C(SPh)Nt-BuH$ (Equation 68) (106).

-68-  $t-BuN=C=Nt-Bu + HSPh \rightarrow t-BuN=C(SPh)Nt-BuH$

Hydrogen sulfide, $H_2S$, was reported to react with carbodiimides according to Equation 69 in a recent review (107). Whereas $[W(CO)_5(SH)]^-$ was inert

$$-69- \quad RN=C=NR + H_2S \rightarrow S=C(NRH)_2$$

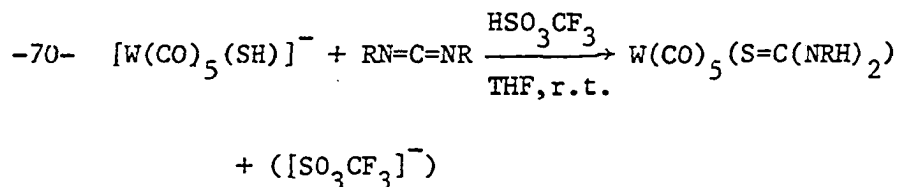to carbodiimides (RN=C=NR), acidification of these mixtures gave dial-kylthiourea complexes which are analogous to the products resulting from the reaction of $H_2S$ with RN=C=NR (Equation 69).

A number of reagents that contained the imide group did not react with $[W(CO)_5(SH)]^-$. Equimolar mixtures of $[W(CO)_5(SH)]^-$ and RN=C=NR (R = i-Pr, $C_6H_{11}$), PhN=C(p-MeOC$_6$H$_4$)H, $CH_2$=N=N, or $\overline{NCH_2CH_2}$ in THF were stirred for 18 hours at room temperature without change in the solution IR spectrum of $[W(CO)_5(SH)]^-$. Similarly, treating $[W(CO)_5(SH)]^-$ with a tenfold excess of $CH_2$=N=N in THF gave no reaction with the complex.

Treating an equimolar mixture of $[W(CO)_5(SH)]^-$ and RN=C=NR where R = i-Pr, $C_6H_{11}$ with an equivalent of $HSO_3CF_3$ gave dialkyl thiourea com-plexes (Equation 70). Reaction took place quickly giving a brown-

$$-70- \quad [W(CO)_5(SH)]^- + RN=C=NR \xrightarrow[\text{THF,r.t.}]{HSO_3CF_3} W(CO)_5(S=C(NRH)_2)$$

$$+ ([SO_3CF_3]^-)$$

yellow reaction mixture. Isolation of $W(CO)_5(S=C(N(C_6H_{11})H)_2)$ was not effected; a solution IR spectrum in $CH_2Cl_2$ (e.g. 2071 cm$^{-1}$(w), 1978(w), 1929(vs), 1895(sh)) of the reaction residue which was obtained by con-centrating the reaction mixture (Equation 70, R = $C_6H_{11}$) in vacuo and of

$W(CO)_5(S=C(Ni-PrH)_2)$ (Table 6) were identical. An authentic sample of

$W(CO)_5(S=C(NPhH)CPh_2H)$ (above) was prepared by Equation 70 substituting

$PhN=C=CPh_2$ for $RN=C=NR$.

Acidification of an equimolar mixture of $[\mu-HS[W(CO)_5]_2]^-$ and

$i-PrN=C=Ni-Pr$ in THF gave $W(CO)_5(S=C(Ni-PrH)_2)$ (Equation 71). After a

mixture of 0.163 g (0.201 mmole) of $NEt_4[\mu-HS[W(CO)_5]_2]$, 32 μl

$$-71-\quad [\mu-HS[W(CO)_5]_2]^- + i-PrN=C=Ni-Pr \xrightarrow[\text{THF,r.t.}]{HSO_3CF_3}$$

$$W(CO)_5(S=C(Ni-PrH)_2) + (W(CO)_5(THF)) + ([SO_3CF_3]^-)$$

(0.211 mmole) of $i-PrN=C=NiPr$, and 10 ml of THF had stirred for an hour

with no change in the solution IR spectrum of $[\mu-HS[W(CO)_5]_2]^-$, the mixture

was treated with 18 μl (0.203 mmole) of $HSO_3CF_3$. Successively, stirring

the mixture for 1 hour, concentrating this mixture to a residue in vacuo,

eluting the $HCCl_3$ soluble portion of the residue over florisil, and

removing the volatile components of the collected yellow eluate in

vacuum resulted in a yellow powder of the product in 58% yield. Its solu-

tion IR spectrum in $CH_2Cl_2$ and melting point were the same as those of

$W(CO)_5(S=C(Ni-PrH)_2)$ (Tables 2 and 6) which was prepared by Equation 70.

b. <u>Fragmentation reactions with $[W(CO)_5(SH)]^-$</u> (Figure 9)

Like the reaction of $H_2S$ with ketones or aldehydes in acid conditions

giving gem-dithiols (this chapter, Section B.1.c), ketimines react with

$H_2S$ to yield gem-dithiols (Equation 72) (108). Thiols also react with

$$-72-\quad Et_2C=Nn-Bu + ex. \ H_2S \rightarrow Et_2C(SH)_2 + BuNH_2$$

Figure 9. Reactivity of imide, C=N, containing reagents with [W(CO)$_5$(SH)]$^-$

Shiff bases (Equation 73) (109). These reactions are not paralleled by

-73-  $ArN=CArH + RSH \rightleftharpoons HArNC(SR)ArH$

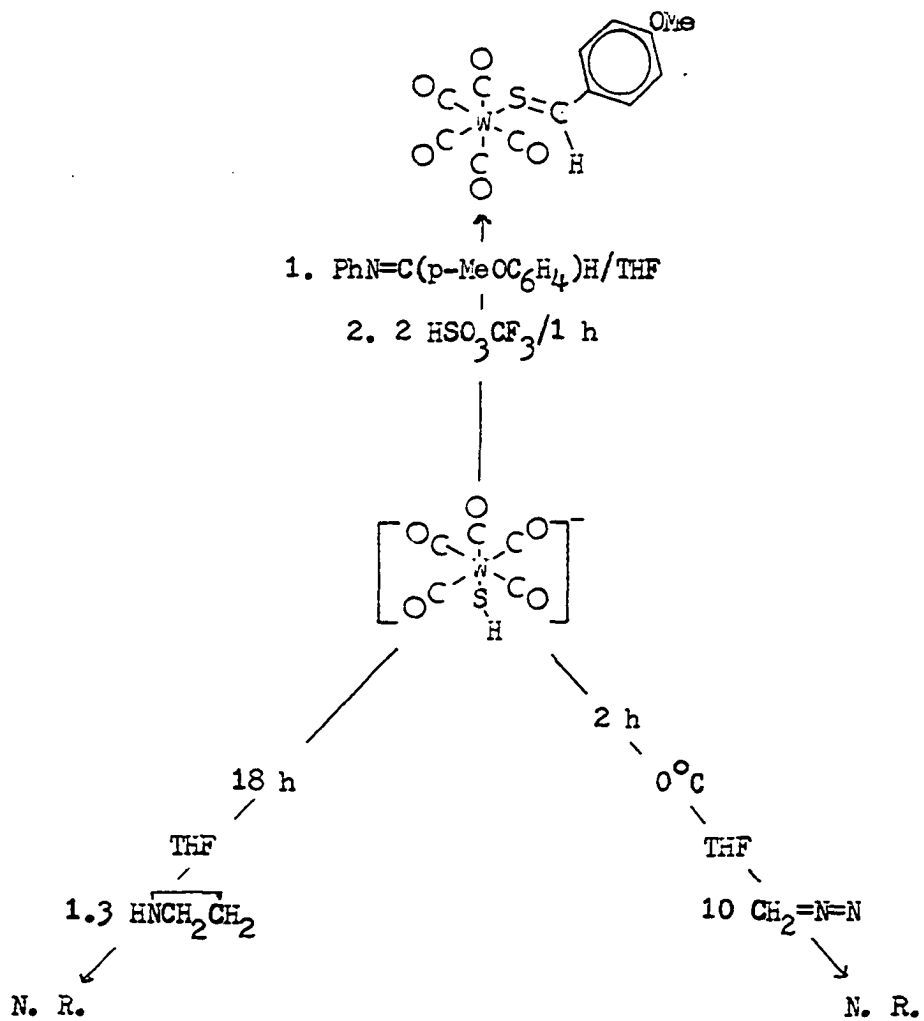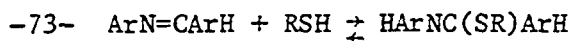the reactions of $[W(CO)_5(SH)]^-$ with Shiff bases.

A thioaldehyde complex was prepared in accordance with Equation 74. A purple suspension of the product was obtained with the addition of 0.1

-74-  $[W(CO)_5(SH)]^- + PhN=C(p-MeOC_6H_4)H \xrightarrow[\text{THF,r.t.}]{2HSO_3CF_3}$

$W(CO)_5(S=C(p-MeOC_6H_4)H + ([PhNH_3][SO_3CF_3]) + ([SO_3CF_3]^-)$

ml (1.13 mmole) of $HSO_3CF_3$ to a mixture, which had stirred for 18 hours without reaction, of 0.501 g (0.559 mmole) of $[(Ph_3P)_2N][(W(CO)_5(SH)]$, 0.120 g (0.570 mmole) of $PhN=C(p-MeOC_6H_4)H$, and 10 ml of THF. After the resultant mixture had stirred for 40 minutes, it was reduced to a residue in vacuo. The 10/90 (V/V) $CH_2Cl_2$/hexanes soluble portion of the residue was eluted through a column of florisil, and the purple eluate was collected under an atmosphere of PPN and concentrated slowly in vacuum giving purple needles of $W(CO)_5(S=C(p-MeOC_6H_4)H)$ in 9% yield. A solution IR spectrum in hexanes and melting point of this product were the same as those of an authentic sample (Tables 2 and 6). Addition of a second equivalent of $HSO_3CF_3$ to remove $PhNH_2$ as $[PhNH_3][SO_3CF_3]$ was unnecessary, no reaction took place between equivalent amounts of $W(CO)_5(S=C(p-Me_2NC_6H_4)H)$ and $PhNH_2$ in THF at room temperature over an 18 hour period. Substituting t-BuN=CMeH, PhN=CPhH, $PhN=C(p-O_2NC_6H_4)H$,

PhN=C(p-Me$_2$NC$_6$H$_4$)H, or HON=CMe$_2$ for PhN=C(p-MeOC$_6$H$_4$)H in Equation 74 did not give thioaldehyde complexes in appreciable yields.

Imide-containing reagents were observed to undergo addition and fragmentation reactions with [W(CO)$_5$(SH)]$^-$. Additions of [W(CO)$_5$(SH)]$^-$ to the C=N bond of RN=C=O or RN=C=S and to the C=C bond of Ph$_2$C=C=NPh were observed at room temperature in THF; thiols, RSH, also add to these bonds. Carbodimides react with [W(CO)$_5$(SH)]$^-$ or [μ-HS[W(CO)$_5$]$_2$]$^-$ in the presence of acid to give dialkylthiourea complexes. A thioaldehyde complex was obtained by fragmentation of NPh from a Schiff base, PhN=C(p-MeOC$_6$H$_4$)H, by [W(CO)$_5$(SH)]$^-$ in the presence of acid.

The order of reactivity for addition to the C=X bonds where X = O, S, N, C in heterocumulenes by [W(CO)$_5$(SH)]$^-$ followed the order (most reactive to least): C=C>C=N>C=S>C=O. No evidence for addition to the C=O bond was obtained from the reactions of [W(CO)$_5$(SH)]$^-$ with O=C=O, O=C=S, O=C=NR, and O=C=CPh$_2$; addition to the C=N and C=C bonds of O=C=NR and O=C=CPh$_2$ by [W(CO)$_5$(SH)]$^-$ suggests C=N and C=C were more susceptible to addition reactions than C=O. Both O=C=S and O=C=O were inert to [W(CO)$_5$(SH)]$^-$ implying both C=S and C=O were unreactive; however, since S=C=S reacted with [W(CO)$_5$(SH)]$^-$ (below), the C=S bond appeared more reactive than C=O with [W(CO)$_5$(SH)]$^-$. Addition to the C=N bond of PhN=C=S by [W(CO)$_5$(SH)]$^-$ indicated that C=N was more susceptible to addition than C=S. Similarly, addition to C=C of Ph$_2$C=C=NPh by [W(CO)$_5$(SH)]$^-$ suggested that the C=C bond was more reactive than the C=N bond.

3. Reactions of thiocarbonyl (C=S), olefin (C=C), acetylene (C≡C), and nitrile (C≡N) groups with $[W(CO)_5SH]^-$

a. Reactions with thiocarbonyl (C=S) groups    Butler and Fenster have reviewed reactions of S=C=S with transition metal complexes (110). Carbon disulfide inserts into M-X bonds where X = H, R, Ph, $NH_2$, OR, and SR. Addition of S=C=S to $CpM(CO)_2SR$ where M = Mo, W and R = Me, Ph has been observed by Havlin and Knox (Equation 75), reaction might have taken

-75-   $CpM(CO)_2SR + S=C=S \rightarrow CpM(CO)_2SC(=S)SR$

place by insertion of C=S into the M-S or S-R bonds of $CpM(CO)_2SR$ (111). Reaction between $[W(CO)_5(SH)]^-$ and S=C=S appeared to be more complicated than reaction between $CpM(CO)_2SR$ and S=C=S (Equation 75).

An equimolar mixture of S=C=S and $[W(CO)_5(SH)]^-$ was stirred in THF at room temperature for 18 hours, a solution IR spectrum of the resultant mixture in THF revealed that reaction had occurred giving a number of $[W(CO)_5X]^-$ complexes. Repeated attempts to isolate the products by partitional crystallization were unsuccessful. Ethylene sulfide $(\overline{SCH_2CH_2})$ did not react with an equivalent amount of $[W(CO)_5(SH)]^-$ in THF at room temperature over an 18 hour period.

b. Reactions with olefins (C=C) (Figure 10)    Both substitutions for $F^-$ by $[SR]^-$ (Equation 76) on fluoro olefins and addition of HSR (Equation 77) to fluoro olefins have been described in a recent review (112). Substitution for the vinylic $F^-$ of perfluorocyclohexene by metal

-76-   $CF_2=CClF + NaSEt \rightarrow (EtS)CF=CClF + NaF$

$^a t_{1/2} = 1.0$ h.

Figure 10. Reactivity of reagents which contain the C=C group with $[W(CO)_5(SH)]^-$

-77-  $F_2$☐F + n-BuSH $\xrightarrow{\text{base}}$ $F_2$☐S(n-Bu) +

$F_2$☐S(n-Bu) + $F_2$☐S(n-Bu)

carbonyl anions (e.g. Equation 78) has been repeatedly cited by Bruce

-78-  $[CpFe(CO)_2]^- + \overline{CF=CF(CF_2)_3CF_2} \rightarrow$

$CpFe(CO)_2 \ (\overline{C=CF(CF_2)_3CF_2}) + F^-$

and Stone in reviews (113, 114). Substitution for a vinylic $F^-$ of

perfluorocyclohexene was also observed when $[W(CO)_5(SH)]^-$ was treated

with $\overline{CF=CF(CF_2)_3CF_2}$.

Preparation of $[(Ph_3P)_2N][W(CO)_5(S\overline{C=CF(CF_2)_3CF_2})]$ was carried out

according to Equation 79. A slight excess of $\overline{CF=CF(CF_2)_3CF_2}$ was employed

-79-  $[W(CO)_5(SH)]^- + \overline{CF=CF(CF_2)_3CF_2} \xrightarrow[\text{r.t.}]{\text{THF}}$

$[W(CO)_5(S\overline{C=CF(CF_2)_3CF_2})]^- + (HF)$

to guarantee complete conversion of the organometallic reactant to

product. The half-life for the reaction was 1.0 hour (Chapter II,

Section A.9); no evidence was obtained to confirm that HF was a

product in Equation 79.

No reaction took place between equimolar amounts of $CH_2=C=CH_2$ and

$[W(CO)_5(SH)]^-$ in THF at room temperature for 18 hours. Similarly, equimolar mixtures of $[W(CO)_5(SH)]^-$ and $CH_2=C(C\equiv N)H$ or, $CH_2=C(C(=O)OMe)Me$, which are activated to nucleophilic attack by inductive and resonance effects (115), were stirred in THF at room temperature for 18 hours without change.

c. <u>Reactions with acetylenes ($C\equiv C$)</u> (Figure 11)    Acetylenes are more readily attacked by nucleophiles than by electrophiles. The ease of nucleophilic attack is enhanced by electron withdrawing or resonance stabilizing groups adjacent to the C-C triple bond (116). Both PhC≡CPh and PhC≡CH which undergo reaction with $CpNi(PBu_3)(SH)$ (Chapter I, Section C) (37) did not react with an equimolar amount of $[W(CO)_5(SH)]^-$ in THF at room temperature over an 18 hour period. A green mixture of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ and THF was treated with one part of PhC≡CPh; the resultant mixture was stirred at room temperature. No reaction seemed to occur as the reaction mixture was still green 18 hours later. Neither $Me_3SiC\equiv C\text{-}C\equiv CSiMe_3$ nor HC≡CC(=O)OEt appeared to react with an equivalent amount of $[W(CO)_5(SH)]^-$ in THF at room temperature over an 18 hour period.

d. <u>Reactions with nitriles ($C\equiv N$)</u> (Figure 12)    Under acidic conditions, addition of thiols, RSH, to nitriles gives iminothioesters, Equation 30 (117). Reaction between nitriles and $[W(CO)_5(SH)]^-$ in an

$$-80-\quad N\equiv CR + R'SH \xrightarrow{H+} R(R'S)C=NH\cdot HCl$$

N. R.

HC≡CC(=O)OEt

THF

18 h

N. R.

PhC≡CPh

THF

18 h

$$\left[ \begin{array}{c} O_C \overset{\overset{\displaystyle O}{\displaystyle C}}{\underset{\underset{\displaystyle H}{\displaystyle S}}{\overset{\displaystyle |}{W}}} CO \\ OC \end{array} \right]^-$$

18 h

THF

Me₃SiC≡CC≡CSiMe₃

N. R.

18 h

THF

PhC≡CH

N. R.

$$\left[ (CO)_5 W \overset{S}{\diagdown} W(CO)_5 \right]^{2-} \xrightarrow[\text{18 h}]{\begin{array}{c}\text{PhC≡CPh}\\\text{THF}\end{array}} \text{N. R.}$$

Figure 11.    Reactivity of $[W(CO)_5(SH)]^-$ and $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ with reagents that contain the C≡C group

Figure 12. Reactivity of nitrile, C≡N, containing reagents with
[W(CO)$_5$(SH)]$^-$

acidic environment did not parallel the organic reactions above

(Equation 80).

Stirring an equimolar mixture of $[W(CO)_5(SH)]^-$ and $N{\equiv}CCH{=}CH_2$ (above),

$N{\equiv}CSMe$, or $N{\equiv}CNH_2$ in THF at room temperature for 18 hours had no effect

on the solution IR spectrum of $[W(CO)_5(SH)]^-$. No reaction occurred when

$[W(CO)_5(SH)]$ was stirred in MeCN for 4 hours at room temperature. Acidifi-

cation of the above unreacted mixtures with one equivalent of $HSO_3CF_3$

resulted in nitrile complexes (Equation 81). Treating a mixture of

$$-81-\quad [W(CO)_5(SH)]^- + N{\equiv}CR \xrightarrow[\text{THF, r.t.}]{HSO_3CF_3} W(CO)_5(N{\equiv}CR) + (H_2S{\uparrow})$$

0.177 g (0.198 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$, 10 ml of THF, and 0.0104 g

(0.248 mmole) of $N{\equiv}CNH_2$, 14 µl (0.204 mmole) of $N{\equiv}CSMe$, or 16 µl (0.237

mmole) of $N{\equiv}CCH{=}CH_2$ with 20 µl (0.225 mmole) of $HSO_3CF_3$ immediately gave

a brown mixture. After the mixture was stirred for 1 hour, the mixture

was reduced to a residue in vacuo. Eluting the 50/50 (V/V) $CH_2Cl_2$/hexanes

soluble portion of the residue over florisil and concentrating the

yellow eluate under a stream of PPN gave yellow powders of the products

(e.g. $W(CO)_5N{\equiv}CNH_2$, 54% yield; $W(CO)_5(N{\equiv}CSMe)$, 17% yield; and

$W(CO)_5(N{\equiv}CCH{=}CH_2)$, 11% yield; respectively). Similarly, $W(CO)_5(N{\equiv}CMe)$

was prepared in 10 ml of $N{\equiv}CMe$ and isolated in 62% yield. Solution IR and

$^1H$ NMR spectra of the products and of $W(CO)_5(N{\equiv}CNH_2)$ (Chapter II, Section

C.11 (50, 118), Tables 6 and 14), $W(CO)_5(N{\equiv}CSMe)$ (118), and

$W(CO)_5(N{\equiv}CMe)$ (118) were the same. Acrylonitrilepentacarbonyltungsten,

$W(CO)_5(N{\equiv}CCH{=}CH_2)$, was identified by its IR (solution and solid phase)

and $^1H$ NMR spectra (e.g. in hexanes 2076 $cm^{-1}$(w), 1984(w), 1949(vs),

1932(m); in a KBr pressed disk 2940 cm$^{-1}$(vw), 2200(vw) ($\nu$C$\equiv$N),1400(vw)

($\nu$C=C), 953(vw), 588(w), 545(vw), 474(vw); and in DCCl$_3$ 6.22 $\tau$ (m)

vinylic H̲'s; respectively).

Preparation of [(Ph$_3$P)$_2$N][W(CO)$_5$(NCS)] was effected according to

Equation 82. A mixture of 0.0445 g (0.0497 mmole) of [(Ph$_3$P)$_2$N][W(CO$_5$(SH)],

$$-82- \quad [W(CO)_5(SH)]^- + N\equiv COPh \xrightarrow[r.t.]{THF} [W(CO)_5(NCS)]^- + (HOPh)$$

6 $\mu$l (0.0548 mmole) of N$\equiv$COPh, and 5 ml of THF was stirred for 18 hours.

The resultant reaction mixture was reduced to a residue in vacuum.

Washing the residue with three 10 ml portions of diethylether gave a

yellow powder of the product in 59% yield. Solution and solid phase IR

spectra of the product and of an authentic sample of [(Ph$_3$P)$_2$N][W(CO)$_5$(NCS)]

(118, 119) were identical. Observation of a vibrational absorption at

818 cm$^{-1}$(w) confirmed that the [N=C=S]$^-$ ligand was coordinated through

N (120).

Presumably, reaction by Equation 82 took place in a number of steps:

1. substitution of [OPh]$^-$ on N$\equiv$COPh by [W(CO)$_5$(SH)]$^-$, 2. transfer of a

hydrogen from W(CO)$_5$(SHC$\equiv$N) to ⌊OPh]$^-$ (Equation 83), and 3. rearrange-

ment of the S bound [NCS]$^-$ to the N bound product (Equation 84). No

$$-83- \quad [W(CO)_5(SH)]^- + N\equiv COPh \rightarrow [W(CO)_5(SCN)]^- + (HOPh)$$

$$-84- \quad [W(CO)_5(SCN)]^- \xrightarrow{} [W(CO)_5(NCS)]^-$$

evidence to support this reaction path was obtained directly; acyl

transfer reactions (e.g. Equation 36 and Scheme IV) proceeded by a path

similar to that of Equation 83.

Addition of $[W(CO)_5(SH)]^-$ to olefins, acetylenes, and nitriles was not observed to occur with a variety of reagents containing these groups. Substitution for $F^-$ or $[OPh]^-$ by $[W(CO)_5(SH)]^-$ occurred when $\overline{CF=CF(CF_2)_3CF_2}$ or $N\equiv COPh$ were treated with $[W(CO)_5(SH)]^-$.

4.  Reactions of halogenated reagents with $[\mu-S[W(CO)_5]_2]^{2-}$ and $\overline{[W(CO)_5(SH)]^-}$

a.  Reactions with $[\mu-S[W(CO)_5]_2]^{2-}$ (Figure 13)    Substitution of various groups, $X^-$, that were bonded to a variety of main group atoms by $[SR]^-$ were reviewed by Peach (89). Thiolate, $[SR]^-$, substitutions were executed with C-Cl, Si-Cl, Sn-Cl, Ge-Cl, Pb-Cl, B-Cl, N-Cl, P-Cl, and S-Cl. Rate constants for the replacement of various groups X in $p-XC_6H_4SO_2CF_3$ by $Na[SPh]$ in MeOH decreased in the order:  X = $SO_2CH_3>NO_2>F>Cl$ (121). Substitutions for $Cl^-$ or $Br^-$ in a variety of compounds by $[\mu-S[W(CO)_5]_2]^{2-}$ paralleled reactions by $[SR]^-$ (above).

Preparations of $[\mu-PhCH_2S[W(CO)_5]_2]^-$, $[\mu-Ph_2PS[W(CO)_5]_2]^-$, $[\mu-PhS[W(CO)_5]_2]^-$, $[\mu-Me_3SnS[W(CO)_5]_2]^-$, and $[\mu-MeHgS[W(CO)_5]_2]^-$ were carried out according to Equations 85, 86, 87, 88, and 89, respectively. A green suspension of the binuclear dianion, $[\mu-S[W(CO)_5]_2]^{2-}$, was prepared

$$-85-\quad [\mu-S[W(CO)_5]_2]^{2-} + PhCH_2X \xrightarrow[\text{r.t.}]{\text{THF}} [\mu-PhCH_2S[W(CO)_5]_2]^- + (X^-)$$

$$X=Cl, Br$$

$$-86-\quad [\mu-S[W(CO)_5]_2]^{2-} + Ph_2PCl \xrightarrow[\text{r.t.}]{\text{THF}} [\mu-Ph_2PS[W(CO)_5]_2]^- + (Cl^-)$$

Figure 13. Reactivity of $[\mu-S[W(CO)_5]_2]^{2-}$ with reagents that contain halogens

-87-  $[\mu\text{-}S[W(CO)_5]_2]^{2-} + PhSO_2Cl \xrightarrow[\text{r.t.}]{THF} [\mu\text{-}PhS[W(CO)_5]_2]^- + (Cl^-)$

$+ (SO_2\uparrow)$

-88-  $[\mu\text{-}S[W(CO)_5]_2]^{2-} + Me_3SnCl \xrightarrow[\text{r.t.}]{THF} [\mu\text{-}Me_3SnS[W(CO)_5]_2]^- + (Cl^-)$

-89-  $[\mu\text{-}S[W(CO)_5]_2]^{2-} + MeHgCl \xrightarrow[\text{r.t.}]{THF} [\mu\text{-}MeHgS[W(CO)_5]_2]^- + (Cl^-)$

following Equation 19 and was employed in situ. A slight excess of the halogenated reagents was used; reactions were generally fast (ca. 2 hours). A green mixture of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ (ca. 0.50 mmole) and THF (10 ml) appeared to react with $PhCH_2Br$ (ca. 0.50 mmole) faster than with $PhCH_2Cl$ (ca. 0.50 mmole) at room temperature (e.g. 0.5 hour and 4, respectively). With the addition of $PhSO_2Cl$ in Equation 87, a gas was released that was presumably $SO_{2(g)}$. The products were precipitated from a concentrated aqueous solution of $[NEt_4]Br$.

Attempts to obtain products by substitution for $Cl^-$ on other reagents failed to give the desired compounds. No reaction took place between $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ and $Me_3CCH_2Cl$ in THF at room temperature for 18 hours. Treating 2 parts of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ with 1 part of $SCl_2$ in THF at room temperature did not yield metal carbonyl containing products (desired product, $[[(CO)_5W]_2SSS[W(CO)_5]_2]^{2-}$). Similarly, NOCl decomposed an equimolar amount of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$. Stirring 2 parts of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$, 1 part of $t\text{-}Cl_2Pd(PPh_3)_2$, and 10 ml of THF for 1 hour at

room temperature gave $W(CO)_5(PPh_3)$ (68% yield) and $NEt_4[W(CO)_5Cl]$

(49% yield) (Equation 90).

$$-90- \quad 2\,[\mu-S[W(CO)_5]_2]^{2-} + t\text{-}Cl_2Pd(PPh_3)_2 \xrightarrow[\text{r.t.}]{\text{THF}}$$

$$W(CO)_5(PPh_3) + NEt_4[W(CO)_5Cl] + (PdS)$$

  b. <u>Reactions with $[W(CO)_5(SH)]^-$ (Figure 14)</u>  Treating a mixture

of $[W(CO)_5(SH)]^-$ and THF with an equimolar amount of MeHgCl or $Me_3SnCl$

and stirring the resultant mixture for 6 hours yielded $[W(CO)_5Cl]^-$

quantitatively (Equation 91 and 92). This product was identified via

$$-91- \quad [W(CO)_5(SH)]^- + MeHgCl \xrightarrow[\text{r.t.}]{\text{THF}} [W(CO)_5Cl]^- + (MeHgSH)$$

$$-92- \quad [W(CO)_5(SH)]^- + Me_3SnCl \xrightarrow[\text{r.t.}]{\text{THF}} [W(CO)_5Cl]^- + (Me_3SnSH)$$

its solution IR and visible spectra (87).

  Two additional attempts to prepare a methylmercury mercaptan complex,

$W(CO)_5(HSHgMe)$, failed by Equations 93 and 94. Treatment of a suspension

of 1.00 mmole of $MeHg[BF_4]$ and 10 ml of $CH_2Cl_2$ or of 1.07 mmole of

$$-93- \quad [W(CO)_5(SH)]^- + MeHg[NO_3] \xrightarrow[\text{r.t.}]{\text{MeCN}} W(CO)_5(N\equiv CMe) + (MeHgSH) + ([NO_3]^-)$$

$$-94- \quad [W(CO)_5(SH)]^- + MeHg[BF_4] \xrightarrow[\text{r.t.}]{CH_2Cl_2} W(CO)_6 + (MeHgSH) + ([BF_4]^-) + (W)$$

$MeHg[NO_3]$ and 10 ml of $N\equiv CMe$ with 0.945 mmole of $[(Ph_3P)_2N][W(CO)_5(SH)]$

rapidly resulted in a brown-black reaction mixture which was stirred for

Figure 14. Reactivity of [W(CO)$_5$(SH)]$^-$ with halogenated and related electrophilic reagents

2 hours. Successively, reducing the resultant suspension to a residue

in vacuo, filtering the hexanes soluble portion of the residue through a

frit with suction, and concentrating the filtrate under a stream of PPN

gave the products (W(CO)$_5$(N≡CMe), 44% (Equation 93) and W(CO)$_6$, 64%

(Equation 94)).

Whereas substitution for halides, X$^-$, by [μ-S[W(CO)$_5$]$_2$]$^{2-}$ took place

with a variety of halogenated reagents (e.g. PhCH$_2$Cl, PhCH$_2$Br, Me$_3$SnCl,

MeHgCl, and Ph$_2$PCl), [W(CO)$_5$(SH)]$^-$ reacted with halogenated reagents by

an unknown mechanism giving [W(CO)$_5$Cl]$^-$ (e.g. MeHgCl and Me$_3$SnCl). In

addition, [μ-S[W(CO)$_5$]$_2$]$^{2-}$ appeared to be a well-behaved nucleophile in

that it reacted with PhCH$_2$Br faster than with PhCH$_2$Cl; the less basic

the substituent, the more easily it is pulled off by solvent or pushed off

by an attacking nucleophile (Br less basic than Cl) (122).

## 5. Miscellaneous reactions

a. Reactions with [W(CO)$_5$(SH)]$^-$ (Figure 15)    Magic methyl,

MeSO$_3$F, reacted with [W(CO)$_5$(SH)]$^-$ in accordance with Equation 95. Addi-

tion of 2 drops (ca. 0.066 mmole) of MeSO$_3$F to a solution of [W(CO)$_5$(SH)]$^-$

$$-95- \quad [W(CO)_5(SH)]^- + ex.\ MeSO_3F \xrightarrow[\text{r.t.}]{HCCl_3} W(CO)_5(SMe_2) + ([SO_3F])^- + (HSO_3F)$$

(ca. 0.020 mmole) and 0.6 ml of DCCl$_3$ in an $^1$H NMR tube resulted in a

brown yellow mixture. An $^1$H NMR spectrum that was obtained from the

mixture after 30 minutes showed chemical shifts which were assigned to

[(Ph$_3$P)$_2$N]$^+$, MeSO$_3$F, and W(CO)$_5$(SMe$_2$) (minor peaks were observed at 6.13 τ

and 6.67 τ). Successively, concentrating the reaction mixture to a residue

Figure 15.  Reactivity of $[W(CO)_5(SH)]^-$ with miscellaneous reagents

under a stream of PPN and obtaining a solution IR spectrum of the yellow

hexanes soluble portion of the residue confirmed that $W(CO)_5(SMe_2)$ had

been formed as a reaction product. The yield of $W(CO)_5(SMe_2)$ was 33%

by relative integrated intensities (^{1}H NMR). Values for the chemical

shift in $DCCl_3$ and $C\equiv O$ stretching frequencies in hexanes for $W(CO)_5(SMe_2)$

were identical to reported values (123).

Treating two parts of $[W(CO)_5(SH)]^-$ with one part of $HSO_3CF_3$ yielded

$[\mu-HS[W(CO)_5]_2]^-$ and $H_2S$ (Equation 96). To a solution of 0.0493 g

$$-96- \quad [W(CO)_5(SH)]^- + 1\ HSO_3CF_3 \xrightarrow[\text{r.t.}]{HCCl_3} [\mu-HS[W(CO)_5]_2]^- + H_2S$$

$$+ ([SO_3CF_3]^-)$$

(0.0550 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$ and 0.6 ml of $DCCl_3$ in an

^{1}H NMR tube was added 2.0 μl (0.023 mmole) of $HSO_3CF_3$. An ^{1}H NMR spectrum

was obtained 18 hours later revealing chemical shifts that were assigned

to $[(Ph_3P)_2N]^+$ (2.50 τ (m)), $[\mu-HS[W(CO)_5]_2]^-$ (11.74 τ (s) (Table 15)),

and $H_2S$ (9.20 τ (s) (124)). A solution IR spectrum in $CH_2Cl_2$ of the

reaction residue, which resulted from removing the volatile components of

the reaction mixture under a stream of PPN, verified that

$[\mu-HS[W(CO)_5]_2]^-$ (Table 7) was a product of Equation 96. By relative

integrated intensities $[\mu-HS[W(CO)_5]_2]^-$ was formed in 43% yield.

Preparation of $W(CO)_5(SH_2)$ by acidification of $[W(CO)_5(SH)]^-$ did not

appear possible.

An attempt to prepare $[W(CO)_5(SSPh)]^-$ according to Equation 97 was

unsuccessful. A mixture of 0.445 g (0.497 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$,

-97-  $[W(CO)_5(SH)]^- + PhSSPh \xrightarrow[\text{r.t.}]{THF} [W(CO)5(SPh)]^- + (HSSPh)$

0.108 g (0.496 mmole) of PhSSPh, and 15 ml of THF was stirred for 18 hours. Consecutively, filtering the resultant reaction mixture and partitionally crystallizing the filtrate with diethylether and hexanes resulted in a yellow powder of the product in 29% yield. The product, $[(Ph_3P)_2N]W(CO)_5(SPh)]$, was identified by its solution and solid phase IR spectra, visible spectrum, conductivity measurement, and elemental analysis (e.g. in $CH_2Cl_2$, 2052 $cm^{-1}$(w), 1908(s), 1846(m); in pressed disk of KBr (omitting $[(Ph_3P)_2N]Cl$ bands) 2055 $cm^{-1}$(w), 1963(sh), 1902(s), 1846(m), 1580(vw), 1473(vw), 1082(vw), 1029(vw), 979(vw), 819(w); in MeCN, 456 nm (664), 405(sh), 375 (1210); in MeCN, 136; and calcd. for $[(Ph_3P)_2N][W(CO)_5(SPh)]$: S, 3.35, found: S, 3.09; respectively). Values of the C$\equiv$O stretching absorptions for $[W(CO)_5(SPh)]^-$ (above) were the same as reported values (125).

Addition of 0.0163 g (0.0642 mmole) of $I_2$ to a solution of 0.113 g (0.126 mmole) of $[(Ph_3P)_2N][W(CO)_5(SH)]$ and 5 ml of THF resulted in a gas release and brown reaction mixture (Equation 98). Reaction was

-98-  $[W(CO)_5(SH)]^- + I_2 \xrightarrow[\text{r.t.}]{THF} [W(CO)_5I]^- + (HSSH)$

fast. After the resultant mixture was stirred for 2 hours, it was reduced to a residue in vacuum. Solution IR (in $CH_2Cl_2$) and visible (in MeCN) spectra of portions of the residue were identical to the spectra of an authentic sample of $[W(CO)_5I]^-$ (Chapter II, Section B.1 (14)) and indicated that $[W(CO)_5I]^-$ was the sole carbonyl containing product formed.

No evidence for the desired product, $[(CO)_5WSSW(CO)_5]^{2-}$, was obtained from the spectrophotometric data.

b. Reactions of $[W(CO)_5(SC(=O)Me)]^-$ and $[W(CO)_5(SC(=O)NMeH)]^-$

(Figure 16)     Preparation of $[(Ph_3P)_2N][\mu-MeC(=O)S[W(CO)_5]_2]$ was accomplished according to Equation 99. A slight excess of $W(CO)_5$(acetone)

$$-99- \quad [W(CO)_5(SC(=O)Me)]^- + W(CO)_5(acetone) \xrightarrow[0°C]{acetone}$$

$$[\mu-MeC(=O)S[W(CO)_5]_2]^-$$

was employed to guarantee complete conversion of $[W(CO)_5(SC(=O)Me)]^-$ to products. Reaction took place in less than 1 hour.

Similarly, $[(Ph_3P)_2N][\mu-HMeNC(=O)S[W(CO)_5]_2]$ was prepared by treating a mixture of 0.480 g (0.504 mmole) of $[(Ph_3P)_2N][W(CO)_5(SC(=O)NMeH)]$ and 10 ml of acetone with a suspension containing 0.555 mmole of $W(CO)_5$(acetone) $AgI_{(s)}$, and $NEt_4[BF_4]$ in 10 ml of acetone (Equation 100). This

$$-100- \quad [W(CO)_5(SC(=O)NMeH)]^- + W(CO)_5(acetone) \xrightarrow[r.t.]{acetone}$$

$$[\mu-HMeNC(=O)S[W(CO)_5]_2]^-$$

yellow mixture was stirred for 1 hour at room temperature. Consecutively, filtering the resultant reaction suspension through a fritted funnel with suction and partitionally crystallizing the filtrate with diethylether and hexanes gave yellow oils of the product. Foams which resulted from these oils in vacuo were found to be composed primarily of $[(Ph_3P)_2N][\mu-HMeNC(=O)S[W(CO)_5]_2]$ by solution (in $CH_2Cl_2$) and solid phase

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Figure 16. Reactivity of [W(CO)$_5$(SC(=O)Me)]$^-$ and [W(CO)$_5$(SC(=O)NMeH)]$^-$ with electrophiles

(in a pressed disk of KBr) IR spectra of portions of the foams. Spectral features of the above spectra were identical to the spectra of $NEt_4[\mu-HMeNC(=O)S[W(CO)_5]_2]$ (Tables 7 and 11 (omitting $[(Ph_3P)_2N]Cl$ bands)).

Acidification of $[W(CO)_5(SC(=O)Me)]^-$ or $[W(CO)_5(SC(=O)NMeH)]^-$ seemingly will not give $W(CO)_5(S=C(OH)Me)$ (Equation 101) or

$$-101-\ 2\ [W(CO)_5(SC(=O)Me)]^- + HSO_3CF_3 \xrightarrow[\text{r.t.}]{\text{THF}}$$

$$[\mu-MeC(=O)S[W(CO)_5]_2]^- + (HSC(=O)Me) + ([SO_3CF_3]^-)$$

$$-102-\ 2\ [W(CO)_5(SC(=O)NMeH)]^- + HSO_3CF_3 \xrightarrow[\text{r.t.}]{\text{HCCl}_3}$$

$$[\mu-HMeNC(=O)S[W(CO)_5]_2]^- + (HSC(=O)NMeH) + ([SO_3CF_3]^-)$$

$W(CO)_5(S=C(OH)NMeH)$ (Equation 102), respectively. Treating a mixture of 0.464 g (0.494 mmole) of $[(Ph_3P)_2N][W(CO)_5(SC(=O)Me)]$ and 10 ml of THF in a 25 ml flask or of 0.27 mmole of $[(Ph_3P)_2N][W(CO)_5(SC(=O)NMeH)]$ and 0.6 ml of $DCCl_3$ in an $^1H$ NMR tube with 50 µl (0.563 mmole) or 12 µl (0.135 mmole) of $HSO_3CF_3$, respectively, gave brown mixtures. After this mixture (Equation 101) was stirred for 18 hours, a solution IR spectrum in THF (e.g. 2073 $cm^{-1}$(vw), 2063(w), 1977(m), 1940(vs), 1917(m), 1873(m)) of the reaction mixture demonstrated that $[(Ph_3P)_2N][\mu-MeC(=O)S[W(CO)_5]_2]$ was the only metal carbonyl containing product present. An $^1H$ NMR spectrum of the reaction mixture (Equation 102) which was spun in a centrifuge to remove insoluble materials demonstrated that

[(Ph$_3$P)$_2$N][μ-HMeNC(=O)S[W(CO)$_5$]$_2$] was prepared in 31% yield by relative

integrated intensities. No other peaks were observed in the spectrum;

apparently HMeNC(=O)SH was incorporated with the insoluble material.

Neither HOC(=S)Me nor HOC(=S)NMeH are found in appreciable concentra-

tion at room temperature; the tautomeric equilibrium is markedly shifted

to the thiol form (e.g. HSC(=O)Me (126) or HSC(=O)NMeH (127)). The

Lewis acid, W(CO)$_5$, coordinated a loan pair of electrons on S in the

[W(CO)$_5$(SC(=O)Me)]$^-$ and [W(CO)$_5$(SC(=O)NMeH)]$^-$ complexes rather than an

O loan pair of electrons (Equation 99 and 100). Acidification of

[W(CO)$_5$(SC(=O)Me)]$^-$ or [W(CO)$_5$(SC(=O)NMeH)]$^-$ did not give

W(CO)$_5$(S=C(OH)Me) or W(CO)$_5$(S=C(OH)NMeH), complexes with the less abundant

tautomeric forms of the free ligands (e.g. HOC(=S)Me and HOC(=S)NMeH,

respectively).

    c.  Reactions with [μ-MeC(=O)S[W(CO)$_5$]$_2$]$^-$ (Figures 17 and 18)

The binuclear anion, [μ-MeC(=O)S[W(CO)$_5$]$_2$]$^-$, was inert to a variety of

electrophiles. An equimolar mixture of [μ-MeC(=O)S[W(CO)$_5$]$_2$$^-$ and MeI in

acetone was stirred for 18 hours at room temperature without change.

No reaction took place between equivalent amounts of EtSO$_3$F and

[μ-MeC(=O)S[W(CO)$_5$]$_2$]$^-$ in diethylether at room temperature over an 18

hour period. Treatment of one part of [μ-MeC(=O)S[W(CO)$_5$]$_2$]$^-$ with 1.4

parts of BF$_3$·OEt$_2$ in diethylether at room temperature gave a yellow

mixture. After the mixture was stirred for 18 hours, 90% of the

original amount of [μ-MeC(=O)S[W(CO)$_5$]$_2$]$^-$ was recovered by diluting the

N. R.
↖
1.4 BF$_3$/ether

N. R.
↗
MeI

ether

acetone

18 h

18 h

$$\left[ (CO)_5 W \overset{\overset{\displaystyle C(=O)Me}{|}}{\underset{}{S}} W(CO)_5 \right]^-$$

16 h

18 h

acetone

ether

1.5 W(CO)$_5$(acetone)

EtSO$_3$F

N. R.

N. R.

Figure 17. Reactivity of [μ-MeC(=O)S[W(CO)$_5$]$_2$]$^-$ with electrophiles

$$\left[(CO)_5W \overset{\overset{\displaystyle H}{\big|}}{\underset{\phantom{.}}{S}} W(CO)_5\right]^- \ + \ \left[\begin{matrix} O \\ C \\ OC \searrow \overset{|}{C} \overset{O}{\nearrow} \\ OC \nearrow \overset{|}{\underset{C}{W}} \searrow S \overset{O}{-} \overset{\|}{C} - Me \\ O \end{matrix}\right]^-$$

$$\Big[W(CO)_5(SH)\Big]^-$$

HCCl$_3$

$t_{\frac{1}{2}}$ = 36 h

$$\left[(CO)_5W \overset{\overset{\displaystyle S \nearrow C(=O)Me}{}}{\underset{\phantom{.}}{\big\backslash}} W(CO)_5\right]^-$$

137 h

HCCl$_3$

S=C(NH$_2$)$_2$

$$\Big[W(CO)_5(SC(=O)Me)\Big]^- +$$
$$W(CO)_5(S=C(NH_2)_2)$$

120 h

HCCl$_3$

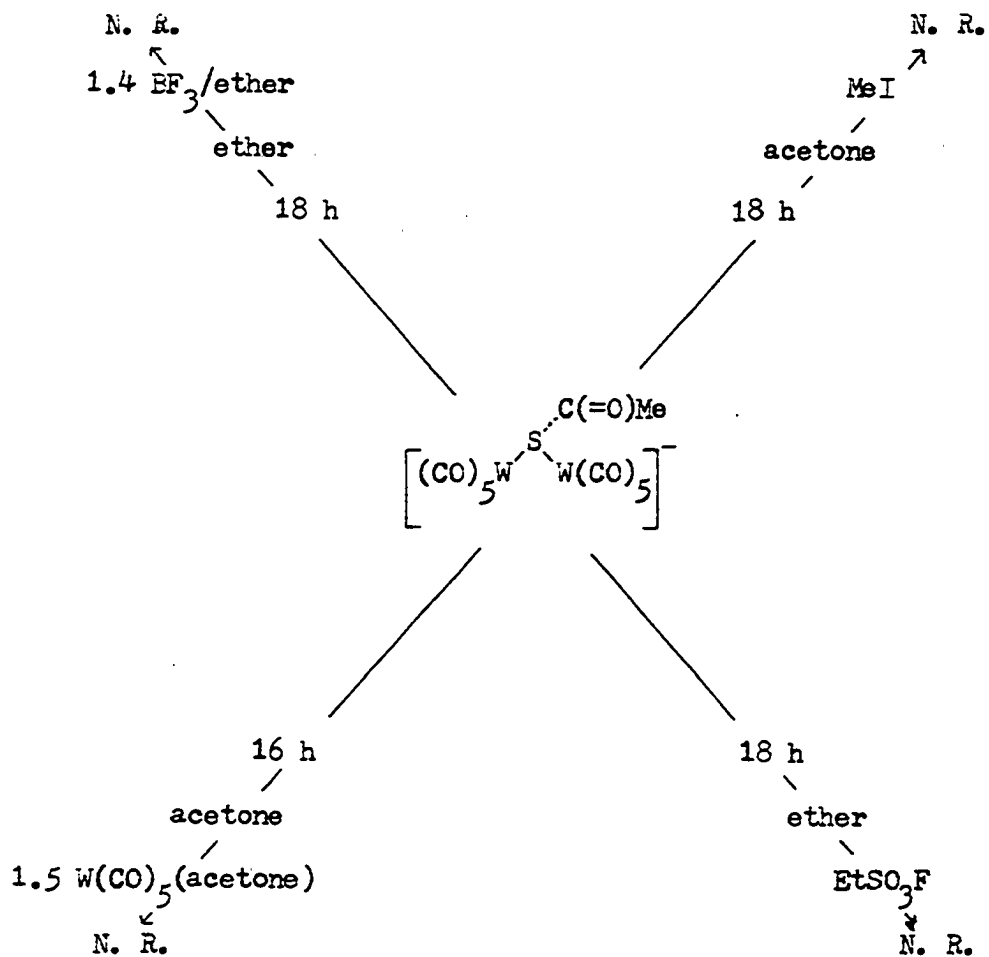1.3 SMe$_2$

$$\Big[W(CO)_5(SC(=O)Me)\Big]^- +$$
$$W(CO)_5(SMe_2)$$
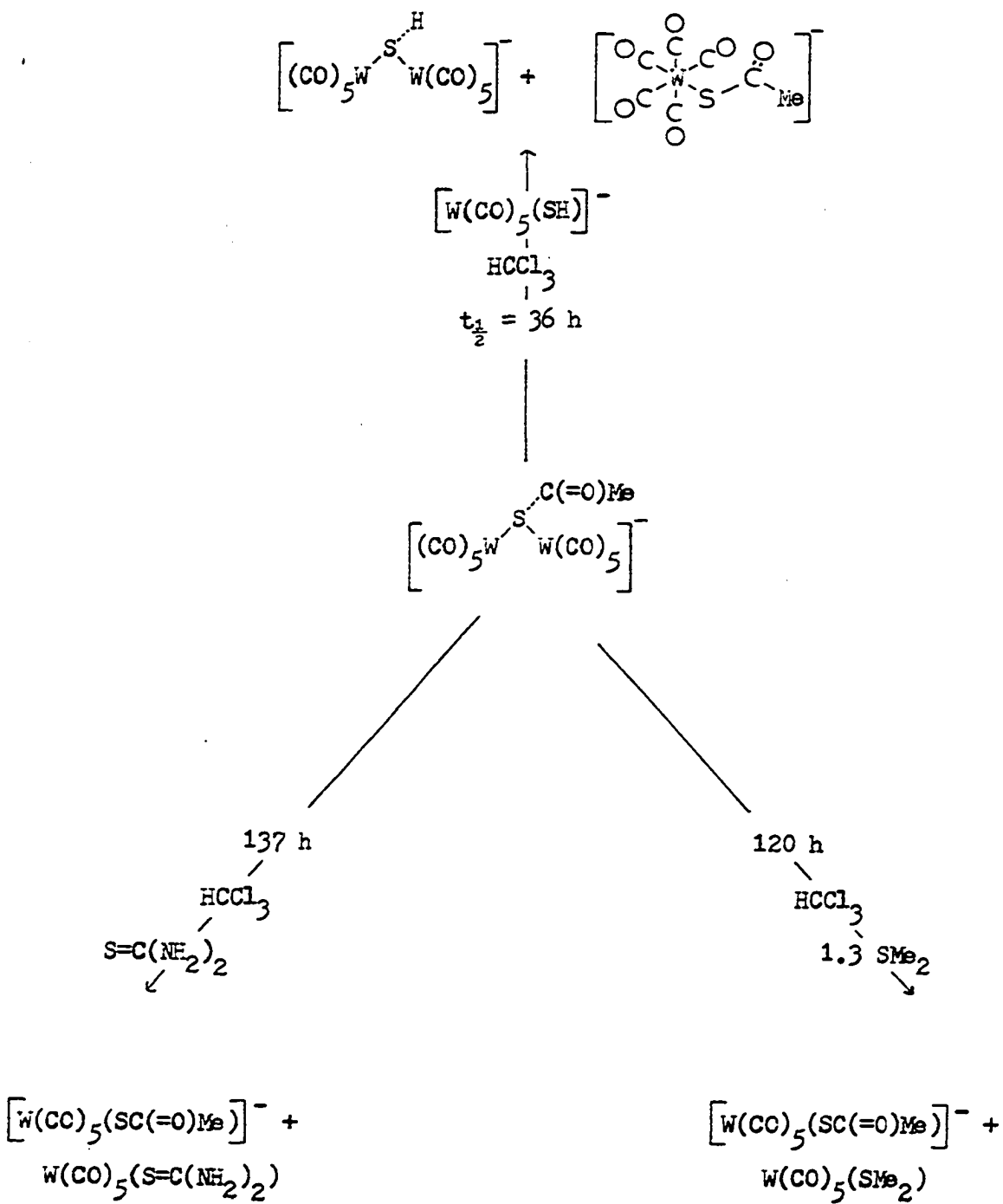
Figure 18. Reactivity of $[\mu\text{-}MeC(=O)S[W(CO)_5]_2]^-$ with nucleophiles

resultant mixture with hexanes. Addition of 1.5 parts of $W(CO)_5$(acetone) in acetone to one part of $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^-$ in acetone at room temperature returned 75% of the initial amount of $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^-$ after the mixture was stirred for 16 hours and then diluted with hexanes.

Nucleophiles reacted with $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^-$ according to Equations 103, 104, and 105. Reactions were conducted in capped $^1$H NMR

-103-  $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^- + [W(CO)_5(SH)]^- \xrightarrow[\text{r.t.}]{HCCl_3}$

$[W(CO)_5(SC(=O)Me)]^- + [\mu\text{-HS}[W(CO)_5]_2]^-$

-104-  $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^- + S=C(NH_2)_2 \xrightarrow[\text{r.t.}]{HCCl_3}$

$[W(CO)_5(SC(=O)Me)]^- + W(CO)_5(S=C(NH_2)_2)$

-105-  $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^- + SMe_2 \xrightarrow[\text{r.t.}]{HCCl_3}$

$[W(CO)_5(SC(=O)Me)]^- + W(CO)_5(SMe_2)$
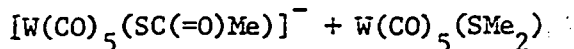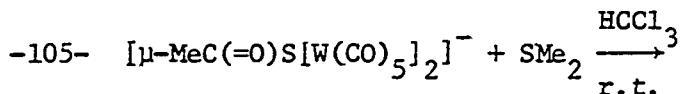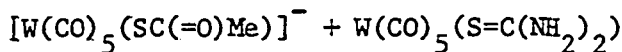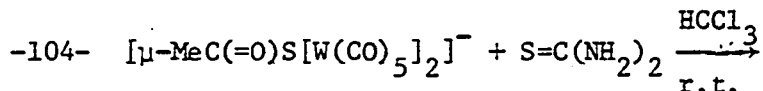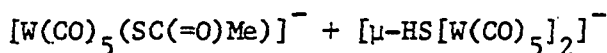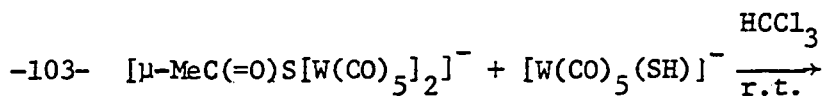
tubes with equimolar amounts of the reactants over long reaction periods. For example, the half-life for the reaction of 0.033 mmole of $[(Ph_3P)_2N][\mu\text{-MeC}(=O)S[W(CO)_5]_2]$ with 0.033 mmole of $[(Ph_3P)_2N][W(CO)_5(SH)]$ in 0.6 ml of $HCCl_3$ at room temperature was 36 hours. Products were identified by their solution $^1$H NMR and IR (in $CH_2Cl_2$) spectra which were identical to spectra that were obtained from authentic samples $([W(CO)_5(SH)]^-$ and $[W(CO)_5(SC(=O)Me)]^-$ (Tables 4 and 12), $W(CO)_5(S=C(NH_2)_2)$ (Chapter II, Section C.11 (50), Table 6), and

$W(CO)_5(SMe_2)$ (123)).

## 6. Stabilities of the compounds

a. _Mercapto complexes_    Stabilities of the mercapto complexes toward air and heat were observed to follow the order (most stable to least):   $[W(CO)_5(SH)]^- > [\mu-HS[W(CO)_5]_2]^- > [Cr(CO)_5(SH)]^- >>$ $[Mo(CO)_5(SH)]^-$. Solids of $[W(CO)_5(SH)]^-$ were manipulated and stored in air for a month with no observable decomposition. Yellow solids of $[\mu-HS[W(CO)_5]_2]^-$ and $[Cr(CO)_5(SH)]^-$ developed a green coloration when exposed to air for 12 hours and 4 hours, respectively. Crystalline solids of $[Mo(CO)_5(SH)]^-$ could not be obtained under an atmosphere of $N_2$ from solution apparently due to its thermal instability.

In a solution of THF under a $N_2$ atmosphere at room temperature, $[\mu-HS[W(CO)_5]_2]^-$ was unaffected for 18 hours, but $[Cr(CO)_5(SH)]^-$ and $[W(CO)_5(SH)]^-$ were partially decomposed to insoluble yellow solids which did not contain metal carbonyls. The stability of $[W(CO)_5(SH)]^-$ in solution was dependent upon the solvent and followed the series (most stable to least):   $HCCl_3 \simeq$ acetone > MeCN = THF >> $CH_2Cl_2$.

Water and oxygen did not affect $[W(CO)_5(SH)]^-$ in solution. Treating a solution of 0.030 mmole of $[(Ph_3P)_2N][W(CO)_5(SH)]$ and 0.6 ml of $DCCl_3$ with a drop of $H_2O$ and obtaining an $^1H$ NMR spectrum of the resultant mixture 4 hours later demonstrated that no reaction had taken place. Obtaining a solution IR spectrum in the 2200 $cm^{-1}$ to 1700 region of a mixture of $[W(CO)_5(SH)]^-$ and $HCCl_3$ which had been kept under an atmosphere

of $O_2$ for 2 hours showed that $O_2$ had not affected $[W(CO)_5(SH)]^-$.

b. <u>Sulfido complex</u>    Oxygen and $H_2O$ reacted with $[\mu\text{-}S[W(CO)_5]_2]^{2-}$.
Addition of a 19-fold molar excess of $O_2$ to $[\mu\text{-}S[W(CO)_5]_2]^{2-}$ in THF at
room temperature in a sealed reaction flask gave in 1.5 hours a colorless
mixture which did not contain any soluble metal carbonyl compounds
(by solution IR in THF). Treatment of a solution of $[\mu\text{-}S[W(CO)_5]_2]^{2-}$
and THF with 15 equivalents of $H_2O$ at room temperature gave in 24 hours
$[\mu\text{-}HS[W(CO)_5]_2]^-$ (quantitatively) and white solids (presumably NaOH).
This product, $[\mu\text{-}HS[W(CO)_5]_2]^-$, was identified from its solution IR spec-
trum in THF (Table 7).

c.  $W(CO)_5L$ complexes    Neutral complexes, $W(CO)_5L$, appeared to
be infinitely stable as solids in vacuo. Solids of these complexes were
not adversely affected by short exposures to the air at room temperature.
In solution stabilities of the neutral complexes toward air or heat
seemed to follow the sequence (most stable to least): thioureas = thio-
amides > thioaldehydes = cyanamide > thioketones. The thioacetone complex,
$W(CO)_5(S=CMe_2)$, was slowly sublimed under vacuum (0.1 torr) at 60°C;
thiourea, thioamide, and thioaldehyde complexes decomposed under the
same conditions.

d.  $[W(CO)_5L]^-$ and $[\mu\text{-}RS[W(CO)_5]_2]^-$ complexes    Mononuclear and
binuclear anionic complexes appeared to be infinitely stable in vacuum
and were unaffected by short exposures to the air. In a solution of MeCN,
$[\mu\text{-}Me_3SnS[W(CO)_5]_2]^-$ and $[\mu\text{-}MeHgS[W(CO)_5]_2]^-$ decomposed to unidentified

products at room temperature in 1 hour; however, no evidence for de-composition of other mononuclear or binuclear anionic complexes in MeCN was observed over a 1 hour period.

e.  Anionic complexes with $[NEt_4]^+$ or $[(Ph_3P)_2N]^+$     A few ionic compounds were obtained with either $[(Ph_3P)_2N]^+$ or $[NEt_4]^+$ as counter-cation (e.g. $[(Ph_3P)_2N][W(CO)_5(SH)]$, $NEt_4[W(CO)_5(SH)]$ and $[(Ph_3P)_2N][\mu-MeC(=O)S[W(CO)_5]_2]$, $NEt_4[\mu-MeC(=O)S[W(CO)_5]_2]$); there did not seem to be any significant differences between the stabilities of these compounds in solution or the solid state.  Other ionic complexes have been shown to be more stable with $[(Ph_3P)_2N]^+$ as a counter cation than with $Na^+$ in the solid state (128, 129, 130, 131) and solution (132).

## C.  Physical Properties of the Compounds

### 1.  Solubilities

Ionic compounds were soluble in polar organic solvents (e.g. $HCCl_3$, $CH_2Cl_2$, THF, acetone, and MeCN).  Mononuclear ionic complexes, e.g. $[cation][W(CO)_5L]$ and $[cation][W(CO)_4L]$, were insoluble in diethyl-ether and hydrocarbons.  Solubilities of binuclear ionic complexes, e.g. $NEt_4[\mu-RS[W(CO)_5]_2]$, in $HCCl_3$ appeared to follow the sequence (most soluble to least): (R=) $PhCH_2$ = $Me_3Sn$ = MeHg = $MeC(=O)$ > Ph = $HPh_2C(=O)$ > $HMeNC(=O)$ > H > $PPh_2$.  Binuclear ionic complexes were insoluble in saturated hydrocarbons and $H_2O$.  Countercations affected the solubility of the ionic complexes; saturated solutions of compounds with

$[(Ph_3P)_2N]^+$ as a countercation were more concentrated (moles/liter) than with $[NEt_4]^+$.

Neutral complexes, $W(CO)_5L$, were also soluble in polar organic solvents. Solubilities of neutral complexes in saturated hydrocarbons followed the order (most soluble to least): (L=) thioketones > $S=C(NPhH)CPh_2H$ > $S=C(p-MeC_6H_4)H$ > $S=C(p-MeOC_6H_4)H$ > $S=C(p-Me_2NC_6H_4)H$ > $S=C(Ni-PrH)_2$ > $N\equiv CNH_2$ > $S=C(NH_2)_2$. The least soluble compounds in the above series (e.g. (L=)$N\equiv CNH_2$ and $S=C(NH_2)_2$) were virtually insoluble in saturated hydrocarbons.

## 2. Conductivity

Molar conductivity values (Tables 1 and 3) of the ionic compounds were observed in the range that was expected for 1 to 1 electrolytes in acetonitrile or nitromethane solvent (133). Both $NEt_4[\mu-Me_3Sn[W(CO)_5]_2]$ and $MEt_4[\mu-MeHgS[W(CO)]_2]$ were unstable in MeCN; accordingly, measurements for these compounds were obtained in $MeNO_2$.

## 3. Infrared spectra

a. <u>Solution IR spectra</u>  Solution infrared spectra of the compounds in the CO stretching region are reported in Tables 4, 5, 6 and 7. Assignments for the bands were based on a $C_{4v}$ symmetry for $M(CO)_5L$ and a $C_{2v}$ symmetry for $W(CO)_4L$. The $C_{4v}$ symmetry of $M(CO)_5L$ complexes allows three vibrational absorptions ($2A_1$ and $E$) (134, 135, 136). A fourth band of weak intensity was also observed and was assigned to a $C_{4v}$ unallowed vibrational mode ($B_1$) (137). Four vibrational absorptions ($2A_1 + B_1 + B_2$)

are IR-active for a $C_{2v}$ symmetry (138). Band positions and relative

intensities conformed with the CO stretching absorptions of numerous

$M(CO)_5L$ and $cis\text{-}M(CO)_5L_2$ complexes (137). Assignments for the vibrational

absorptions were not made for the binuclear anions, e.g. $[\mu\text{-RS}[W(CO)_5]_2]^-$;

however, the observed six band pattern in $CH_2Cl_2$ matched the pattern of the

CO stretching absorptions that was described for $[\mu\text{-I}[Cr(CO)_5]_2]^-$ (139).

Structure XIX has been determined for $[\mu\text{-I}[Cr(CO)_5]_2]^-$ by Handy et al.

by x-ray techniques (140); by analogy, $[\mu\text{-RS}[W(CO)_5]_2]^-$ was tentatively
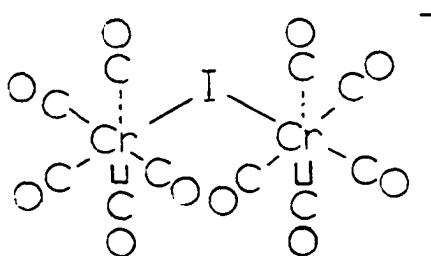


XIX

given structure XX. Solution IR spectra of $[\mu\text{-PhS}[W(CO)_5]_2]^-$ and
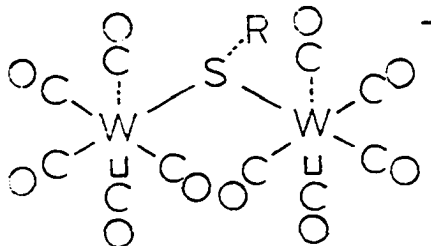


XX

$[\mu\text{-PhCH}_2S[W(CO)_5]_2]^-$ were the same as those that were reported

previously (141).

Band positions for the ionic compounds moved to higher wave numbers

as more strongly electron-withdrawing fragments were placed on S.

Changes in the E CO stretching absorptions were representative for the

following $[W(CO)_5L]^-$ complexes: (L,E) SH, 1912 $cm^{-1}$; SC(=O)Me, 1917; and

$SCF_2C(=O)CF_3$, 1924. Similarly, the 4th CO vibrations of the

$[\mu-RS[W(CO)_5]_2]^-$ compounds demonstrated this trend (e.g. (R, 4) H, 1933

$cm^{-1}$; Ph, 1935; C(=O)Me, 1938). This effect has been observed with other

$W(CO)_5L$ complexes (142).

Vibrational absorptions were not altered by changing the solvent or

the countercation. Solution infrared spectra of $[(Ph_3P)_2N][W(CO)_5(SH)]$

in $CH_2Cl_2$ or THF (Table 4) and $[NEt_4][\mu-HS(W(CO)_5]_2]$ in $CH_2Cl_2$ or THF

(Table 7) were virtually identical. Exchanging the countercation,

$[(Ph_3P)_2N]^+$ for $[NEt_4]^+$, had little effect on the CO stretching ab-

sorptions, e.g. $[(Ph_3P)_2N][W(CO)_5(SC(=O)NMeH)]$., $NEt_4[W(CO)_5(SC(=O)NMeH)]$

(Table 4) and $[(Ph_3P)_2N][\mu-MeC(=O)S[W(CO)_5]_2]$, $NEt_4[\mu-MeC(=O)S[W(CO)_5]_2]$

(Table 7).

b. <u>Solid phase IR spectra (ligand absorptions)</u>    Solid phase

infrared spectra of the complexes omitting the CO stretching region

bands are reported in Tables 8, 9, 10, and 11. Countercation absorptions

that were observed in the solid phase IR spectra of $[(Ph_3P)_2N]Cl$ or $[NEt_4]Br$

were also omitted. Structural information that was ascertained from

these absorptions is described below.

Mercapto complexes $([M(CO)_5(SH)]^-$ where M=Cr, W) did not manifest

a stretching vibration for S-H. Other authors who have reported

mercapto complexes were also unable to locate this absorption (16, 22,

35, 36). Bands that were observed in the 700 $cm^{-1}$ to 400 region resulted

from $\nu(M-C)$ and $\delta(M-C-O)$ (143); assignments were not made. The

proposed structure XXI of $[M(CO)_5(SH)]^-$ was inferred from the solution IR



XXI
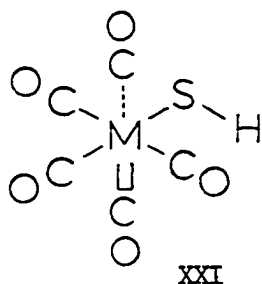
and NMR spectra (see below) which are indicative of a $C_{4v}$ symmetry about the central metal.

Both monodentate and bidentate dialkylthiocarbamate and thioacetate ligands have been observed in transitions metal complexes (144, 145, 146, 147); spectrophotometric data pointed unequivocally to structures XXII and XXIII for the complexes containing these ligands. Weak bands that were observed at 1620 $cm^{-1}$, 1590, 1605, 1604, and 1680 for $[W(CO)_5(SC(=O)NRH)]^-$ where R = Ph, Me (XXI), $[W(CO)_5(SC(=O)CR_2H]^-$ where R = Ph, H (XXII), and $[W(CO)_5(SCF_2C(=O)CF_3)]^-$, respectively, were tenta-



XXII



XXIII
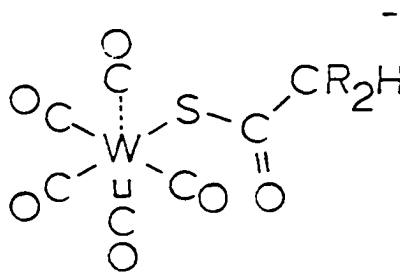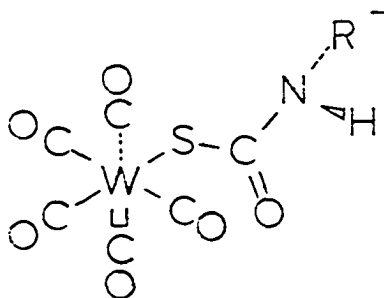
tively assigned to an uncoordinated $\nu(C=O)$. This assignment was the basis for the differentiation between tungsten-sulfur and tungsten-oxygen bonding; an uncoordinated C=O has a stretching vibration near 1600 $cm^{-1}$ (144). A $\nu(N-H)$ which was indicative of a transfer of the S's hydrogen to N (Equation 27) was observed at 3440 $cm^{-1}$ and 3240 for the alkylmono-

thiocarbamate complexes, XXII. A relatively high value for the $\nu(C=O)$, 1680 cm$^{-1}$, of $[W(CO)_5(SCF_2C(=O)CF_3)]^-$ XXIV reflected the influence of F (e.g. $[W(CO)_5(OC(=O)Me)]^-$, $\nu(C=O)$ = 1600 cm$^{-1}$; $[W(CO)_5(OC(=O)CF_3)]^-$, $\nu(C=O)$ = 1683 cm$^{-1}$ (148)).

Bands that were observed in the 1300 cm$^{-1}$ to 1000 region for $[W(CO)_5(SCF_2C(=O)CF_3)]^-$ XXIV and $[W(CO)_5(SC=CF(CF_2)_3CF_2)]^-$ XXV were characteristic of $\nu(C-F)$ (149). An absorption at 1639 cm$^{-1}$, that was observed in an IR spectrum obtained from a concentrated solution of XXV in $CH_2Cl_2$, was tentatively assigned to $\nu(C=C)$; $Mn(CO)_5(C=CF(CF_2)_3CF_2)$ was assigned a $\nu(C=C)$ at 1633 cm$^{-1}$ (150). Additional spectrophotometric
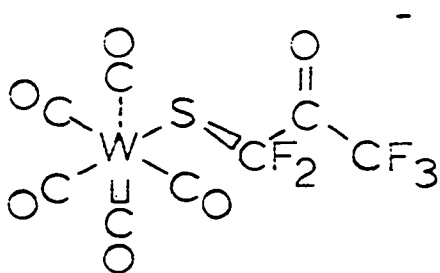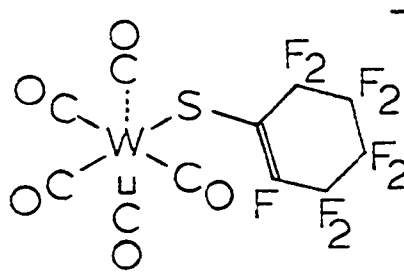


XXIV                           XXV

data (see above and below) supported the proposed structures, XXIV and XXV.
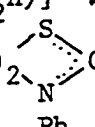
Monodentated dialkyldithiocarbamate ligands in transition metal complexes were reported to contain a characteristic $\nu(C-N)$ at 1480 cm$^{-1}$ to 1460 (151, 152) and bidentate dialkyldithiocarbamates a $\nu(C-N)$ at 1550 cm$^{-1}$ to 1500 (152, 153). Stretching absorptions at 1500 cm$^{-1}$ and 1525 for $[W(CO)_4(S_2CNRH)]^-$ where R = Me, Ph, respectively, suggested structure XXVI for these complexes. By the same argument, the structure

123
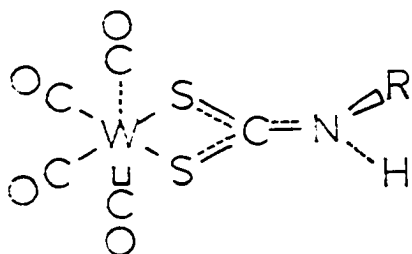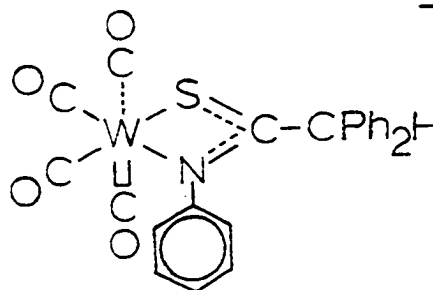
XXVI                                    XXVII

of $[W(CO)_4(SC(=NPh)CPh_2H)]^-$ with a $\nu(C-N)$ at 1500 cm$^{-1}$ was thought to

be XXVII (e.g. $CpMo(CO)_2$ ⟨S⟩CMe, $\nu(C-N)$ = 1484 cm$^{-1}$ (154)). Support for

these structures XXVI and XXVII, was also obtained from solution IR

(above) and $^1$H NMR (below) spectra.

Binuclear complexes, $[\mu-RS(W(CO)_5)_2]^-$, had structures XX based on

their solution IR spectra; solid phase IR spectra of these complexes

demonstrated that the substituent R was present. A $\nu(S-H)$ was not observed

for $[\mu-HS[W(CO)_5]_2]^-$ (see $[W(CO)_5(SH)]^-$ above for discussion). Stretching

vibrations at 1643 cm$^{-1}$ and 1664 for $[\mu-MeC(=O)S[W(CO)_5]_2]^-$ and

$[\mu-HMeNC(=O)S[W(CO)_5]_2]^-$, respectively, which were tentatively assigned

to $\nu(C=O)$ demonstrated that the metals, W, were bound to S. A $\nu(N-H)$

was observed at 3342 cm$^{-1}$ for $[\mu-HMeNC(=O)S[W(CO)_5]_2]^-$. Other vibrations

in these spectra were characteristic of the organic fragments bonded to

the ligands.

Comparisons between mononuclear and binuclear complexes with the

same ligand were possible. Stretching absorptions assigned to (C=O) for

$[W(CO)_5(SC(=O)Me)]^-$, $[\mu-MeC(=O)S[W(CO)_5]_2]^-$ and $[W(CO)_5(SC(=O)NMeH)]^-$,
$[\mu-HMeNC(=O)S[W(CO)_5]_2]^-$ underwent shifts of 39 cm$^{-1}$ and 74 cm$^{-1}$,
respectively, to higher wave numbers upon coordination to a second
$W(CO)_5$ group. This movement was indicative of greater double bond
character in the C-O bond as a result of removal of electron density from
the ligand (e.g. $[SC(=O)Me]^-$ and $[SC(=O)NMeH]^-$). A similar shift in CO
stretching vibrations, that occurred upon coordination to a second $W(CO)_5$
group was also suggestive of a diminishing of electron density through-
out the complex.

Thioaldehyde complexes, $W(CO)_5(S=C(p-RC_6H_4)H)$ where R = $Me_2N$, MeO,
Me whose structure (XXVIII) was based by analogy on the structure of
$W(CO)_5(S=CMe_2)$, XXIX (155) had $\nu(C=S)$ at 1321 cm$^{-1}$ and 1269,



| XXVIII | XXIX |
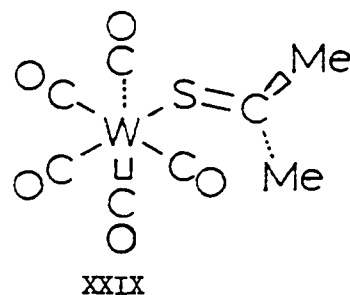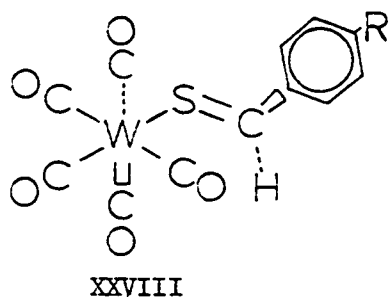
respectively. These bands were tentatively assigned by their relative
intensities and positions which were close to the $\nu(C=S)$, 1253 cm$^{-1}$, of
$W(CO)_5(S=CMe_2)$ (97). A $\nu(C=S)$ band was not distinguishable from the
numerous bands that were observed in the spectra of $W(CO)_5(S=C(p-MeC_6H_4)H)$,
$W(CO)_5(S=C(NPhH)CPh_2H)$, $W(CO)_5(S=C(NH_2)_2)$, and $W(CO)_5(S=C(Ni-PrH)_2)$.
The last three compounds did exhibit stretching vibrations for N-H.

Tripathi reported $\nu$(C=S) of $Mo(CO)_5(S=C(NH_2)(NPhH))$ at 670 cm$^{-1}$ (156); other authors have not reported $\nu$(C=S) for transition metal carbonyl thioacetamide (157, 158), thiourea (157, 158, 159), or alkylthioureas (156, 160, 161).

The proposed structure of $W(CO)_5(N\equiv CNH_2)$ (XXX) was based on information that was obtained from the solid phase IR spectrum of the complex. A $\nu$(C$\equiv$N) was observed at 2270 cm$^{-1}$ with a shoulder at 2315 cm$^{-1}$; in the free



XXX
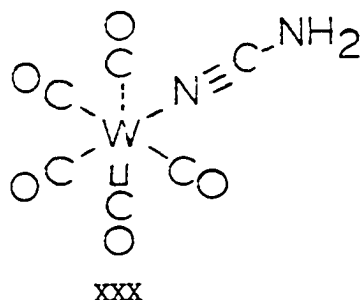
ligand, $N\equiv C-NH_2$, the $\nu$(C$\equiv$N) occurred at 2190 cm$^{-1}$ and 2150 (162). This dramatic increase in $\nu$(C$\equiv$N) (ca. 120 cm$^{-1}$) upon coordination of $N\equiv CNH_2$ was indicative of coordination of the N loan pair of C$\equiv$N rather than of $NH_2$ (163). Additional evidence for coordination of the N loan pair of C$\equiv$N was ascertained from the small change in $\nu$(N-H) upon coordination of $N\equiv CNH_2$ (e.g. $\nu$(N-H) for $W(CO)_5(N\equiv CNH_2)$ = 3425 cm$^{-1}$ and 3335 and $\nu$(N-H) for $N\equiv CNH_2$ = 3430 cm$^{-1}$ and 3342 both in $CH_2Cl_2$ solution) (164).

4. $^1$H NMR spectra

In Tables 12, 13, 14, and 15 hydrogen NMR spectra of the complexes are reported with their assignments. Assignments of the chemical shifts were based on splittings and relative integrated intensities. Just as solution

IR spectra were an invaluable aid in diagnosing the symmetry about the group VIA transition metal, NMR spectra were of comparable value in determining the structure of the organic fragments that were bound to S.

Chemical shifts for the hydrogen of the mercapto ligand in mononuclear complexes, $[M(CO)_5(SH)]^-$, were found above TMS with the highest field resonance occurring with the Cr complex and the lowest with the W complex (e.g. Cr, 14.67 $\tau$; Mo, 13.38; W, 12.93). Frequently chemical shifts for the hydrogen of mercapto ligands have been found above TMS (16, 28, and 35). A resonance for the hydrogen of the mercapto ligand in the binuclear complex, $[\mu-HS[W(CO)_5]_2]^-$, was also found above TMS at lower field than the chemical shift for the hydrogen of $[W(CO)_5(SH)]^-$ (e.g. binuclear, 11.70 $\tau$; mononuclear, 12.93). Whereas the chemical shift of the hydride ligand in $[\mu-H[W(CO)_5]_2]^-$ was found at 22.52 $\tau$ (165), the resonance of the hydrogen of the mercapto ligand in the binuclear complex was found at lower field conclusively demonstrating that the hydrido complex was not the product of Equation 18 (see this Chapter, Section A.1 for further discussion).

Sp$^3$ carbon hydrogens of $[W(CO)_5(SC(=O)Me)]^-$ (XXIII), $[W(CO)_5(SC(=O)CPh_2H)]^-$ (XXIII), and $[W(CO)_4(SC(=NPh)CPh_2H)]^-$ (XXV) were observed as singlets. Coordination of $[SC(=O)Me]^-$ with 1 or 2 $W(CO)_5$ groups resulted in a movement of the methyl's chemical shift to lower field (e.g. $[SC(=O)Me]^-$, 7.70 $\tau$; $[W(CO)_5(SC(=O)Me)]^-$, 7.55; and $[\mu-MeC(=O)S[W(CO)_5]_2]^-$, 7.39).

Exchange of the hydrogen which was bound to N in $[W(CO)_5(SC(=O)NMeH)]^-$ (XXII) and $[W(CO)_4(S_2CNMeH)]^-$ (XXVI) did not allow the hydrogen to couple

with the methyl hydrogens in these complexes. Accordingly, the chemical

shifts that were assigned to the methyl hydrogens in XXII and XXVI were

not observed as doublets. In anhydrous $HCCl_3$, the expected doublet was

observed for the methyl hydrogens of XXII at 7.23 $\tau$. Coordination of a

second $W(CO)_5$ group to XXII again resulted in a movement of the chemical

shift to lower field (e.g. XXII (in $DCCl_3$), 7.23 $\tau$ and

$[\mu\text{-HMeNC}(=O)[W(CO)_5]_2]^-$ (in $DCCl_3$), 7.15).

$^1$H NMR spectra of the binuclear complexes, XX where R = Ph, $CH_2Ph$,

$PPh_2$, $SnMe_3$, and HgMe, confirmed that the appropriate organic fragments

were present in the complexes. Due to the limited solubilities of XX

where R = $SnMe_3$ and HgMe, $J_{(117_{Sn-H})}$, $J_{(118_{Sn-H})}$, and $J_{(199_{Hg-H})}$ were

not observed.

Hindered rotation around the C-N bond of amides, thioamides, etc.

(166, 167) or the C-S bond of HSC(=O)Me (168) resulted in cis and trans

isomers of the compounds (e.g. XXXI and XXXII). No evidence for more than
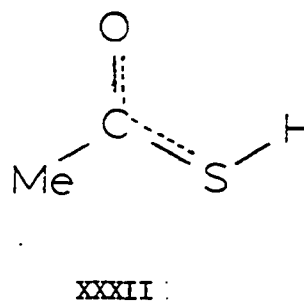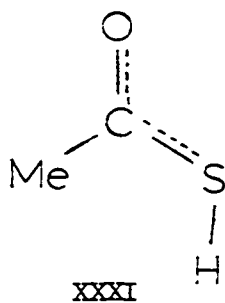


one isomer of $[W(CO)_5(SC(=O)NMeH)]^-$ (XXII), $[\mu\text{-HMeNC}(=O)S[W(CO)_5]_2]^-$,

or $[W(CO)_5(SC(=O)Me)]^-$ (XXIII) was obtained from the $^1$H NMR spectra of the

complexes at r.t. Furthermore, low temperature studies that were per-

formed with $[\mu\text{-HMeNC}(=O)S[W(CO)_5]_2]^-$ or $[W(CO)_5(SC(=O)Me)]^-$ from 300°K to

215 had no affect on the chemical shifts of the methyl hydrogens of these complexes.

Whereas chemical shifts of the hydrogens of the ligands were insensitive to changes in the countercation, resonances were affected by solvent changes. Chemical shifts for the methyl hydrogens of $[\mu-MeC(=O)S\lfloor W(CO)_5\rfloor_2]^-$ in $DCCl_3$ were observed at 7.40 $\tau$ and 7.39 with $[(Ph_3P)_2N]^+$ and $[NEt_4]^+$, respectively. A singlet that was assigned to the methyl hydrogens of $[(Ph_3P)_2N]\lfloor W(CO)_5(SC(=O)Me)\rfloor$ was observed at 7.55 $\tau$ in $DCCl_3$ and at 7.28 $\tau$ in $(CD_3)_2C=O$.

Coordination of a $W(CO)_5$ group to a ligand resulted in a down field movement of the chemical shift for the hydrogens that were bonded to the ligand. Examples of this effect have been cited (above) for the mercapto, thioacetate, and methylmonothiocarbamate ligands. This effect probably resulted from a reduction of electron density on the ligand (note changes in $v(C=O)$ upon coordination of a $W(CO)_5$ group (above)).

^{1}H NMR spectra of the neutral complexes showed chemical shifts that were expected for the organic substituents present. Resonances for the hydrogen of the coordinated thioaldehyde, S=C-H, were at unusually low field (e.g. -1.11 $\tau$ to -0.58) but were comparable to those of the $\alpha,\beta$-unsaturated monomeric thioaldehyde compounds (e.g. -1.11 $\tau$ through -0.15) (169). Proposed structures of $W(CO)_5(S=C(NH_2)_2)$ (XXXIII) and $W(CO)_5(S=C(Ni-PrH)_2)$ (XXXIV), which were assumed to be isostructural with
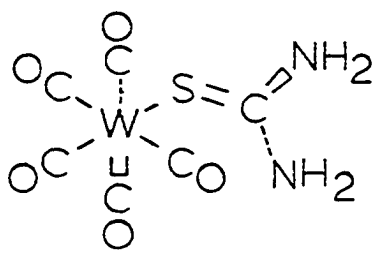
XXXIII
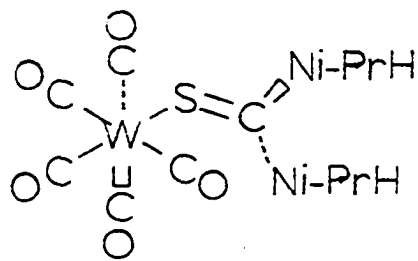
XXXIV

$W(CO)_5(S=CCH_2SCH_2CH_2NH)$ (170) $W(CO)_5(S=CNHCH_2CH_2S)$ (171), and XXIX

(155) appeared to be at variance with the observed resonances of these

complexes. In XXXIII the $NH_2$ fragment and in XXXIV the Ni-PrH group were

in two unique chemical environments; accordingly, the number of resonances

observed should be twice the number actually obtained. A similar problem

occurred with $W(CO)_5(S=CMe_2)$ which has been thoroughly investigated

and discussed (93).

## 5. $^{13}C$ NMR spectra

$^{13}C$ NMR spectra of a few complexes are reported and assigned in

Table 16. Mann (172) and Todd (173) have independently reviewed the

$^{13}C$ NMR spectra of transition metal carbonyl complexes. Assignments were

based on the relative integrated intensities and by analogy to other

reported spectra.

Trans carbonyl resonances were deshielded (down field) relative to

the cis carbonyl resonances (relative intensities 1:4) in the spectra

of the $[M(CO)_5(L)]^-$ and $[\mu-RS[W(CO)_5]_2]^-$ complexes. The same trend has

been observed for other $LM(CO)_5$ complexes and confirmed a $C_{4v}$ symmetry

for $[M(CO)_5L]$ (174). Whereas solution IR spectra of $[\mu\text{-RS}[W(CO)_5]_2]^-$

was complex, $^{13}C$ NMR spectra were simple and supported a $C_{4v}$ local sym-

metry about W. Chemical shifts for two unique carbonyl carbons (relative

intensities 1:1) were not assigned for the $[W(CO)_4(S_2CNPhH)]^-$ complex

(XXVI).

Resonances for the methyl carbons of $[W(CO)_5(SC(=O)Me)]^-$ (-34.4$\delta$)

and $[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^-$ (-30.8$\delta$) were near the reported chemical shift

for the fragment in MeC(=O)SH (-32.6$\delta$) (175). Chemical shifts for the

organic carbonyl carbons of $[W(CO)_5(SC(=O)Me)]^-$ (-206.2$\delta$) and

$[\mu\text{-MeC}(=O)S[W(CO)_5]_2]^-$ (-203.3$\delta$) were down field from the resonance that

was reported for this carbon in MeC(=O)SH (194.5$\delta$) (175). Coordina-

tion of $W(CO)_5$ to $[W(CO)_5(SC(=O)Me)]^-$ resulted in a down shift for the

resonance of the methyl hydrogens; however in the $^{13}C$ NMR spectra of these

complexes an up field shift occurred for the resonances of both the

methyl carbon and the organic carbonyl carbon (above).

## 6. $^{19}F$ and $^{31}P$ NMR spectra

In Table 17 $^{19}F$ NMR spectra are reported and assigned for the new

compounds. Assignments for the chemical shifts that were obtained from

the spectrum of $[W(CO)_5(S\overline{C=CF(CF_2)_3}CF_2)]$ (XXV) were based by analogy to

reported spectra for $X\overline{C=CF(CF_2)_3}CF_2$ where X = halogen, $CH_3$, $CF_3$ (176,

177) and relative integrated intensities. Resonance assignments for

$[W(CO)_5(SCF_2C(=O)CF_3)]^-$ (XXIV) were made by comparison with the reported

spectra of $CF_3C(=O)CF_2X$ where X = $NF_2$, $CF_2C(=O)OH$ (178) and relative

integrated intensities. $^{19}F$ NMR spectra (above) were an invaluable aid in

determining the structure of the organic ligands in the complexes and confirmed the loss of $F^-$ from the organic reagents (Equation 43 and 79).

A $^{31}P$ NMR spectrum of $[\mu-Ph_2PS[W(CO)_5]_2]^-$ (XXXV) was obtained



XXXV                                    XXXVI
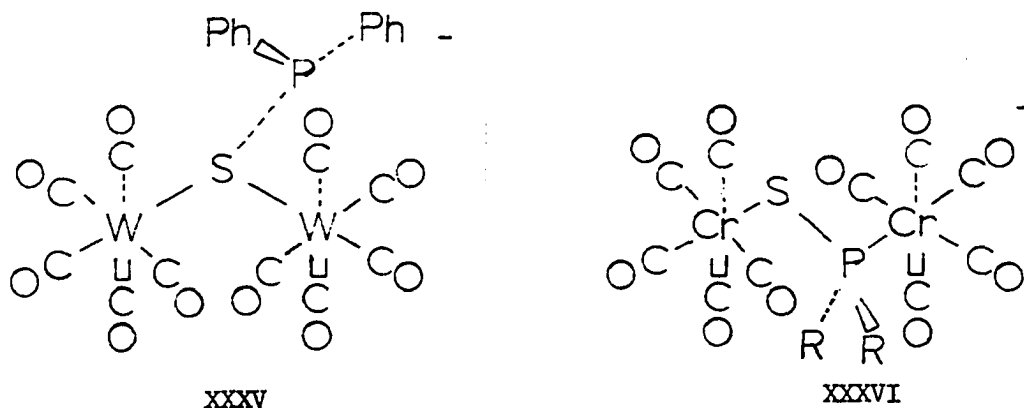
to confirm the proposed structure. A solution IR spectrum of

$[NEt_3H][(CO)_5CrSP(Me)_2Cr(CO)_5]$ which was tentatively given structure XXXVI

(M=Cr) was interpreted as a composite of two $C_{4v}$ spectra (e.g. absorptions

in the spectrum were assigned to the $\cdot SCr(CO)_5$ and $Me_2\dot{P}Cr(CO)_5$ fragments)

(179). The similarity of the solution IR spectrum of $[\mu-Ph_2PS[W(CO_5]_2]^-$

(which was different from the spectrum of XXXVI) to the spectra of other

binuclear complexes (XX) suggested that $[\mu-Ph_2PS[W(CO)_5]_2]^-$ had structure

XXXV. Observation of a singlet which was unaffected in the temperature

range 300°K to 200 at $-35.5\delta$ (down field from $H_3PO_4$) and a doublet which

resulted from $J_{(183_W-31_P)}$ (242 Hz) confirmed that one isomer was present

with the structure XXXV (e.g. a structure like XXXVI would have contained

two $J_{(183_W-31_P)}$ giving a 5 band pattern rather than the 3 bands that were

observed).

## 7. Mass spectra

Mass spectra are reported in Table 18 for the complexes that were volatile. The best conditions for clean fragmentation with relatively intense molecular ions for organometallics is an ionizing potential of 50 ev with a vacuum lock (180). Fragmentation patterns demonstrated a facile loss of carbonyls from the $W(CO)_5L$ complexes suggesting that the W-S bond was stronger than the W-C bond (178).

## 8. Visible spectra

Visible spectra of the $W(CO)_5L$ and $[\mu-RS[W(CO)_5]_2]^-$ complexes (Tables 19, 20 and 21) generally evidenced two bands; extinction coefficients for the higher wavelengths absorptions were normally lower than those of the other band. Other authors have observed the same spectral pattern for $W(CO)_5L$ complexes (181, 182, 183). The extraordinarily high extinction coefficient for the 570 nm band of $W(CO)_5(S=C(p-Me_2NC_6H_4)H)$ was an exception to the above pattern and was responsible for the metallic luster of this complexes crystals. Assignments were not made for the observed bands.

IV. CONCLUSIONS

Pentacarbonylmercapto group 6A metal anionic complexes,

$[M(CO)_5(SH)]^-$ where M = Cr, W, and a binuclear complex, $[\mu-HS[W(CO)_5]_2]^-$,
were stable isolable substances whose physical and chemical properties
were investigated. An investigation of the chemical properties of

$[\mu-S[W(CO)_5]_2]^{2-}$ which was not isolated was also conducted.

Both $[W(CO)_5(SH)]^-$ and $[\mu-S[W(CO)_5]_2]^{2-}$, paralleling the reactivity
of $[RS]^-$ and $[HS]^-$, underwent addition, substitution, and fragmentation
reactions with electrophiles; $[\mu-HS[W(CO)_5]_2]^-$ was inert to most
electrophiles (Figure 6). Addition reactions occurred between

$[W(CO)_5(SH)]^-$ (Figures 2 and 8) or $[\mu-S[W(CO)_5]_2]^{2-}$ (Figure 7) and
heterocumulenes (e.g. $Ph_2C=C=O$, $RN=C=O$, $RN=C=S$, and $Ph_2C=C=NPh$). Acyl
transfer reactions took place between $[W(CO)_5(SH)]^-$ and $MeC(=O)OC(=O)Me$ or

$MeC(=O)O(2,4-(NO_2)_2C_6H_3)$ (Figure 3) and between $[\mu-S[W(CO)_5]_2]^{2-}$ and

$MeC(=O)Cl$ (Figure 7). Substitutions for halides transpired between

$[W(CO)_5(SH)]^-$ and $\overline{CF=CF(CF_2)_3CF_2}$ (Figure 10) or $CF_3C(=O)CF_3$ (Figure 3)
and between $[\mu-S[W(CO)_5]_2]^{2-}$ and $PhCH_2Cl$, $PhCH_2Br$, $Me_3SnCl$, $MeHgCl$, or

$Ph_2PCl$ (Figure 13). Thioketone (Figure 4) and thioaldehyde (Figures
5, 7, and 9) complexes were obtained by acidifying mixtures of

$[W(CO)_5(SH)]^-$ and a ketone or aldehyde (also a Schiff base) or of

$[\mu-S[W(CO)_5]_2]^{2-}$ and an aldehyde. Reactivity of these compounds with
electrophiles followed the order (most reactive to least):

$[\mu-S[W(CO)_5]_2]^{2-} > [W(CO)_5(SH)]^- >>> [\mu-HS[W(CO)_5]_2]^-$.

Physical properties of the new complexes which resulted from the

above reactions were investigated. Thioaldehyde complexes, .
$W(CO)_5(S=C(p-RC_6H_4)H)$ where $R = Me_2N$, MeO, Me, were the first compounds
with these monodentate ligands. The free ligands, $S=C(p-RC_6H_4)H$, are
not stable at room temperature.

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## VI. ACKNOWLEDGMENTS