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Synthesis and reactivity of some tungsten carbene complexes

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SYNTHESIS AND REACTIVITY OF SOME TUNGSTEN CARBENE COMPLEXES

Iowa State University PH.D. 1980

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Synthesis and reactivity of some tungsten carbene complexes

by

Ruth A. Pickering

A Dissertation Submitted to the
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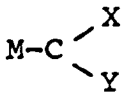
GENERAL INTRODUCTION

The first transition metal carbene complex, $W(CO)_5$-[$C(OCH_3)Ph$], recognized as such was prepared by Fischer and Massböl[1] in 1964. The carbene ligand may be considered as a two electron donor, which when bound to a metal center has the general formula:

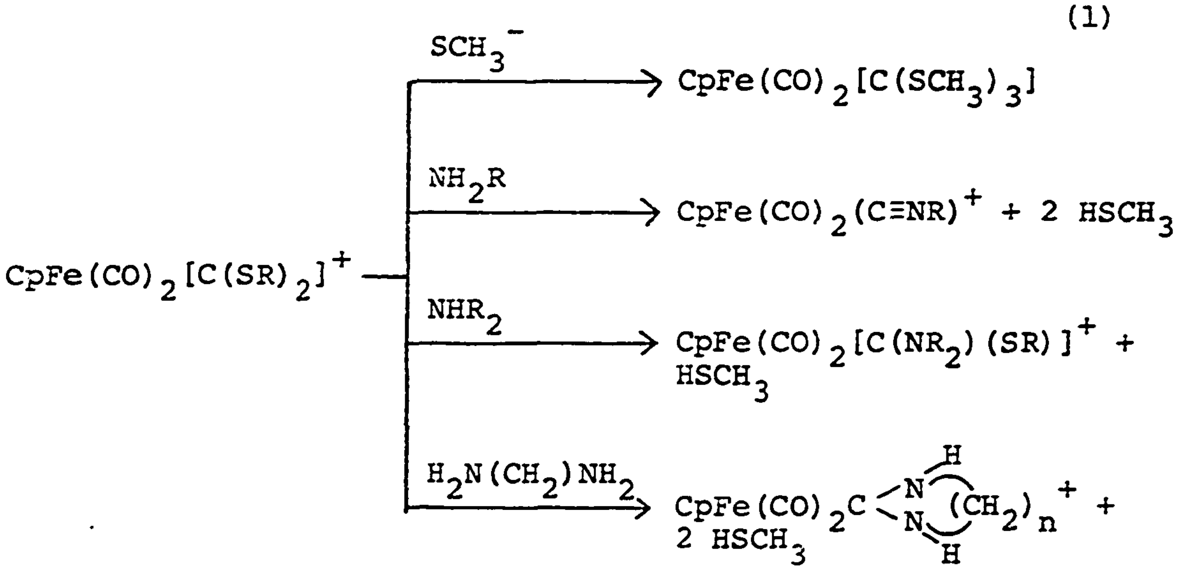


In most stable carbenes the X and or Y group contain a heteroatom; OR, SR, NR_2 or SeR. These heteroatoms help to stabilize the complex by donating π electron density to the p_z orbital of the carbene carbon. The metal atom also helps to stabilize the carbene by donation of electron density from its filled d orbitals. However, the $d_\pi \rightarrow p_\pi$ donation from the metal is generally considered to be not as important in stabilizing carbene complexes as the $p_\pi \rightarrow p_\pi$ donation of the heteroatoms.[2-8]

Much interest has developed in metal stabilized carbene complexes since they were first discovered, and they are thought to be intermediates in several catalytic processes including Fischer-Tropsch,[7] and olefin metathesis[8,9] reactions. However, dithiocarbene complexes have received very little attention. This may be due to the fact that until recently there were no general methods for their preparation and that most of the known preparations gave low yields.[10-19] A complete listing of known dithiocarbene complexes may be found in Fred McCormick's Ph.D. Dissertation.[20]

The only systematic study of the reactivity of dithiocarbene complexes to date was carried out by McCormick and Angelici.[21-24] They recently wrote a series of papers that discuss the high yield preparation of some cyclopentadienyl(dithiocarbene)iron complexes, as well as their reactivity. They found that $CpFe(CO)_2[C(SR)_2]^+$ [21,22] ($Cp=\eta^5-C_5H_5$) are very reactive toward amines and SCH_3^- (eq 1):

(1)



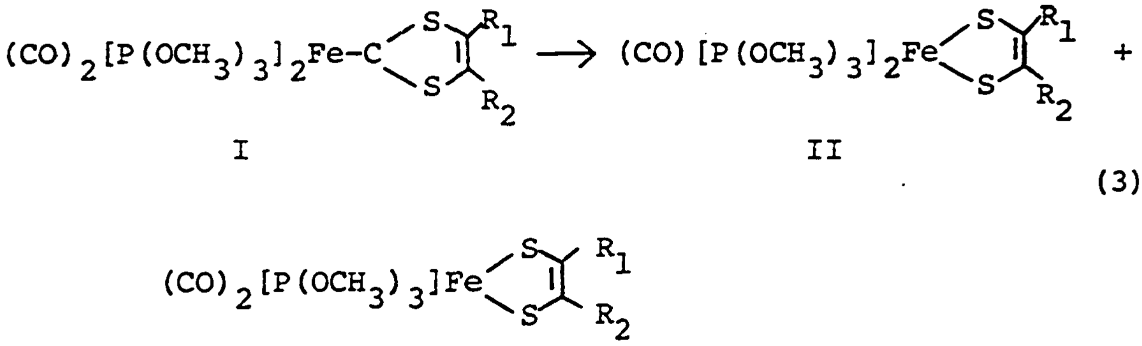
A series of substituted iron dithiocarbene complexes, $CpFe(CO)L[C(SCH_3)_2]^+$,[25] were prepared by photolysis of $CpFe(CO)_2$-

$[C(SCH_3)_2]^+$ in CH_3CN forming $CpFe(CO)(NCCH_3)[C(SCH_3)_2]^+$, which is then reacted with $P(OPh)_3$, $P(OCH_3)_3$, PPh_3, $AsPh_3$, $SbPh_3$, CH_3NC or NC_5H_5 (Ph=phenyl) to form the substituted dithiocarbene iron complexes (eq 2):

$$CpFe(CO)_2[C(SCH_3)_2]^+ \xrightarrow[CH_3CN]{h\nu} CpFe(CO)(NCCH_3)[C(SCH_3)_2]^+ \qquad (2)$$

$$\xrightarrow{L} CpFe(CO)L[C(SCH_3)_2]^+ + NCCH_3$$

The only other reported reaction of dithiocarbene complexes is the air oxidation of some cyclic dithiocarbene iron species,[19] which undergo the loss of the carbene carbon atom (eq 3):


I

II

IIIa

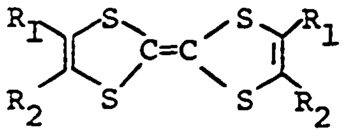
(3)

$R_1=H$, $R_2=CO_2(C_2H_5)$ (Ia)

$R_1=$p-ClC_6H_4, $R_2=CHO$ (Ib)

$R_1=R_2=CO_2(CH_3)$ (Ic)

In the case of Ia and c, the olefin is also formed.

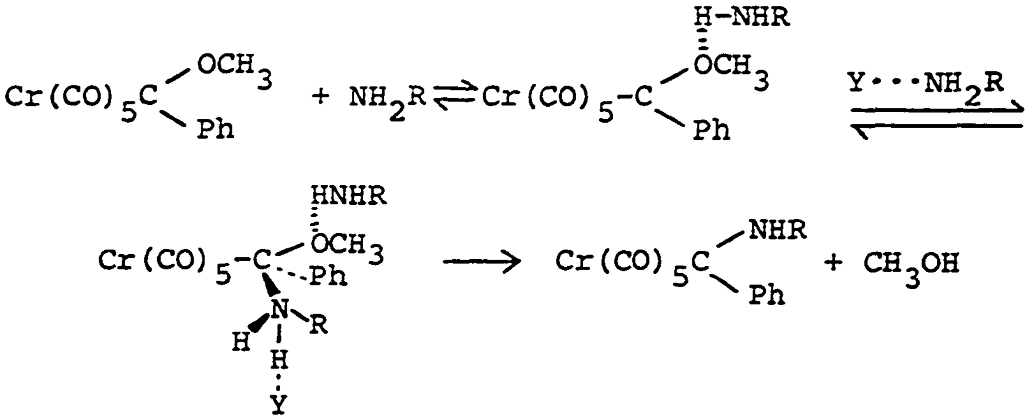


Only a few kinetic and mechanistic studies on the reactivity of carbenes[25-34] have been reported and none of these involved dithiocarbene complexes. However, since some of the work presented in this dissertation is the mechanistic study of the reaction of $W(CO)_5[C(SCH_3)_2]$ with phosphines, we would like to provide a short summary of the previous studies.

The carbene complex $Cr(CO)_5[C(OCH_3)Ph]$ reacts with primary amines to yield $Cr(CO)_5[C(NHR)Ph]$[25,26] (R=n-C_4H_9, CH_2Ph and C_6H_{11}) (eq 4):

$$Cr(CO)_5[C(OCH_3)Ph] + H_2NR \longrightarrow Cr(CO)_5[C(NHR)Ph] + CH_3OH \qquad (4)$$

This reaction is second or third order in amine depending on the nature of the solvent. The reason for this may be seen in the mechanism described in equation 5:



(5)

When the reaction takes place in n-decane solvent, Y is an amine molecule. However, if a solvent capable of hydrogen bonding, dioxane, is used Y is a solvent molecule; thus, reducing the reactions dependence on amine from third to second order.

The reaction of $Cr(CO)_5[C(OCH_3)R]$ ($R=CH_3$ or Ph) with phosphines ($P(C_6H_{11})_3$, $P(p\text{-}C_6H_4CH_3)_3$, PPh_3, $PPh_2(C_2H_5)$, $PPh(C_2H_5)_2$, $P(C_2H_5)_3$ and $P(n\text{-}C_4H_9)_3$)^{27,29} yields $Cr(CO)_4L$-$[C(OCH_3)R]$ and $Cr(CO)_{6-n}L_n$ (n=1 or 2) (eq 6):

$$Cr(CO)_5[C(OCH_3)R] + PR'_3 \longrightarrow Cr(CO)_4PR'_3[C(OCH_3)R] + Cr(CO)_{6-n}(PR'_3)_n \qquad (6)$$

This reaction follows a mechanism with two parallel pathways (eq 7):

$$\begin{tikzcd}
 & Cr(CO)_5L & \\
Cr(CO)_5[C(OCH_3)R] \arrow[ru, "L"] \arrow[rd, "-CO"'] & & \\
 & Cr(CO)_4[C(OCH_3)R] \arrow[r, "L"] & \underline{cis}\text{-}Cr(CO)_4L[C(OCH_3)R]
\end{tikzcd} \qquad (7)$$

The rate law for this reaction is given in equation 8:

$$-d[Cr(carbene)]/dt = k_1[Cr(carbene)] + k_2[Cr(carbene)][L] \qquad (8)$$

The upper pathway in equation 7 is assumed to be associative and gives rise to the second order term. It is important only for the nucleophilic trialkylphosphines, $P(C_2H_5)_3$ and $P(\underline{n}\text{-}C_4H_9)_3$. The lower pathway (eq 7) gives rise to the first order term, and depends only on the rate of dissociation of a cis-CO.

The insertion reaction of $Cr(CO)_5[C(OCH_3)Ph]$[33,34] with ER_3H (E=Si, Ge or Sn; R=C_2H_5, $\underline{i}\text{-}C_3H_7$, $\underline{n}\text{-}C_4H_9$ or Ph) in the presence of pyridine, henceforth referred to as py, gave $Cr(CO)_5(Ph)$, cis-$Cr(CO)_4(py)_2$ and $ER_3[CH(OCH_3)Ph]$ (eq 9):

$$Cr(CO)_5[C(OCH_3)Ph] + ER_3H \longrightarrow Cr(CO)_5(py) + \underline{cis}\text{-}Cr(CO)_4\text{-}(py)_2 + ER_3[CH(OCH_3)Ph] \quad (9)$$

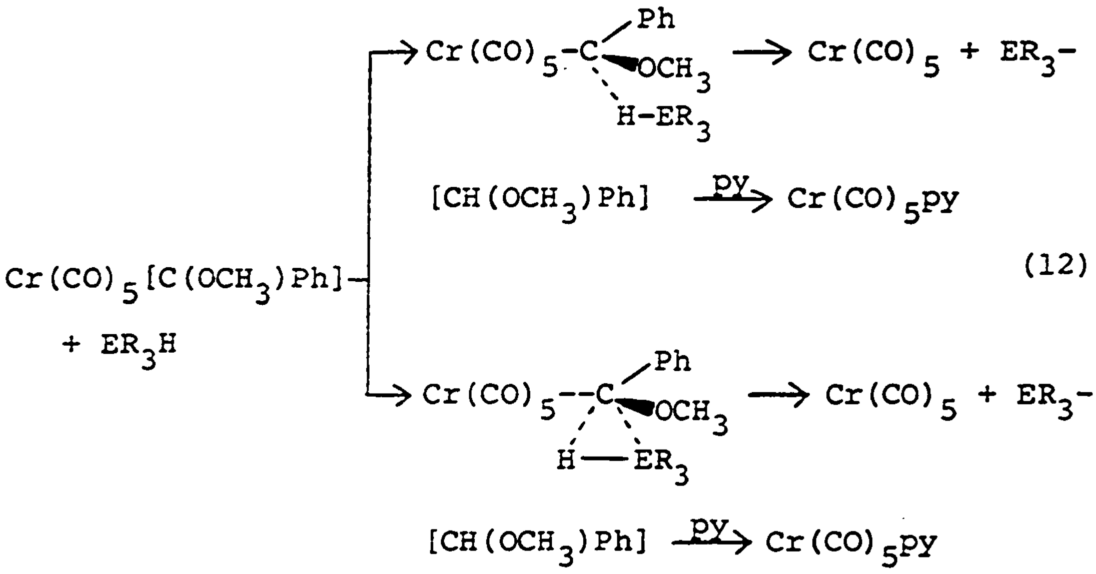
This reaction (eq 9) follows a three term rate law (eq 10):

$$-d[Cr(carbene)]/dt = k_1[Cr(carbene)] + k_2[Cr(carbene)]\text{-}[ER_3H] + k_3[Cr(carbene)][py] \quad (10)$$

However, at the concentrations of py used in these reactions the k_3 term is negligible and the rate law reduces to equation 11:

$$-d[Cr(carbene)]/dt = k_1[Cr(carbene)] + k_2[Cr(carbene)]\text{-}[ER_3H] \quad (11)$$

The second order term arises from an associative pathway, which is thought to involve nucleophilic attack on the carbene-carbon by R_3EH in either a two step or a concerted process (eq 12):



(12)

The rate of reaction was found to increase with E in the order, Si<Ge<Sn, and to decrease upon changing the heteroatomic group of the carbene from OCH_3 to NC_4H_8.

Darensbourg and Conder[31] report the substitution reaction of trans-$LFe(CO)_3[C(OC_2H_5)R]$ (L=PPh_3, $P(OPh)_3$ or $P(\underline{n}-C_4H_9)_3$, R=$CH_3$or Ph) with $P(OPh)_3$, $P(\underline{n}-C_4H_9)_3$ and PPh_3 (eq 13):

$$\underline{\text{trans}}\text{-}LFe(CO)_3[C(OC_2H_5)R] + L' \longrightarrow \underline{\text{trans}}\text{-}L'Fe(CO)_3\text{-}[C(OC_2H_5)R] \qquad (13)$$

The mechanism for this reaction (eq 13) involves a rate-determining dissociation of the phosphorus ligand, L, followed by rapid replacement of the substituting phosphorus ligand, L', (eq 14):

$$\underline{\text{trans}}\text{-LFe(CO)}_3[\text{C(OCH}_3)\text{R}] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Fe(CO)}_3[\text{C(OCH}_3)\text{R}] + \text{L} \underset{k_{-2},\ -\text{L}'}{\overset{k_2,\ +\text{L}'}{\rightleftharpoons}} \underline{\text{trans}}\text{-L}'\text{Fe(CO)}_3[\text{C(OCH}_3)\text{R}] \qquad (14)$$

If k_{-2} is considered to be negligible then the reaction follows the rate law seen in equation 15:

$$\text{rate} = \frac{k_1k_2[\text{L}']}{k_{-1}[\text{L}] + k_2[\text{L}']}\ [\underline{\text{trans}}\text{-LFe(CO)}_3[\text{C(OCH}_3)\text{R}] \qquad (15)$$

Since carbene complexes have proven to be useful in synthetic organic chemistry as stoichiometric reagents[2-6, 35-40] and as intermediates in catalytic processes,[7-9] and since little is known about the preparation and reactivity of dithiocarbene complexes, we decided to undertake a study of pentacarbonyl(dithiocarbene)tungsten complexes. Our purpose was first, to develop a general method for the preparation of these complexes and second to study their reactivities.

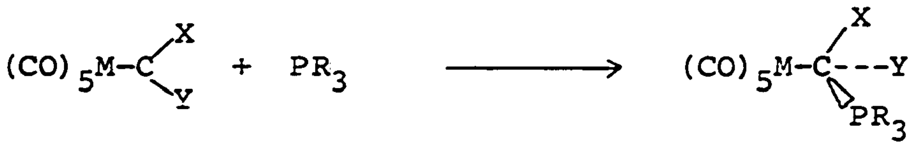
Explanation of Dissertation Format

The material in this dissertation was written so that each section is a manuscript suitable for publication. The numbering of figures and tables apply only to those contained within that section. The literature references cited in the General Introduction and Summary are given at the end under Literature Cited.

SECTION I. REACTIONS OF THE DITHIOCARBENE COMPLEX $W(CO)_5[C(SCH_3)_2]$ WITH PHOSPHINES: CRYSTAL STRUCTURE OF A PHOSPHORANE PRODUCT $W(CO)_5[(CH_3S)_2C{=}PPh_2(CH_3)]$

INTRODUCTION

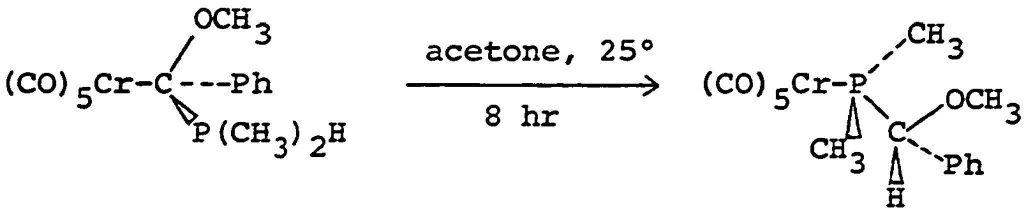
Although the first group VI transition metal carbene was reported by Fischer and Maasböl in 1964,[1] it is only recently that dithiocarbene complexes, $M(CO)_5[C(SPh)_2]$[2,3] and $M(CO)_5[C(SC_2H_5)_2]$,[4] where M=Cr or W, were prepared. Their yields, however, were low, ranging from 2[3] to 15%.[2] While little is known about the reactivity of dithiocarbene complexes, group VI transition metal carbenes of other types are known to react with nucleophiles to form a variety of products.[5-15] Of special relevance to the present report are the reactions of secondary and tertiary phosphines[9-14] with group VI metal carbenes according to equation 1:



(1)

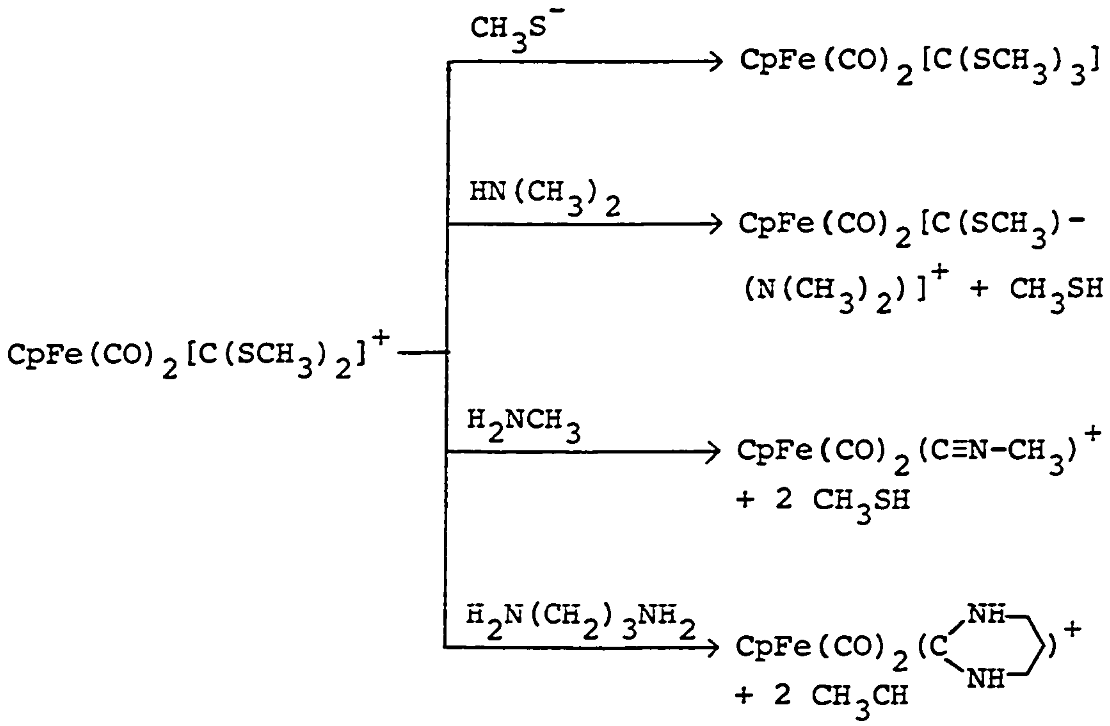
where M=Cr or W, R=alkyl or H, X=OCH_3, SCH_3, or Ph, and Y=CH_3 or aryl

With secondary phosphines a rearrangement product is also formed[11] (eq 2):



(2)

The only reported systematic study of the reactivity of dithiocarbene complexes was that carried out on the cyclopentadienyl dithiocarbene iron cationic complexes, $CpFe(CO)_2[C(SR)_2]^+$.[16-19] McCormick and Angelici[16-19] found that the dithiocarbene ligand in these complexes was highly reactive toward amines and CH_3S^- (eq 3):



(3)

Under the mild conditions of these reactions there was no reaction with secondary or tertiary phosphines. In the present paper we report some surprising reactions of phosphines with the new dithiocarbene complex, $W(CO)_5[C(SCH_3)_2]$, whose high yield synthesis is also described.

EXPERIMENTAL SECTION

General All reactions were performed under prepurified N_2 using Schlenk ware and standard inert atmosphere techniques. The thiocarbonyl complex, $W(CO)_5CS$,[20] was prepared according to the published procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone under N_2 immediately before use. Tertiary phosphines and phosphites were fractionally distilled under N_2 or, when appropriate, recrystallized from hexanes. All other chemicals were reagent grade and used without further purification.

$W(CO)_5[C(SCH_3)_2]$ (II) A solution of $NaSCH_3$ was prepared by bubbling $HSCH_3$ through a THF (80 mL) suspension of NaH (0.0636 g of a 57% oil dispersion, 1.51 mmol) for 30 min. The bubbling was discontinued, and the solution was allowed to stir for an additional 30 min. A mixture[20] of 74.8% $W(CO)_5CS$ (0.669 g, 1.36 mmol) in $W(CO)_6$ was dissolved in 20 mL of THF. This solution was added to the $NaSCH_3$ solution resulting in a color change from yellow to orange. The orange solution was allowed to stir for 5 min followed by addition of CH_3I (0.22 g, 1.5 mmol). After the solution was stirred for approximately 20 min, it was evaporated to dryness under a stream of N_2. The resulting residue was extracted with hexanes, and the hexane extracts were evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CS_2 and placed on a 2 x 36 cm Florisil column. Slow elution with CS_2 led to the separation of two bands. The first eluted band was yellow and was identified as a mixture of $W(CO)_5CS$ and $W(CO)_6$. The second band was orange-red and contained $W(CO)_5[C(SCH_3)_2]$ (0.49 g, 84%). An analytically pure red sample was obtained by recrystallization from pentane at -20° C: mp 63-65° C; IR(hexanes) ν(CO) 2067(m), 1984(vw), 1950(s), 1941(s) cm^{-1}; ^1H NMR($CDCl_3$) τ 7.04(S, CH_3); ^{13}C NMR($CDCl_3$) ppm 300.0(carbene C), 204.4(trans CO), 197.4(cis CO), 29.5 (CH_3); MS m/e 430.02(M^+), 402.04, 374.06, 346.02, 318.04, 290.02 (M^+-$(CO)_n$, n=1-5); Anal. Calcd for $C_8H_6O_5S_2W$: C, 22.34; H, 1.41; S, 14.91. Found: C, 22.64; H, 1.48; S, 14.75.

$W(CO)_5[(CH_3S)_2C{=}PPh_2(CH_3)]$ (IVa) To a solution of $W(CO)_5[C(SCH_3)_2]$ (0.101 g, 0.234 mmol) in 15 mL of THF was added PPh_2CH_3 (0.050 g, 0.25 mmol). After stirring the solution six hours, it was evaporated to an oil under a stream of N_2. The oil was recrystallized from pentane at -20° C to give 0.12 g (82%) of yellow product crystals, which decompose upon standing at room temperature for a few days: mp 95-105° C; IR(hexanes) ν(CO) 2073(w), 1937(s), 1922(m) cm^{-1}; ^1H NMR($CDCl_3$) τ 2.38(m, phenyl), 7.48(S, SCH_3), 7.75(d, J=12 Hz, PCH_3), 7.91(S, SCH_3); ^{13}C NMR($CDCl_3$) ppm

202.1(trans CO), 198.6(cis CO), 132.0, 131.6, 129.2, 128.6, 127.8(phenyl), 37.1(SCH_3), 28.4(J=132.8 Hz, PCS_2), 26.1(SCH_3), 14.0(J=68.4 Hz, PCH_3); Anal. Calcd for $C_{21}H_{19}O_5PS_2W$: C, 40.01; H, 3.04. Found: C, 40.31; H, 3.07.

$W(CO)_5[(CH_3S)_2C{=}P(CH_3)_2Ph]$ (IVb) This complex was prepared by the same method as IVa, starting with $W(CO)_5$-$[C(SCH_3)_2]$ (0.102 g, 0.237 mmol) and $P(CH_3)_2Ph$ (0.033 g, 0.24 mmol). The solution was evaporated to dryness after ten min. A yield of 81% of yellow needles recrystallized from pentane was obtained: mp 45-49° C; IR(hexanes) ν(CO) 2069(w), 1931(s), 1916(m) cm^{-1}; ^1H NMR($CDCl_3$) τ 2.34(m, phenyl), 7.39(S, SCH_3), 7.83(S, SCH_3), 8.02(d, J=13 Hz, PCH_3).

$W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ (IVc) The method used to prepare IVa was also used for this complex, starting with $W(CO)_5[C(SCH_3)_2]$ (0.102 g, 0.237 mmol) and $P(C_2H_5)_3$ (0.028 g, 0.24 mmol). Yellow crystals of $W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ (0.12 g, 89%) were obtained after recrystallization from pentane: mp 81-85° C; IR(hexanes) ν(CO) 2069(w) 1931(s), 1917(m); ^1H NMR ($CDCl_3$) τ 7.35(S, SCH_3), 7.80(S, SCH_3), 8.06(m, PCH_2), 8.81(d of t, J=13 Hz, CH_3); ^{13}C NMR($CDCl_3$) ppm 201.9(trans CO), 198.2(cis CO), 38.6(SCH_3), 26.8(PCS_2), 21.2(SCH_3), 15.7(d, J=56.6 Hz, PCH_2), 5.7(d, J=3.9 Hz, CH_3); Anal. Calcd for $C_{14}H_{21}O_5PS_2W$: C, 30.67; H, 3.87. Found: C, 30.68; H, 3.99.

$W(CO)_5[(CH_3S)_2C{=}P(OCH_3)_3]$ (IVd) This complex was prepared by a route analogous to that used for IVa, starting with $W(CO)_5[C(SCH_3)_2]$ (0.101 g, 0.234 mmol) and $P(OCH_3)_3$ (0.145 g, 1.17 mmol) in 15 mL of cyclohexane. This solution was evaporated to an oil after being stirred for approximately 27 h. This product was always contaminated with some $W(CO)_5P(OCH_3)_3$: mp 49-54° C; IR(hexane) ν(CO) 2074(w), 1937(s), 1924(m) cm^{-1}; ^1H NMR($CDCl_3$) τ 6.18 (d, J=13 Hz, OCH_3), 7.34(S, SCH_3), 7.79(S, SCH_3).

$W(CO)_5[(CH_3S)_2C{=}PPh_3]$ (IVe) This complex was prepared by the method used for IVa, starting with $W(CO)_5[C(SCH_3)_2]$ (0.100 g, 0.232 mmol) and PPh_3 (0.305 g, 1.16 mmol) in 15 mL of cyclohexane. The solution was evaporated to dryness after being stirred for three days. The product was never obtained pure: IR(hexanes) ν(CO) 2070(w), 1938(s), 1930(sh), 1917(m).

$W(CO)_5\{PPh_2[CH(SCH_3)_2]\}$ (v) This compound was prepared in the same manner as IVa, from the reaction of $W(CO)_5$-$[C(SCH_3)_2]$ (0.0953 g, 0.222 mmol) and $PHPh_2$(0.0413 g, 0.222 mmol) in 5 mL of hexanes. The solution was allowed to stir for 8 h at approximately 35° C. After crystallization from pentane, 0.094 g of $W(CO)_5\{PPh_2[CH(SCH_3)_2]\}$ (69%) was obtained: mp 104-107° C; IR(hexanes) ν(CO) 2072(w), 1949(s) 1945(s), 1939(sh); ^1H NMR($CDCl_3$) τ 2.39(m, phenyl), 5.56

(d, J=8 Hz, CH), 8.02(S, SCH_3); ^{13}NMR(CH_3CN) ppm 200.9 (d, J=22 Hz, trans CO), 198.7(d, J=5 Hz, cis CO), 137.0 135.1, 134.6, 132.4, 130.3, 129.9(phenyl), 57.2(d, J=14, Hz PCS_2), 17.1(d, J=2 Hz, SCH_3): Anal. Calcd for $C_{21}H_{12}O_5PS_2W$: C, 38.97; H, 2.79. Found: C, 38.84; H, 2.82.

Spectral Data Proton NMR spectra were recorded at room temperature on a Varian HA 100 spectrometer in $CDCl_3$ with $CHCl_3$ as the internal reference and TMS as the internal lock; temperature dependent ^{1}H NMR were recorded on a Jeol FX-90Q spectrometer. The ^{13}C NMR spectra were also recorded on the Jeol FX-90Q spectrometer; $Cr(acac)_3$ (~0.1M) was added to the solutions to reduce data collection time. Infrared spectra were determined on a Perkin-Elmer 281 spectrometer. Mass spectra were recorded on a Finnigan 4000.

Crystal Data $W(CO)_5[(CH_3S)_2C=PPh_2(CH_3)]$ mol wt 630.34, monoclinic $P2_1/n$, a=13.681(3) Å, b=11.064(1) Å, c=15.913(2) Å, β=94.42(2)°, V=2401.53 $Å^3$, ρ calcd=1.743 g/cm^3, Z=4, μ=53.49 cm^{-1} for Mo Kα.

A single crystal of pentacarbonyl(bis(thiomethyl)methylene diphenylmethylphosphorane)tungsten, $W(CO)_5[(CH_3S)_2$-$C=PPh_2CH_3]$, of approximate dimensions 0.6 x 0.4 x 0.3 mm was mounted on a glass fiber. The fiber was subsequently positioned on a standard goniometer head. Four preliminary ω-oscillation photographs at various χ and ϕ settings, were taken on an automated four-circle x-ray diffractometer, and the coordinates of twelve independent reflections were input to the automatic indexing program ALICE.[21] The resulting cell and reduced-cell scalars indicated $P2_1/n$ (monoclinic) symmetry. Inspection of the axial ω-oscillation photographs confirmed this symmetry. The lattice constants were obtained using least squares refinement based on precise ± 2θ measurements of 15 independent reflections on a previously aligned diffractometer (Mo Kα radiation, λ= 0.70954 Å) at 25° C.

Collection and Reduction of X-ray Intensity Data The data were collected at 25° C with graphite-monochromated Mo Kα radiation on an automated four-circle diffractometer designed and built at the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[22] All data (4575 reflections) within a 2θ sphere of 50° in the hkl and $\bar{h}\bar{k}l$ octants were measured by using an ω-stepscan technique.

As a general check on electronic and crystal stability, the intensities of the three standard reflections were remeasured every 75 reflections. These standards did not vary significantly throughout the entire data collection period. Examination of the data revealed systematic absences for 0k0, k=2n + 1, and h0l, h + l=2n + 1, thus uniquely defining the space group as $P2_1/n$.

The measured intensities were corrected for Lorentz and polarization effects, and an absorption correction was also applied. The estimated error in each intensity was calculated by $\sigma_I{}^2=C_T + K_tC_B + (0.03C_T)^2 + (0.03C_B)^2$ where C_T, K_t and C_B represent the total count, a counting time factor, and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors. The estimated deviations in the structure factors were calculated by the finite difference method.[23] Equivalent data were averaged and yielded 3726 reflections with $I_o > 3\sigma(I)$ which were retained for structural solution and refinement.

Solution and Refinement of the Structure The position of the tungsten atom was obtained by analysis of a sharpened three-dimensional Patterson function. All the remaining atoms (except the H atoms on C8) were found by successive structure factor [24] and electron density map calculations.[25] The atomic positional parameters for the nonhydrogen atoms were refined by using anisotropic parameters by a block matrix least-squares procedure,[26] with final refinement using a full matrix least-squares procedure[24] and minimizing the functions $\Sigma w(|Fo|-|Fc|)^2$ where $w=1/\sigma(F)^2$ to a conventional residual index of $R=\Sigma\big||Fo|-|Fc|\big|/\Sigma|Fo|=0.043$ and the associated weighted index $R_2=0.062$. The hydrogen positions were included but not refined during the least-squares refinement cycles. The scattering factors were those of Hanson et al.,[27] modified for the real and imaginary parts of anomalous dispersion.[28]

RESULTS AND DISCUSSION

Preparation and Characterization of $W(CO)_5[C(SCH_3)_2]$

When a solution of $W(CO)_5CS$ in THF is added to a THF solution of $NaSCH_3$ at room temperature, an immediate color change from yellow to orange-red is observed. The red coloration is presumably due to the formation of the tungsten methyldithio ester anion (eq 4).

$$NaSCH_3 + W(CO)_5CS \longrightarrow \underset{\text{I}}{Na^+[W(CO)_5C(=S)SCH_3^-]} \qquad (4)$$

Fortunately, $W(CO)_6$ does not react with $NaSCH_3$ under these conditions. Thus, the $W(CO)_5CS$ can be used as it is obtained directly from its preparation[20] without separating it from $W(CO)_6$. No attempts have been made to isolate the anionic methyldithio ester. However, it is methylated _in situ_ with either methyl fluorosulfonate or methyl iodide (eq 5) to give $W(CO)_5[C(SCH_3)_2]$ in a yield of about 84%:

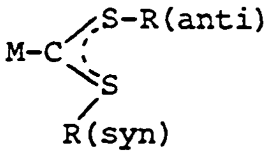
$$Na^+[W(CO)_5C(=S)SCH_3^-] \xrightarrow[\text{or } CH_3I]{CH_3SO_3F} NaX + \underset{\text{II}}{W(CO)_5[C(SCH_3)_2]} \qquad (5)$$

$X = SO_3F$ or I

The carbene complex shows no noticeable decomposition upon exposure to air for a period of several months in the solid state. It is soluble in nonpolar solvents such as hexanes and $(C_2H_5)_2O$ as well as in more polar solvents such as $CHCl_3$, THF, CH_2Cl_2, acetone and C_2H_5OH, but it is insoluble in H_2O. Solutions of II exposed to air at room temperature are stable for a period of 3 or 4 days.

The IR spectrum of II is composed of four ν(CO) absorptions at 2067(m), 1984(vw) 1950(s) and 1941(s) cm^{-1}, which yield approximate C-O stretching force constants[29] of k_1= 15.6(trans) and k_2=15.9(cis) mdyn/Å. While the constants are lower then those of the corresponding carbonyl ($W(CO)_6$, k=17.7 mdyn/Å)[30] indicating that the carbene ligand has a lower π acceptor/σ donor ratio than CO[16], they are very similar to those of $W(CO)_5(PPh_3)$ (k_1=15.5, k_2=15.9).[31] This result indicates that the π acceptor/σ donor ratio of the $C(SCH_3)_2$ carbene ligand is comparable to that of PPh_3; a similar conclusion was reached previously for the analogous $CpFe(CO)_2L^+$ complexes.[17]

The ^1H NMR spectrum of II in acetone-d_6 shows a singlet at τ 6.95 for the two methyl groups. Equivalent alkyl groups in the carbene ligands were also observed in the NMR spectra of other tungsten and chromium dithiocarbenes ($M(CO)_5[C(S\text{-}Ph)_2]$[3] and $M(CO)_5[C(SC_2H_5)_2]$,[4] where M=W or Cr) and iron dithiocarbenes[16,17] $(CpFe(CO)L[C(SCH_3)_2]^+$, where L=CO, CH_3CN, PPh_3, $AsPh_3$, $P(OCH_3)_3$, $SbPh_3$, C_5H_5N). In the cases of $\{PtCl[C(SCH_3)_2](PPh_3)_2\}BF_4$[32] $\{PtI[C(SCH_3)_2](PPh_3)_2\}I$[33] and $\{PtI[C(SC_2H_5)_2](PPh_3)_2\}I$[33] the carbene alkyl groups were nonequivalent in their room temperature ^1H NMR spectra. This nonequivalence presumably results from restricted rotation about the C(carbene)-S bond giving rise to syn and anti alkyl groups.[32,33]



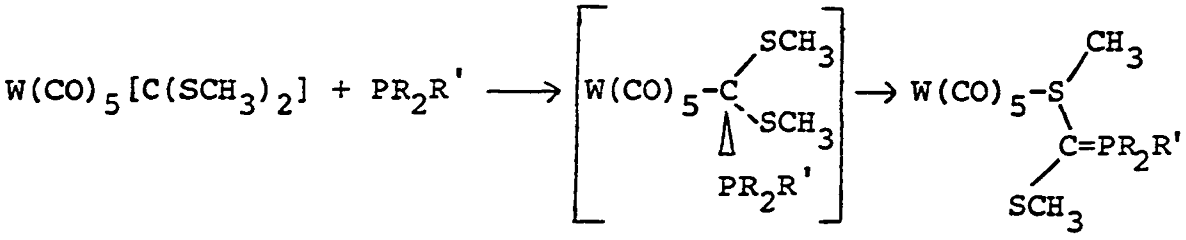
Such restricted rotation is presumably favored by the positive Pt which promotes pπ electron donation from the S to the p_z orbital of the C(carbene) atom.[16] Restricted rotation is also observed in $W(CO)_5[C(SCH_3)_2]$. Although the CH_3 groups occur as a singlet in the room temperature spectrum, two sharp singlets at τ 6.75 and 7.15 are observed upon cooling an acetone-d_6 solution to -22° C. These singlets broaden and coalesce at -4° C as the solution is warmed. Similar behavior has previously been observed for $\{CpFe(CO)L[C(SCH_3)_2]\}PF_6$[16,17] (L=CO, CH_3CN, PPh_3, $AsPh_3$, $P(OCH_3)_3$, $P(OPh)_3$, $SbPh_3$, C_5H_5N).

McCormick and Angelici[16] rationalized the difference in the rate of rotation in the platinum and iron carbenes by suggesting that the $Cl(PPh_3)_2Pt^+$ moiety is probably more electron withdrawing than the $CpFe(CO)_2^+$. This suggestion is supported by the higher ν(CO) force constant of $[Cl(PPh_3)_2Pt(CO)^+]BF_4^-$ (18.2 mdyn/Å)[34] as compared to $[CpFe(CO)_3^+]PF_6^-$ (17.6 mdyn/Å).[35] Since the force constant (17.7 mdyn/Å)[30] for $W(CO)_6$ is very similar to that of $CpFe(CO)_3^+$, both $W(CO)_5[C(SCH_3)_2]$ and $CpFe(CO)_2[C(SCH_3)_2]^+$ should have similar rotational barriers. Qualitatively, this is observed to be true since their coalescence temperatures (-4° and -2.5° C[16], respectively) are nearly identical.

Reactions of $W(CO)_5[C(SCH_3)_2]$ with Tertiary Phosphines

The reaction (eq 6) of II with tertiary phosphines and phosphites provides a general, high yield synthesis of a new class of compounds, IV.

(6)



III IV

PR_2R' = PPh_2CH_3(IVa), $P(CH_3)_2Ph$(IVb), $P(C_2H_5)_3$(IVc), $P(OCH_3)_3$(IVd), PPh_3(IVe)

The reaction at room temperature proceeds almost instantaneously with $P(C_2H_5)_3$ but requires about 3 days with PPh_3. It presumably proceeds by initial attack of the phosphine or phosphite on the empty p_z orbital of the carbene C, followed by rapid rearrangement to the final product IV. The net effect is to transfer the $C(SCH_3)_2$ carbene unit from the tungsten to the phosphorus. The complexes IV decompose upon standing at room temperature when exposed to air over a period of one or two days. However, they may be stored in air at -20° C for a period of months without noticeable decomposition. They are soluble in most common organic solvents ranging in polarity from hexane to acetone.

Because there is no precedent in the literature for a complex having structure IV or for the rearrangement leading to it, an x-ray diffraction study of IVa was undertaken. The unit cell contains four molecules and has $P2_1/n$ symmetry. A stereo view of the unit cell is shown in Figure 1. Figure II shows IVa as discrete molecules having a slightly distorted octahedral symmetry around the tungsten atom in which the bis(thiomethyl)methylene diphenylmethylphosphorane ligand is bound to the tungsten atom <u>via</u> S1. Final positional and thermal parameters, bond distances, bond angles and equations of least squares planes are given in Tables I-V respectively.

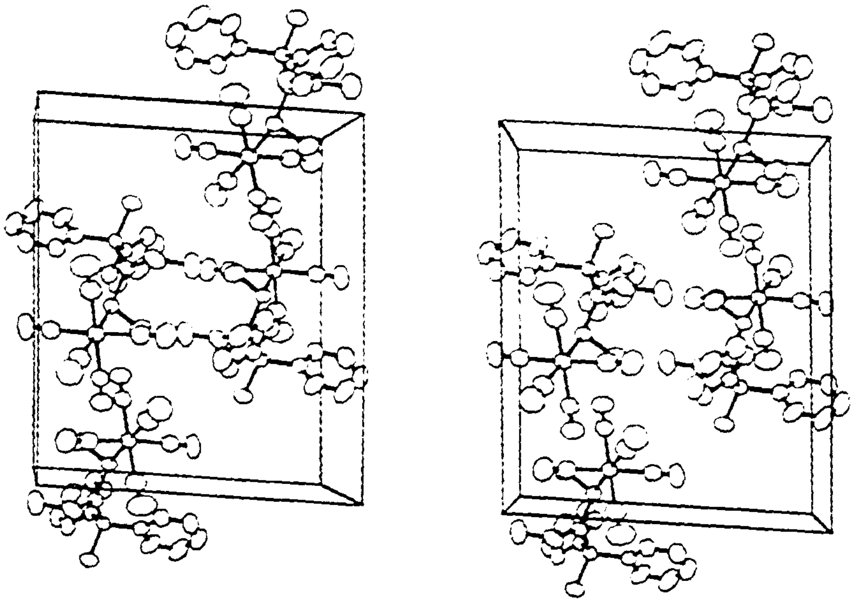


Figure 1. Stereoscopic view of the unit cell with the a axis horizontal and the c axis vertical

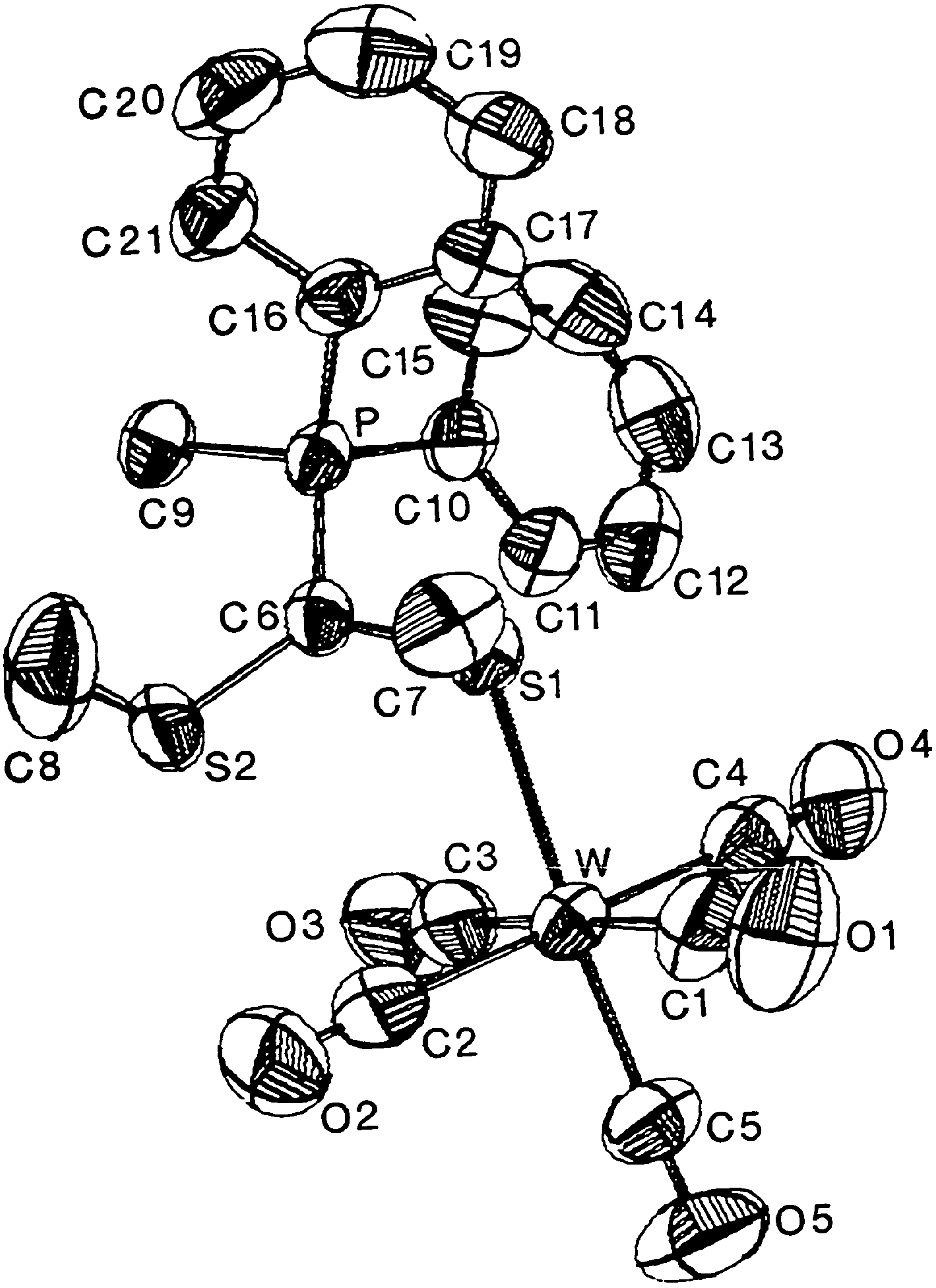


Figure 2. Structure of $W(CO)_5[(CH_3)_2C{=}PPh_2(CH_3)]$

Table I. Final positional parameters and their estimated standard deviations (in parentheses)[a] for $W(CO)_5$-$[(CH_3S)_2C{=}PPh_2(CH_3)]$

	x	y	z
W	0.81663(2)	0.15098(2)	0.60537(1)
S1	0.75843(13)	0.34431(13)	0.52920(10)
S2	0.62625(17)	0.20412(21)	0.40102(12)
P	0.74280(11)	0.41913(15)	0.35371(9)
O1	0.85297(65)	0.02115(58)	0.43410(42)
O2	0.60213(51)	0.03911(70)	0.59897(43)
O3	0.79181(51)	0.27030(76)	0.78347(35)
O4	1.03554(43)	0.24077(66)	0.59713(44)
O5	0.90347(57)	0.92867(67)	0.70472(46)
C1	0.83581(62)	0.06878(71)	0.49431(49)
C2	0.67755(64)	0.08285(75)	0.60052(45)
C3	0.79895(58)	0.22972(84)	0.71871(47)
C4	0.95654(61)	0.21288(70)	0.60216(41)
C5	0.87111(62)	0.00908(81)	0.66752(50)
C6	0.70984(47)	0.31690(60)	0.42642(36)
C7	0.66062(65)	0.41011(81)	0.58467(48)
C8	0.50614(74)	0.27244(150)	0.41036(73)
C9	0.69132(62)	0.37570(73)	0.25073(42)
C10	0.87365(47)	0.42817(59)	0.34548(37)

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[a] The positional parameters are presented in fractional unit cell coordinates.

Table I. (continued)

	x	y	z
C11	0.93618(59)	0.34356(66)	0.38430(51)
C12	1.03656(69)	0.34716(82)	0.37335(65)
C13	1.07166(64)	0.43634(106)	0.32391(66)
C14	1.00900(75)	0.51828(87)	0.28422(66)
C15	0.91079(60)	0.51627(67)	0.29568(50)
C16	0.70450(46)	0.57344(59)	0.37297(39)
C17	0.75273(60)	0.63923(59)	0.43804(51)
C18	0.72038(64)	0.75254(70)	0.45774(56)
C19	0.63935(75)	0.80056(85)	0.41363(64)
C20	0.59141(62)	0.73656(85)	0.34928(60)
C21	0.62263(56)	0.62286(77)	0.32838(52)
H1	0.60625	0.35625	0.57188
H2	0.63756	0.47500	0.55625
H3	0.67500	0.45312	0.63125
H4	0.72812	0.29687	0.24219
H5	0.61406	0.38437	0.24843
H6	0.70625	0.44375	0.21094
H7	0.91875	0.26875	0.41250
H8	1.07812	0.26562	0.41406
H9	1.14375	0.42344	0.30703
H10	1.02812	0.58125	0.24219
H11	0.86563	0.59062	0.26719
H12	0.83475	0.60312	0.46094
H13	0.77187	0.80000	0.51250
H14	0.60625	0.89062	0.42187
H15	0.53125	0.77500	0.32187
H16	0.59062	0.57969	0.27187

Table II. Final thermal parameters (x 10) and their estimated standard deviations (in parentheses) for the nonhydrogen atoms of $W(CO)_5[(CH_3S)_2C{=}PPh_2(CH_3)]$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	46.6(2)	47.8(2)	34.3(1)	-3.29(9)	-3.6(1)	5.12(7)
S1	45.6(7)	45.7(8)	31.8(6)	-3.3(5)	-2.7(5)	0.4(4)
S2	76(1)	64(1)	52.8(8)	-31.2(9)	-17.7(8)	6.5(8)
P	39.9(6)	44.3(8)	31.1(6)	-3.4(6)	-4.8(5)	2.6(5)
O1	140(6)	69(3)	71(3)	-10(3)	11(3)	-26(3)
O2	74(3)	105(5)	87(4)	-34(3)	10(3)	19(3)
O3	85(4)	140(6)	46(2)	6(4)	1(2)	-22(3)
O4	44(2)	99(4)	97(4)	-6(2)	-5(2)	0(3)
O5	101(4)	86(5)	91(4)	21(3)	-2(3)	37(3)
C1	72(4)	50(4)	52(3)	-5(3)	-3(3)	-5(3)
C2	67(4)	58(4)	50(3)	-5(3)	1(3)	10(3)
C3	54(4)	86(5)	43(3)	-1(3)	-4(3)	4(3)
C4	61(4)	56(4)	42(3)	6(3)	-3(3)	1(2)
C5	65(4)	70(4)	55(3)	1(3)	-6(3)	20(3)
C6	45(3)	45(3)	34(2)	-10(2)	-6(2)	2(2)
C7	75(4)	66(4)	52(3)	12(4)	11(3)	-4(3)

Table II. (continued)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C8	52(4)	171(11)	96(7)	-23(6)	-5(4)	15(7)
C9	66(4)	64(4)	35(3)	-4(3)	-7(3)	-2(2)
C10	45(3)	50(3)	37(2)	-1(2)	2(2)	-3(2)
C11	50(3)	66(4)	52(3)	0(3)	-2(3)	2(3)
C12	53(4)	85(6)	71(5)	8(3)	-6(4)	-11(4)
C13	49(4)	92(6)	85(5)	-17(4)	-17(4)	-27(5)
C14	72(5)	65(5)	92(5)	-16(4)	37(4)	-11(4)
C15	70(4)	46(3)	65(4)	-2(3)	26(3)	-2(3)
C16	43(3)	47(3)	40(2)	0(2)	3(2)	8(2)
C17	54(3)	40(3)	55(3)	-3(2)	3(3)	0(2)
C18	65(4)	45(4)	77(4)	-7(3)	8(3)	-1(3)
C19	79(5)	55(4)	82(5)	1(4)	28(5)	7(4)
C20	52(3)	69(5)	84(5)	16(3)	8(3)	28(4)
C21	44(3)	62(4)	61(4)	6(3)	-1(3)	13(3)

Table III. Interatomic distances (Å) and their estimated standard deviations (in parentheses) for $W(CO)_5[(CH_3S)_2C{=}PPh_2(CH_3)]$

W-S1	2.555(2)	C14-C15	1.370(13)
W-C1	2.022(8)	C15-C17	1.390(10)
W-C2	2.043(9)	C16-C21	1.391(10)
W-C3	2.034(8)	C17-C18	1.373(10)
W-C4	2.037(8)	C18-C19	1.373(13)
W-C5	1.972(9)	C19-C20	1.371(14)
S1-C6	1.744(6)	C20-C21	1.391(12)
S1-C7	1.812(9)	C7-H1	0.963(9)
S2-C6	1.719(7)	C7-H2	0.893(9)
S2-C8	1.825(12)	C7-H3	0.890(8)
P-C6	1.704(6)	C9-H4	1.021(8)
P-C9	1.799(7)	C9-H5	1.059(9)
P-C10	1.808(7)	C9-H6	1.015(8)
P-C16	1.819(7)	C11-H7	0.979(8)
O1-C1	1.134(10)	C12-H8	1.224(9)
O2-C2	1.139(11)	C13-H9	1.052(9)
O3-C3	1.135(10)	C14-H10	1.014(10)
O4-C4	1.133(10)	C15-H11	1.015(8)
O5-C5	1.138(11)	C17-H12	1.221(8)
C10-C11	1.382(10)	C18-H13	1.118(9)
C10-C15	1.377(10)	C19-H14	1.105(9)
C11-C12	1.398(12)	C20-H15	0.997(9)
C12-C13	1.373(15)	C21-H16	1.080(8)
C13-C14	1.368(15)		

Table IV. Bond angles (deg) and their estimated standard deviations (in parentheses) for W(CO)$_5$-[(CH$_3$S)$_2$C=PPh$_2$(CH$_3$)]

S1-W-C1	91.1(2)	C6-P-C9	109.6(3)
S1-W-C2	92.0(2)	C6-P-C10	113.7(3)
S1-W-C3	90.5(3)	C6-P-C16	114.5(3)
S1-W-C4	88.1(2)	C9-P-C10	105.6(3)
S1-W-C5	175.4(3)	C9-P-C16	107.9(3)
C1-W-C2	89.1(3)	C10-P-C16	105.1(3)
C1-W-C3	178.5(3)	S1-C6-P	114.8(4)
C1-W-C4	86.8(3)	S1-C6-S2	123.1(4)
C1-W-C5	90.6(3)	S2-C6-P	121.9(4)
C2-W-C3	91.0(3)	P-C10-C11	120.8(5)
C2-W-C4	175.9(3)	P-C10-C15	119.5(5)
C2-W-C5	92.3(3)	P-C16-C17	119.4(5)
C3-W-C4	93.1(3)	P-C16-C21	121.0(5)
C3-W-C5	87.9(3)	C10-C11-C12	120.3(7)
C4-W-C5	87.8(3)	C10-C15-C14	119.8(8)
W-S1-C6	112.4(2)	C11-C12-C13	118.8(8)
W-S1-C7	108.7(3)	C11-C10-C15	119.6(7)
W-C1-01	175.4(8)	C12-C13-C14	120.5(9)
W-C2-02	176.4(8)	C13-C14-C15	120.9(9)
W-C3-03	177.1(8)	C16-C17-C18	120.4(7)
W-C4-04	175.4(7)	C16-C21-C20	119.2(8)
W-C5-05	178.4(8)	C17-C18-C19	119.9(8)
C6-S1-C7	106.5(3)	C17-C16-C21	119.4(7)
C6-S2-C8	105.5(5)	C18-C19-C20	120.1(9)

Table IV. (continued)

C19-C20-C12	120.9(8)	C14-C13-H9	122.7(10)
S1-C7-H1	103.6(6)	C14-C15-H11	117.1(8)
S1-C7-H2	108.8(7)	C15-C14-H10	113.9(9)
S1-C7-H3	119.8(8)	C16-C17-H12	115.1(6)
P-C9-H4	100.8(5)	C16-C21-H16	120.6(7)
P-C9-H5	109.0(5)	C17-C18-H13	112.6(7)
P-C9-C6	106.6(6)	C18-C17-H12	122.4(7)
C10-C11-H7	127.8(8)	C18-C19-H14	127.7(9)
C10-C15-H11	122.9(7)	C19-C18-H13	127.4(8)
C11-C12-H8	109.5(8)	C19-C20-H15	116.0(9)
C12-C11-H7	110.9(8)	C20-C19-H14	112.2(9)
C12-C13-H9	115.1(10)	C20-C19-H16	148.3(7)
C13-C12-H8	131.7(9)	C21-C20-H15	123.0(9)
C13-C14-H10	125.1(10)		

Table V. Equations of least squares planes[a] in $W(CO)_5[(CH_3S)_2C{=}PPh_2(CH_3)]$

Atom	D[b]	Atom	D
Plane 1: W-O1-O2-O3-O4-C1-C2-C3-C4			
0.3068 X - 0.8228 Y + 0.4785 Z - 6.4345 = 0			
W	-0.0112	C1	0.0162
O1	0.0875	C2	-0.0102
O2	0.0600	C3	0.0154
O3	0.0833	C4	-0.0102
O4	0.0313		
Plane 2: W-S1-O1-O3-O5-C1-C3-C5			
0.9337 X + 0.3571 Y + 0.0255 Z - 10.6 = 0			
W	-0.0339	O5	0.1242
S1	0.0423	C1	-0.0313
O1	0.0443	C3	-0.0327
O3	-0.0116	C5	0.0557
Plane 3: W-S1-O2-O4-O5-C2-C4-C5-C20			
-0.1764 X + 0.4494 Y + 0.8757 Z - 7.3044 = 0			
W	0.0159	C2	-0.0553
S1	0.0430	C4	-0.0594
O2	-0.1124	C5	0.0558
O4	-0.1826	C20	-0.1420
O5	0.1027		

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[a] Planes are defined as $C_1X + C_2Y + C_3Z + C_4 = 0$ where X, Y, and Z are Cartesian coordinates.

[b] D is the distance (Å) of the given atom from the fitted plane.

Table V. (continued)

Atom	D	Atom	D
Plane 4: S1-S2-P-C6			
0.7811 X - 0.5986 Y - 0.1776 - 4.8442 = 0			
S1	-0.0122	C6	0.0377
S2	-0.0132	O2	0.0743
P	-0.0123		
Plane 5: C10-C11-C12-C13-C14-C15			
0.0829 X + 0.6006 Y + 0.7953 Z - 8.1583 = 0			
P	-0.1036	C12	-0.0027
C6	0.0897	C13	0.0108
C10	0.0018	C14	-0.0131
C11	-0.0035	C15	0.0061
Plane 6: C16-C17-C18-C19-C20-C21			
0.6421 X + 0.4058 Y - 0.6504 Z - 4.6237 = 0			
P	-0.1409	C19	-0.0034
C16	0.0012	C20	0.0025
C17	-0.0021	C21	-0.0013
C18	0.0033		
Dihedral Angles			
Plane 1 and plane 2	89.72		
Plane 1 and plane 3	90.27		
Plane 1 and plane 4	49.67		
Plane 1 and plane 5	95.06		
Plane 1 and plane 6	116.62		

Table V. (continued)

Plane 2 and plane 3	88.96
Plane 2 and plane 4	59.27
Plane 2 and plane 5	71.81
Plane 2 and plane 6	43.29
Plane 3 and plane 4	124.21
Plane 3 and plane 5	17.87
Plane 3 and plane 6	120.03
Plane 4 and plane 5	115.85
Plane 4 and plane 6	68.03
Plane 5 and plane 6	102.73

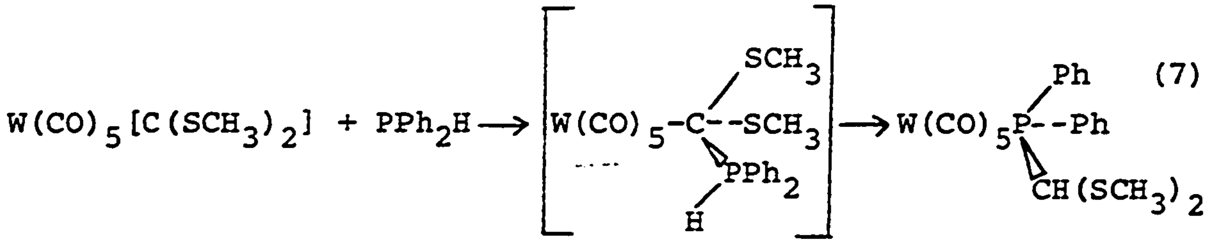
The bond lengths and angles (W-C, 2.043(9)-1.972(9) Å; C-O, 1.139(11)-1.133(10) Å; cis C-W-C, 86.8(3)-93.1(3)°; trans C-W-C 175.9(3)-178.5(3)°; and W-C-O, 175.4(7)-178.4(8)°) for the $W(CO)_5$ portion of the molecule are very similar to values observed in other molecules.[36,37] The bond between W and C5 (C5 is trans to S1) is shorter than the other W-C bonds by at least 0.05 Å indicating that the π acceptor/σ donor ratio is lower for the phosphorane ligand than for CO. The tungsten-sulfur bond length of 2.555(2) Å compares favorably with those in $(CO)_5W-\underline{SCH_2CH_2NH\overset{O}{\overset{\|}{C}}}CH_2$ (2.551(14) Å)[37] and $(CO)_4\underline{W-[S(Bu^t)CH_2CH_2S}(Bu^t)]$ (2.565(4) and 2.559(5) Å).[36]

The methylene carbon C6 and the atoms bound to it S1, S2 and P are coplanar with bond angles ranging from 114.8(4)-123.1(4)° indicating the sp^2 hybridized character of the carbon atom. The P-C6 bond length of 1.704(6) Å is similar to that (1.709(19) Å)[38] found in $Ph_3P=CH[SO_2(C_6H_4CH_3$-p)] and that (1.71(5) Å)[39] found in $Ph_3P=C(I)(C=OPh)$. The S1-C6 and the S2-C6 distances, 1.744(6) and 1.718(7) Å, respectively, are within the range of normal $C(sp^2)$-S bonds.[40-42] The S1-C6 bond distance of the coordinated S atom is slightly longer that the S2-C6 distance of the uncoordinated S.

The spectral characteristics of IVa-c are, in general, very similar and are expected on the basis of the above structural assignment. Their IR spectra are consistent with the pseudo C_{4v} symmetry, found for IVa, containing three ν(CO) absorptions in a weak-strong-medium pattern. Their ^{1}H NMR spectra show a singlet for each of the two different methyl groups on the sulfur atoms, and the ^{13}C NMR spectra of IVa and c also show separate peaks for these different methyl groups. Although spectra of the related complex $M(CO)_5[(PhS)_2C{=}PPh_3]$, where M=Cr or W, were not given in the conference report[2] describing their synthesis from $M(CO)_6$ and $(PhS)_2C{=}PPh_3$, a structure was proposed in which the phosphorane carbon, rather than the S, was coordinated to the metal. It is possible that this complex has a structure analogous to IV.

Since amines cannot form phosphorane analogs, $(CH_3S)_2$-$C{=}NR_3$, it seemed that amines may give stable carbene adducts, III in eq 6. There is, however, no evidence of reaction between $W(CO)_5[C(SCH_3)_2]$ and $N(C_2H_5)_3$ or 1,4-diazabicyclo[2.2.2] octane. Thus it appears that the carbene adduct is unstable relative to the reactants. This result also suggests that it is the formation of the phosphorane product which provides the overall driving force for reaction 6.

With a Secondary Phosphine Reaction of the secondary phosphine PPh_2H with II does not give a phosphorane complex (eq 6) as found with the tertiary phosphines but instead yields the phosphine derivative (eq 7):



(7)

III V

Product (V) is pale yellow in the solid state, is soluble in most common solvents and is stable at -20° C for a period of months. The structure assigned to complex V is based on its ^1H and ^{13}C NMR spectra. Consistent with this structure is the equivalence of both SCH_3 groups in both the ^1H and ^{13}C spectra of the complex. The J_{PCH} coupling constant (8 Hz) is consistent[43] with the hydrogen atom being bound to the carbon rather than remaining on the phosphorus in which case the J_{PH} would be expected to be in the range of 200-700 Hz.[43] The J_{PWC} values for the cis and trans CO groups (5 Hz and 22 Hz, respectively) are very similar to those in related PR_3 complexes.[31,44]

The reaction presumably proceeds by initial attack of the phosphine on the p_z orbital of the carbene C to give intermediate III. This intermediate could rearrange directly to the product by H atom migration to the C and P migration to the W as was suggested[11] for reaction 2 or it could rearrange first to the corresponding phosphorane complex IV which could then convert to V by migration of the H from P to the basic C atom followed by migration of P to the W.

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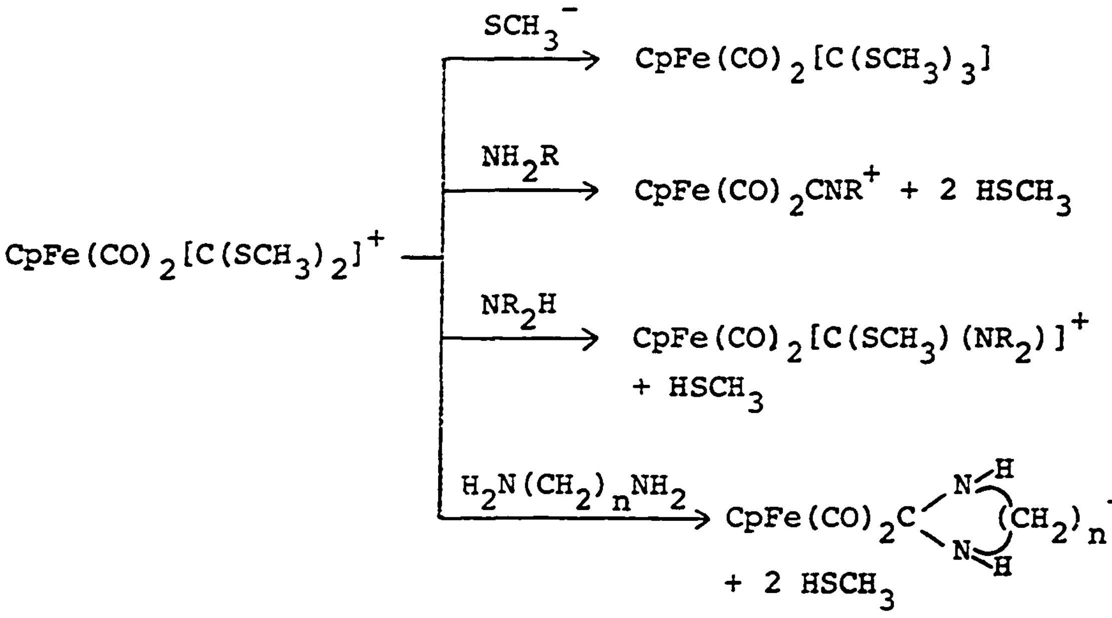
SECTION II. PREPARATION OF SOME DITHIOCARBENE COMPLEXES, $W(CO)_5[C(SR)_2]$, AND THEIR REACTIONS WITH NUCLEOPHILES

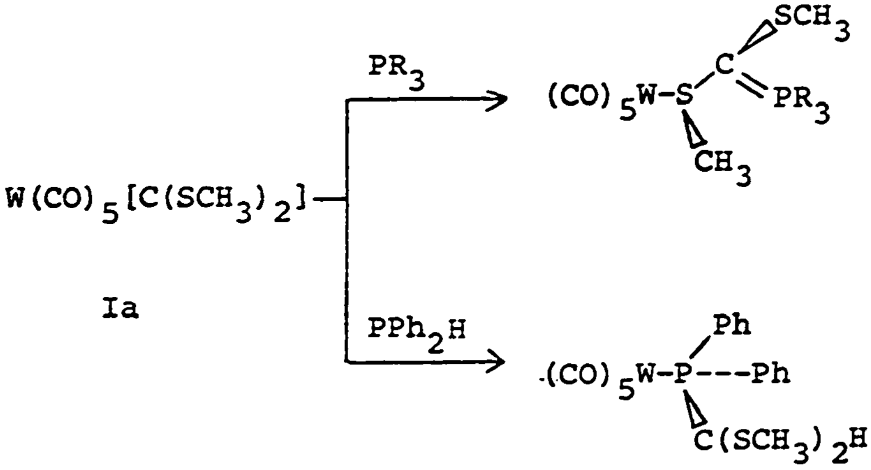
INTRODUCTION

It has been only recently that transition metal complexes containing the dithiocarbene ligand $[=C(SR)_2]$ have been isolated,[1-11] and only a few studies of their reactivity have been reported.[8,10,11] McCormick and Angelici[8] found that $CpFe(CO)_2[C(SCH_3)_2]^+$ $(Cp=\eta^5-C_5H_5)$ reacts with mercaptides and amines according to equation 1:[12]



(1)

Recently, we reported the preparation of $W(CO)_5[C(SCH_3)_2]$[11] and its remarkable reactions with secondary and tertiary phosphines (eq 2):



(2)

We would now like to report the preparations of other dialkyldithiocarbene pentacarbonyl tungsten complexes, $W(CO)_5[C(SR)_2]$, and their reactions with amines and other nucleophiles.

EXPERIMENTAL SECTION

General The thiocarbonyl and carbene complexes, $W(CO)_5CS$,[13] $W(CO)_4(CS)P(OCH_3)_3$,[14] $W(CO)_4(CS)P(OPh)_3$,[14] $W(CO)_5[C(SCH_3)_2]$[11] and $[CpFe(CO)_2(THF)^+][BF_4^-]$[15] were prepared as previously reported. A mixture[13] of $W(CO_5)CS$ ranging from 41 to 78% in $W(CO)_6$ was used in the preparation of the carbene products unless otherwise stated. The NaH used was a 57% oil dispension. The grams and millimoles of $W(CO)_5CS$ and NaH listed below are the amounts of these compounds actually used. Tetrahydrofuran (THF) was distilled from sodium benzophenone under N_2 immediately before use. Hexanes were stored over 4A molecular sieves. All other chemicals were reagent grade and used without further purification. All reactions were performed under prepurified N_2 using Schlenk ware and standard inert atmosphere techniques.

$W(CO)_5[C(SC_2H_5)(SCH_3)]$ (IIb) A solution of $NaSC_2H_5$ was made by adding HSC_2H_5 (0.037 g, 0.63 mmol) to a suspension of NaH (0.016 g, 0.65 mmol) in 15 mL of THF. The solution was allowed to stir for 45 min at room temperature. Then the $W(CO)_5CS$[13] (0.15 g, 0.41 mmol) in 10 mL of THF was added to the $NaSC_2H_5$ solution. The resulting orange solution was allowed to stir for five min. To this solution was added CH_3I (0.089 g, 0.63 mmol), and the mixture was allowed to stir for an additional ten min. At the end of this time the reaction mixture was evaporated to dryness under a N_2 stream. The remaining solid was extracted with hexanes, and the extracts were evaporated to dryness under reduced pressure. The resulting solid was taken up in CS_2 and placed on a 2 x 36 cm Florisil column. Slow elution with CS_2 led to the separation of two bands. The first eluded band was yellow and was identified as a mixture of $W(CO)_6$ and $W(CO)_5CS$. The second band was orange-red and contained $W(CO)_5[C(SC_2H_5)(SCH_3)]$. The $W(CO)_5[C(SC_2H_5)(SCH_3)]$ solution was evaporated to dryness under reduced pressure, and the tungsten dithiocarbene was recrystallized from pentane at -20° C. A 47% (0.088 g, 0.20 mmol) yield of orange flakes was obtained: mp 56-61° C; Anal. Calcd for $C_9H_8O_5S_2W$: C, 24.34; H, 1.82. Found: C, 24.52; H, 1.90.

$\underline{W(CO)_5[C(S\text{-}\underline{i}\text{-}C_3H_7)(SCH_3)]\ (IIc)}$ Following the method of preparation for IIb, the following reactants and quantities were used: NaH (0.015 g, 0.64 mmol), $HSCH(CH_3)_2$ (0.049 g, 0.64 mmol) $W(CO)_5CS$ (0.16 g, 0.44 mmol) and CH_3I (0.091 g, 0.64 mmol). The $W(CO)_5[C(SCH(CH_3)_2)(SCH_3)]$ was obtained as orange crystals in 59% (0.12 g, 0.26 mmol) yield: mp 78-81° C; Anal. Calcd for $C_{10}H_{10}O_5S_2W$: C, 26.21; H, 2.20. Found: C, 26.24; H, 2.16.

$W(CO)_5[C(S\text{-}\underline{n}\text{-}C_4H_9)(SCH_3)]$ (IId) This complex was prepared by the same method as IIb, using NaH (0.015 g, 0.64 mmol), $HS(CH_2)_3CH_3$ (0.067 g, 0.64 mmol), $W(CO)_5CS$ (0.16 g, 0.44 mmol) and CH_3I (0.091 g, 0.64 mmol). The product IId was obtained as a red oil.

$W(CO)_5\{C[SC(CH_3)_3](SCH_3)\}$ (IIe) This complex was prepared by a route analogous to that used for IIb. Starting with NaH (0.016 g, 0.67 mmol), $HSC(CH_3)_3$ (0.060 g, 0.67 mmol) $W(CO)_5CS$ (0.16 g, 0.44 mmol) and CH_3I (0.095 g, 0.67 mmol), 0.072 g (0.15 mmol, 45%) of orange needles of $W(CO)_5\{C[SC(CH_3)_3](SCH_3)\}$ was obtained: mp 113-118° C; Anal. Calcd for $C_{11}H_{12}O_5S_2W$: c, 27.98; H, 2.52. Found: C, 28.44; H, 2.79.

$W(CO)_5[C(SC_2H_5)_2]$ (IIf) A route similar to the one used for the preparation of IIb was used to make this complex. Starting with NaH (0.015 g, 0.64 mmol), HSC_2H_5 (0.037 g, 0.64 mmol), $W(CO)_5CS$ (0.15 g, 0.41 mmol), and C_2H_5I (0.094 g, 0.64 mmol), 0.036 g (0.079 mmol, 19%) of $W(CO)_5[C(SC_2H_5)_2]$ as red crystals were obtained: mp 58-63° C. This complex displayed the same IR and H NMR spectra as were reported earlier.[2a]

$\underline{cis}\text{-}W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$ (IIg) A solution of $NaSCH_3$ was made by bubbling $HSCH_3$ through a suspension of NaH (0.0055 g, 0.23 mmol) in 20 mL of THF for 30 min.

The solution was allowed to stir for an additional 30 min. Then a mixture of *cis*- and *trans*-$W(CO)_4(CS)[P(OCH_3)_3]$[14] (0.17 g, 0.37 mmol) in 15 mL of THF was added. The yellow reaction mixture turned orange after stirring approximately 15 min. At this time CH_3I (0.034 g, 0.24 mmol) was added, stirred for 15 min and then evaporated to dryness. The residue was extracted with hexanes, and the hexane extracts were evaporated to dryness. The residue was taken up in CS_2 and placed on a 2 x 36 cm Florisil column. Elution with CS_2 led to the separation of two bands. A yellow band identified as *cis*- and *trans*-$W(CO)_4[P(OCH_3)_3]CS$ was eluted first. The second band was orange-red and contained 0.042 g (0.076 mmol, 21%) of *cis*-$W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$, as a red oil.

cis-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ (IIh) The same method used to prepare IIg was used for this complex. Starting with NaH (0.048 g, 2.0 mmol), $HSCH_3$ gas, *cis*- and *trans*-$W(CO)_4[P(OPh)_3]CS$[14] (0.920 g, 1.41 mmol) and CH_3I (0.296 g, 2.09 mmol), 0.24 g (0.32 mmol, 24%) of *cis*-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ was obtained as red crystals: mp 106-108° C; Anal. Calcd for $C_{25}H_{21}O_7PS_2W$: C, 42.15; H, 2.98. Found: C, 42.08; H, 3.05.

$W(CO)_5\overline{CS(CH_2)_2S}$ (IIIa) This complex was prepared in the same manner as IIb, by the reaction of NaH

(0.016 g, 0.66 mmol), $HS(CH_2)_2SH$ (0.062 g, 0.66 mmol), $W(CO)_5CS$ (0.15 g, 0.63 mmol) and CH_3I (0.093 g, 0.66 mmol) in THF. After crystallization from hexanes 0.14 g (0.33 mmol, 51%) of $W(CO)_5\overline{CS(CH_2)_2S}$ was obtained as red crystals: mp 110-115° C; Anal. Calcd for $C_8H_4O_5S_2W$; C, 22.44; H, 0.94. Found: C, 22.73; H, 1.03.

$W(CO)_5\overline{CS(CH_2)_3S}$ (IIIb) This complex was prepared from NaH (0.016 g, 0.68 mmol), $HS(CH_2)_3SH$ (0.073 g, 0.68 mmol), $W(CO)_5CS$ (0.24 g, 0.64 mmol) and CH_3I (0.096 g, 0.67 mmol) by a procedure analogous to the one used for IIb. The product $W(CO)_5\overline{CS(CH_2)_3S}$ (0.088g, 0.20 mmol, 31%) was obtained as orange-red crystals: mp 113-128° C; Anal. Calcd for $C_9H_6O_5S_2W$: C, 24.45; H, 1.37. Found: C, 24.42; H, 1.38.

$W(CO)_5\overline{CS(CH_2)_4S}$ (IIIc) The method used for the preparation of IIb was followed for this complex using NaH (0.014, 0.57 mmol), $HS(CH_2)_4SH$ (0.070 g, 0.57 mmol), $W(CO)_5CS$ (0.20 g, 0.55 mmol), and CH_3I (0.082 g, 0.58 mmol). Orange flakes of $W(CO)_5\overline{CS(CH_2)_4S}$ (0.10 g, 0.22 mmol, 41%) were obtained: mp 112-116° C. Anal. Calcd for $C_{10}H_8O_5S_2W$: C, 26.33; H, 1.77. Found: C, 26.33, H, 1.76.

$W(CO)_5\{C(SCH_3)[SFeCp(CO)_2]\}$ (IV) To a solution of $Na[W(CO)_5C(S)(SCH_3)^-]$, prepared from NaH (0.024 g,

1.0 mmol), CH_3SH, and pure $W(CO)_5CS$ (0.38 g, 1.0 mmol) in 25 mL of THF, was added a solution of $[CpFe(CO)_2(THF)][BF_4]$[15] (0.34 g, 1.0 mmol) in 5 mL of CH_2Cl_2. After the solution was stirred for 30 min it was evaporated to dryness. The residue was extracted with hexanes. The remaining solid was taken up in a minimum amount of CH_2Cl_2 and filtered. The product IV was crystallized by adding hexanes to the CH_2Cl_2 filtrate and cooling to -20° C. A yield of 40% (0.23 g, 40 mmol) of IV was obtained: mp 154° C(dec); Anal. Calcd for $C_{14}H_8FeO_7S_2W$: C, 28.40; H, 1.36. Found: C, 28.08; H, 1.43.

Reaction of $W(CO)_5[C(SCH_3)_2]$ with H_2NCH_3 Methyl amine was bubbled through a solution of IIa (0.102 g, 0.238 mmol) in 20 mL of hexane for 30 sec. During this time the solution faded from an orange-red to a pale yellow color. The reaction mixture was allowed to stir for an hour. The solution was then evaporated to a white solid. A 70% yield of $W(CO)_5CNCH_3$ (Va) was obtained after crystallization from hexanes at -20° C. This complex displayed the same IR and H NMR spectra as were reported earlier.[16]

With $H_2N(CH_2)_2CH_3$ To a solution of IIa (0.077g, 0.25 mmol) in 25 mL of hexanes was added $NH_2(CH_2)_2CH_3$

(0.39 g, 6.6 mmol). The solution was allowed to stir for twelve hours. The resulting pale yellow solution was evaporated to dryness under reduced pressure. A yield of 0.083 g (84%) of $W(CO)_5CN(CH_2)_2CH_3$ (Vb) was collected after crystallization from hexanes at -20°C: mp 88-93° C.

With H_2NCH_2Ph Benzylamine (0.073 g, 0.68 mmol) was added to a solution of IIa (0.12 g, 0.29 mmol) in 10 mL of hexanes. The solution was allowed to stir for 10 min. The orange reaction mixture was reduced to dryness and a pale yellow solid remained. The solid residue was crystallized from hexanes at -20°C yielding 0.099 g (77%) of pale yellow $W(CO)_5CNCH_2Ph$ (Vc): mp 79-82° C; Anal. Calcd for $C_{13}H_7NO_5W$: C, 35.40; H, 1.60. Found: C, 35.66; H, 1.63.

With $H_2NC_6H_{11}$ This complex was prepared by the same method as Vc, starting with IIa (0.12 g, 0.27 mmol) and $NH_2C_6H_{11}$ (0.12 g, 1.2 mmol). After crystallization a 52% yield of $W(CO)_5CNC_6H_{11}$ (Vd) was isolated as white crystals: mp 92-95° C; this complex displayed the same IR spectrum as was reported previously.[16]

With $H_2N(CH_2)_2N(CH_3)_2$ Following the method of preparation for Vb, the following reactants and quantities were used: IIa (0.10 g, 0.24 mmol) and $NH_2(CH_2)_2N(CH_3)_2$ (0.043 g, 0.48 mmol) in 20 mL of hexane. Crystallization from hexanes at -20° C yielded 0.062 g (61%) of $W(CO)_5CN(CH_2)_2N(CH_3)_2$ (Ve): mp 36-37° C; Anal. Calcd for $C_{10}H_{10}N_2O_5W$: C, 28.45; H, 2.39. Found: C, 28.22; H, 2.36.

With $HN(CH_3)_2$ The complex $W(CO)_5[C(SCH_3)N(CH_3)_2]$ (VIa) was prepared by a method similar to that used for Va. Dimethylamine was bubbled through a solution of IIa (0.10 g, 0.24 mmol) in 20 mL of hexanes for 10 min. Crystallization from hexanes yielded 0.075 g (74%) of $W(CO)_5[C(SCH_3)N(CH_3)_2]$ (VIa) as yellow crystals: mp 62-69° C; Anal. Calcd for $C_9H_9NO_5SW$: C, 25.31; H, 2.13. Found: C, 25.25; H, 2.16.

With $H\overline{N(CH_2)_4C}H_2$ To a solution of IIa (0.10 g, 0.23 mmol) in 20 mL of hexanes was added piperidine (0.434 g, 5.11 mmol). The solution was allowed to stir for five hours. The reaction mixture was then evaporated to dryness. The residue was taken up in CS_2 and placed on a 2 x 36 cm Woelm Alumina (Activity Grade III) column. A yellow band containing the amino-thiocarbene product developed and was collected. The complex was crystallized from hexane at -20° C. Yellow crystals of $W(CO)_5\{C(SCH_3)[\overline{N(CH_2)_4C}H_2]\}$ (VIb) (0.058 g, 53%) were isolated: mp 97-103° C; Anal. Calcd for $C_{12}H_{13}NO_5SW$: C, 30.85; H, 2.81. Found: C, 31.03; H, 2.84.

With $HN(CH_2)_2OCH_2CH_2$ The method used to prepare VIb was followed in the preparation of $W(CO)_5\{C(SCH_3)-[N(CH_2)_2OCH_2CH_2]\}$ (VIc), using IIa (0.100 g, 0.233 mmol) and morpholine (0.539 g, 6.19 mmol). Yellow crystals of VIc were obtained in a 48% yield.

With $H_2N(CH_2)_3NH_2$ As for Vb, $W(CO)_5CN(CH_2)_3NH_2$ (VIIa), was isolated from the reaction of IIa (0.10 g, 0.24 mmol) and $H_2N(CH_2)_3NH_2$ (0.035 g, 0.48 mmol). Crystallization from hexanes yielded 0.066 g (67%) of VIIa as a white powder: Anal. Calcd for $C_9H_5N_2O_5W$: C, 26.49; H, 1.98. Found: C, 26.83; H, 1.90.

With $[N(C_2H_5)_4{}^+][N_3{}^-]$ A mixture of IIa (0.0763 g, 0.177 mmol) and $[N(C_2H_5)_4{}^+][N_3{}^-]$[17] (0.0305 g, 0.177 mmol) in 20 mL of THF was stirred for approximately 12 h. The resulting yellow solution was evaporated to dryness. The residue was washed with hexanes and crystallized from a mixture of CH_2Cl_2 and hexanes at -20° C. A 61% yield of the yellow crystalline product, $[N(C_2H_5)_4{}^+][W(CO)_5CN^-]$ (VIII) was obtained: mp 119-126° C; Anal. Calcd for $C_{14}H_{20}N_2O_5W$: C, 35.01; H, 4.21. Found: C, 34.85; H, 4.25.

Reaction of cis-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ with H_2NCH_2Ph The complex *cis*-$W(CO)_4[P(OPh)_3]CNCH_2Ph$ (Vf) was prepared in the same manner as Vb, from the reaction of IIh (0.092 g, 0.13 mmol) and H_2NCH_2Ph (0.080 g, 0.75 mmol). The product, Vf (0.068 g, 73%) was obtained as a white powder: mp 68-70° C; Anal. Calcd for $C_{30}H_{22}NO_7PW$: C, 49.81; H, 3.07. Found: C, 49.70; H, 2.96.

With $H_2N(CH_2)_3NH_2$ The complex $W(CO)_4[P(OPh)_3]$-$CN(CH_2)_3NH_2$ (VIIb) was prepared by the same method as Vc. A trace of CH_2Cl_2 was added to 25 mL of hexane to dissolve IIh (0.090 g, 0.13 mmol). To this was added the $NH_2(CH_2)_3NH_2$ (0.057 g, 0.77 mmol); VIIb (0.0560 g, 64%) was isolated as a white powder.

Reactions of $W(CO)_5\overline{CS(CH_2)_2S}$ *with* $H_2N(CH_2)_3NH_2$ Approximately 2-3 mg of IIIa was dissolved in 2 mL of hexanes. A large excess of $H_2N(CH_2)_3NH_2$ was added to the solution. An IR spectrum taken after the solution turned colorless was identical to that of VIIa obtained from the reaction of IIa with $H_2N(CH_2)_3NH_2$.

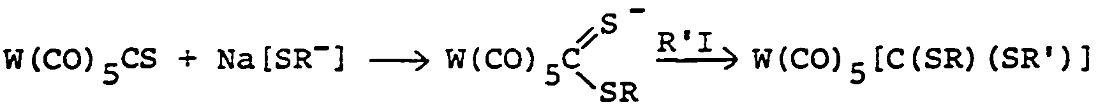
Reactions of $W(CO)_5\overline{CS(CH_2)_3S}$ *with* H_2NCH_3, H_2NCH_2-*Ph,* $H_2N(CH_2)_2N(CH_3)_2$ *and* $H_2N(CH_2)_3NH_2$ Approximately 2-3 mg of IIIb was dissolved in 2 mL of hexanes followed by the addition of a large excess of the primary amine. Although the isocyanide products were never isolated from these reactions, the IR spectra of the reaction mixtures were identical to those of Va, c, e and VIIa obtained from the reaction of the corresponding amine with IIa.

Reactions of $W(CO)_5\{C(SCH_3)[SFeCp(CO)_2]\}$ with H_2NCH_3 Methyl amine was bubbled through a solution of IV (0.0955 g, 0.161 mmol) in 20 mL of CH_2Cl_2 for approximately 45 min. The solution was allowed to stir for an additional hour. It was then evaporated to dryness and the residue was extracted with hexanes. The hexanes extracts contained only Va.

Spectral Data Proton NMR spectra were recorded at room temperature on a Varian HA 100 spectrometer in $CDCl_3$ with $CHCl_3$ as the internal reference and TMS as the internal lock; temperature dependent ^1H NMR spectra were recorded on a Jeol FX-90Q spectrometer. The ^{13}C NMR spectra were also recorded on the Jeol FX-90Q spectrophotometer; $Cr(acac)_3$ (~0.1M) was added to the solutions to reduce data collection time. Infrared spectra were determined on a Perkin-Elmer 281 spectrometer.

RESULTS AND DISCUSSION

Preparation and Characterization of $W(CO)_5[C(SR)(SR')]$ Dithiocarbene Complexes The room temperature preparation of pentacarbonyl(dimethyldithiocarbene)tungsten (IIa), described in a previous paper[11] has been found to be a general method for the preparation of dialkyldithiocarbene tungsten complexes, simply by varying the mercaptide and alkyl halide (eq 3):



$$W(CO)_5CS + Na[SR^-] \longrightarrow \underset{\text{I}}{W(CO)_5C(=S^-)(SR)} \xrightarrow{R'I} \underset{\text{II}}{W(CO)_5[C(SR)(SR')]} \tag{3}$$

I II

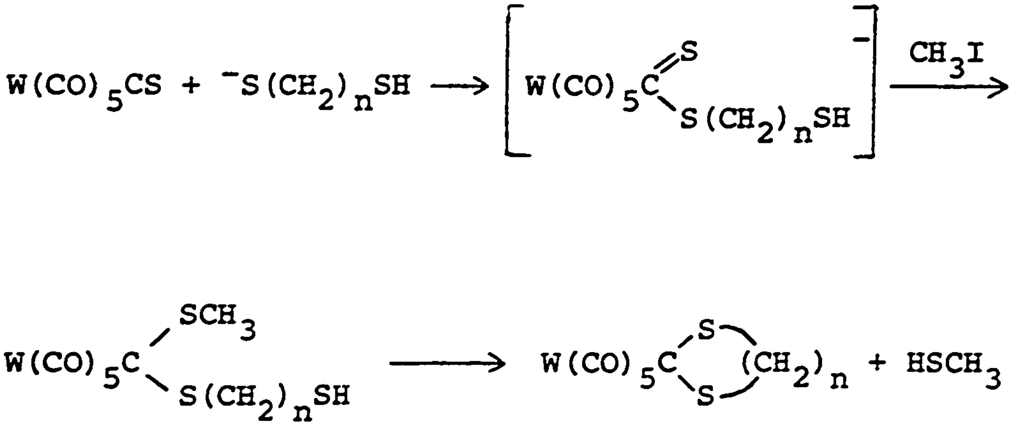
IIa, R = R' = CH_3
IIb, R = C_2H_5 R' = CH_3
IIb, R = CH_3 R' = C_2H_5
IIc, R = i-C_3H_7 R' = CH_3
IIc, R = CH_3 R' = i-C_3H_7
IId, R = n-C_4H_9 R' = CH_3
IId, R = CH_3 R' = n-C_4H_9
IIe, R = t-C_4H_9 R' = CH_3
IIf, R = R' = C_2H_5

In the first step, the mercaptide anion attacks the carbon atom of the thiocarbonyl ligand forming a dithioester anion (I). Preferential attack of nucleophiles on the thiocarbonyl carbon atom, rather than the CO carbon, has been seen before.[16,18-21] Intermediate I has not been isolated, but infrared spectra of reaction mixtures show that I ($R=CH_3$; 2049w, 1911s, 1869m) is formed almost quantitatively. However, when PhS^-, $PhSe^-$, CH_3O^-, Ph_3Sn^-, or Ph_2P^- were used no intermediates of type I were seen. The second step in equation 3 has been found to proceed with CH_3I, C_2H_5I, i-C_3H_7I and n-C_4H_9I, but best results are obtained when CH_3I is used. Yields are lower by approximately 30% when alkyl iodides other than CH_3I are used, and there is often an impurity in these reactions which makes crystallization more difficult. When CH_3COBr, $BrCH_2CO_2H$ or allyl bromide are reacted with $[W(CO)_5C(=S)(SCH_3)^-]$, the only product isolated is IIa. In an attempt to make $W(CO)_5[C(SCH_3)(SH)]$ the methyldithio ester anion was reacted with H_3PO_4 and CF_3SO_3H. In both cases no carbene was formed and $W(CO)_5CS$ was the only isolated carbonyl containing compound.

This same procedure has also been used to make substituted tungsten dithiocarbene complexes, cis-$W(CO)_4L$-$[C(SCH_3)_2]$, ($L=P(OCH_3)_3$ IIg, and $P(OPh)_3$ IIh) by starting with a substituted tetracarbonyl thiocarbonyl tungsten complex, cis and trans-$W(CO)_4L(CS)$. The reaction proceeds satisfactorily where L is $P(OCH_3)_3$ or $P(OPh)_3$ ($\nu(CS)=1247$ and 1257 respectively).[14] However, when L is PPh_3

(ν(CS)=1241,[14]) no reaction occurs. It therefore appears that nucleophilic attack by the mercaptide ion does not occur when ν(CS) is lower than 1247 cm^{-1}. Although a mixture of cis and trans-$W(CO)_4$-L(CS) is used in these reactions, only the cis isomer reacts. The trans isomer together with small amounts of the unreacted cis isomer, is isolated upon work-up of the reaction mixture. The cis configuration of the products, IIg and h, is confirmed by their infrared and ^{13}C NMR spectra. The infrared spectra of IIg and h contain four ν(CO) which is consistent with the cis isomer, but not the trans which should only contain one ν(CO) absorption. The ^{13}C NMR spectrum Table of IIh shows three CO resonances. Again this is consistent only with the cis isomer.

Cyclic dithiocarbenes may be prepared by reacting dimercaptans with half an equivalent of NaH forming the monoanion which is then reacted with $W(CO)_5CS$. Methyl iodide is added to the resulting dithioester anion presumably forming a carbene which then undergoes loss of methylmercaptan to form the cyclic dithiocarbene (eq 4):



(4)

III

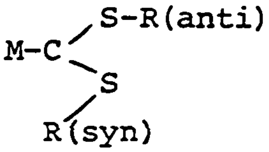
n=2(IIIa); 3(IIIb); 4(IIIc)

This procedure has been used to form five, six and seven membered rings in yields ranging from 30 to 50%.

The solid orange tungsten dithiocarbene complexes are stable for months on exposure to air at room temperature. They are soluble in common organic solvents ranging in polarity from pentane to acetone. Their solutions when exposed to air at room temperature show some decomposition after two or three days.

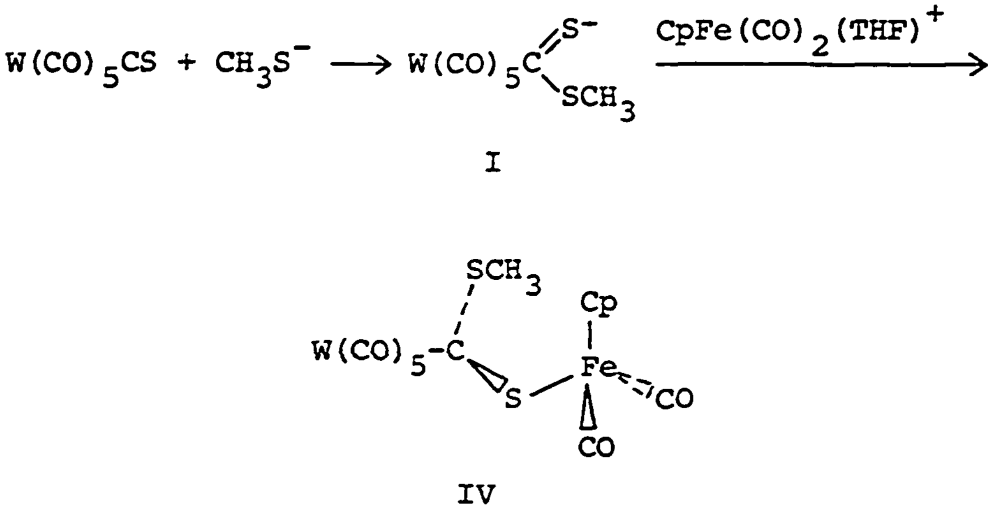
Infrared spectra (Table I) of complexes IIb-f are very similar to that of IIa.[11] The four ν(CO) absorptions for complexes IIa-f are observed in the following ranges 2066-2067m, 1983-1984w, 1948-1950s, and 1939-1941s, with calculated ν(CO) approximate force constants[22] of k_1=15.56-15.60 and k_2=15.90, which indicate that the dialkyldithiocarbene ligand has a π acceptor/σ donor ratio lower than CO ($W(CO)_6$, k=17.7 mdyn/Å [23]), but similar to that of PPh_3 ($W(CO)_5PPh_3$, k=15.5 mdyn/Å, k_2=15.9 mdyn/Å [14]). A similar conclusion was reached previously for the analogous $CpFe(CO)_2L^+$ complexes.[10]

The ^1H NMR spectra (Table II) of the tungsten dithiocarbenes show a single resonance for the alkyl groups of the carbene ligand at room temperature. Other dithiocarbenes of chromium,[1,3] tungsten[1,3,11] and iron[8,9] also show equivalent alkyl groups in their room temperature ^1H NMR spectra. This indicates that the restricted rotation about the C(carbene)-S bond which presumably gives rise to the inequivalent alkyl groups, through syn and anti isomerization in some platinum dithiocarbene complexes,[24,25] is not observed in the chromium, tungsten and iron complexes at this temperature.



However, restricted rotation is observed for some tungsten and iron dithiocarbenes at low temperatures.[8-11] Rationalizations for the difference in the ratio of rotation of the C(carbene)-S bond of platinum versus tungsten and iron complexes have been discussed previously.[8,11] The ^{13}C NMR spectra of IIa-h (Table III) at room temperature show single resonances for the alkyl groups of the carbene ligand, which also indicates rapid rotation about the C(carbene)-S bond. They also show a resonance near 300 ppm for all the dithiocarbene carbon atom, which is consistent with previous reports [8,9,11] of dithiocarbene complexes.

The reaction of the methyldithio ester anion (I) with metal species to form a stable dithiocarbene has so far been limited to a reaction with $[CpFe(CO)_2(THF)^+]$-$[BF_4^-]$ to form IV (eq 5):



(5)

In the solid state, IV is stable for months on exposure to air. It is only slightly soluble in nonpolar solvents (hexane), but is very soluble in polar solvents (CH_2Cl_2, acetone). Solutions of IV at room temperature in air decompose in 3 to 4 hours.

The infrared spectrum of IV (Table I) contains four ν(CO) absorption. The two ν(CO) bands at 2038 and 1997 cm^{-1} correspond to those of IIa in CH_2Cl_2 (Table I). The ^{13}C NMR spectrum contains two resonances (Table III) for both the methyl group and the cyclopentadienyl ring, indicating the presence of more than one isomer. However, the ^{1}H NMR spectrum (Table II) consists of only two resonances, one each for the methyl group and the cyclopentadienyl ring. There is no splitting of these ^{1}H singlets upon cooling an acetone-d_6 solution of IV to -50° C. The reason for the difference between the splitting in the ^{1}H and ^{13}C NMR spectra remains unclear; however, ^{1}H resonances of the methyl groups and the rings in the different isomers may fortuitously occur at the same positions.

Other metal cations, $\{CpFe(CO)[P(OPh)_3](THF)^+\}$ and $[Re(CO)_5(NCCH_3)^+]$, have been tried in reaction (5), but no carbene products were isolated. Group IVA metal halides $[(CH_3)_3C](CH_3)_2SiCl$, Ph_3GeBr, Ph_3SnCl and Ph_3PbCl, have also been reacted with $[W(CO)_5C(=S)(SCH_3)^-]$. The only isolated carbonyl complex was $W(CO)_5CS$ which

Table I. Infrared spectra of the carbene and isocyanide complexes in hexanes

Complex		νCO, cm^{-1}	νCN, cm^{-1}
$W(CO)_5[S(SCH_3)_2]$	IIa[a]	2067m, 1984w, 1950s, 1941s	
$W(CO)_5[S(SCH_3)_2]$	IIa[b]	2066m, 1935s	
$W(CO)_5[C(SC_2H_5)(SCH_3)]$	IIb	2066m, 1984w, 1949s, 1941s	
$W(CO)_5[C(S\text{-}\underline{i}\text{-}C_3H_7)(SCH_3)]$	IIc	2067m, 1983w, 1949s, 1941s	
$W(CO)_5[C(S\text{-}\underline{n}\text{-}C_4H_9)(SCH_3)]$	IId	2067m, 1983w, 1949s, 1940s	
$W(CO)_5\{C[SC(CH_3)_3](SCH_3)\}$	IIe	2066m, 1984w, 1949s, 1939s	
$W(CO)_5[C(SC_2H_5)_2]$	IIf	2066m, 1983w, 1948s, 1941s	
$\underline{\text{cis}}\text{-}W(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$	IIg	2026m, 1946m, 1914s, 1903sh	
$\underline{\text{cis}}\text{-}W(CO)_4[P(OPh)_3][C(SCH_3)_2]$	IIh	2027s, 1944s, 1921s, 1908s	
$w(CO)_5\overline{CS(CH_2)_2S}$	IIIa	2069w, 1950s	
$W(CO)_5\overline{CS(CH_2)_3S}$	IIIb	2067w, 1944s	
$W(CO)_5\overline{CS(CH_2)_4S}$	IIIc	2067w, 1950sh, 1944s	
$W(CO)_5\{C(SCH_3)[SFeCp(CO)_2]\}$	IV[b]	2062m, 2038m, 1997m, 1927s	

$W(CO)_5CNCH_3$	Va	2068w, 1956s	2177w
$W(CO)_5CN(CH_2)_2CH_3$	Vb	2066m, 1955s	2166w
$W(CO)_5CNCH_2Ph$	Vc	2066m, 1956s	2164w
$W(CO)_5CNC_6H_{11}$	Vd	2064m, 1954s	2158w
$W(CO)_5CN(CH_2)_2N(CH_3)_2$	Ve	2066m, 1954s	2166w
$W(CO)_4[P(OPh)_3]CNCH_2Ph$	Vf	2028s, 1949s, 1928vs	2150w
$W(CO)_5\{C(SCH_3)[N(CH_3)_2]\}$	VIa	2064w, 1956m, 1929s	
$W(CO)_5\{C(SCH_3)[\overline{N(CH_2)_4CH_2}]\}$	VIb	2063m, 1927s	
$W(CO)_5\{C(SCH_3)[\overline{N(CH_2)_2OCH_2CH_2}]\}$	VIc	2059w, 1923s	
$W(CO)_5CN(CH_2)_3NH_2$	VIIa	2066m, 1953s	2166w
$W(CO)_4[P(OPh)_3]CN(CH_2)_3NH_2$	VIIb	2028s, 1952s, 1032vs	2164w
$[N(C_2H_5)_4^+][W(CO)_5CN^-]$	VIII[b]	2055w, 1921s, 1886sh	

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[a] Reference 11.

[b] Solvent CH_2Cl_2.

Table II. ^{1}H-NMR spectra of the carbene and isocyanide complexes in $CDCl_3$ (τ)

Complex	SCH_3[a]	SCH_2	NCH_2	Other Resonances
IIa[b]	7.04			
IIb	7.04	6.46(q)		8.47(t, CH_3)
IIc	7.06			5.66(m, SCH); 8.44(d, CH_3)
IId	7.04	6.46(t)		8.28(m, CH_2 $^-CH_2$); 8.94(t, CH_3)
IIe	6.80			8.31(S, CH_3)
IIf		6.48(q)		8.49(t, CH_3)
IIg	7.08			6.36(d, OCH_3)
IIh	7.35			2.78(S, OPh)
IIIa		6.36(s)		
IIIb		7.06(m)		7.48(m, CH_2)
IIIc		6.74(m)		7.63(m, CH_2)
IV	6.76			4.88(C, Cp)
Va				6.52(S, NCH_3)
Vb			6.32(t)	8.16(m, CH_2); 8.88(t, CH_3)

Vc		5.06(s)	2.63(m, Ph)
Ve		6.20(t)	7.24(t, CH_2); 7.60(S, CH_3)
Vf		5.40(s)	2.75(m, Ph)
VIa	7.06		6.06(S, CH_3); 6.45(S, CH_3)
VIb	7.06		5.55, 5.81 and 8.13(m,m,m, $N(CH_2)_4CH_2$)
VIc	7.01		5.46, 5.70 and 6.08(t,t,m, $N(CH_2CH_2)_2O$)
VIIa			7.06(t, CH_2); 8.05(m, CH_2)
VIIb		6.16(t)	2.67(S, Ph); 7.16(t, CH_2); 8.28(m, CH_2)
VIII[c]		6.49(t)	6.47(q, CH_2); 8.58(m, CH_3)

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[a] All resonances are singlets.

[b] Reference 11.

[c] Solvent acetone-d_6.

Table III. ^{13}C-NMR spectra of the carbene complexes in $CDCl_3$ (ppm)[a]

Complex	C-carbene	CO-trans	CO-cis	SCH_3	Other Resonances
IIa[b]	300.0	204.4	197.4	29.5	
IIb	298.9	204.3	197.4	29.5	40.2(SCH_2); 12.1(CH_3)
IIc	296.9	204.2	197.4	29.7	50.8(CH); 22.1(CH_3)
IIe	301.0	204.2	197.6	32.1	62.1(SC); 28.9(CH_3)
IIh	300.1			29.0	207.6[c], 203.1[d], 199.9[e](CO); 151.2[f], 129.4, 124.5, 121.0[g](Ph)
IIIa	282.2	204.6	196.0		47.8(SCH_2)
IIIb	277.5	204.3	196.7		36.3(SCH_2); 17.4(CH_2)
IIIc	291.1	205.3	197.5		44.3(SCH_2); 26.7(CH_2)
IV	323.4	206.6	199.2	31.3, 28.8	211.4($Fe(CO)_2$); 87.6, 86.7(C_5H_5
VIa	249.8	201.9	198.3	25.7	56.3(NCH_3); 45.1(NCH_3)
VIb	245.6	202.0	198.1	25.4	65.6, 54.4(NCH_2); 27.8, 26.4, 23.9(CH_2)
VIc	250.5	209.2	198.1	25.4	67.9, 66.5, 84.3, 54.0; (OCH_2), (NCH_2)

[a] All resonances are singlets unless otherwise noted.

[b] Reference 11.

[c] $J_{PWC} = 9.8$.

[d] $J_{PWC} = 9.8$.

[e] $J_{PWC} = 52.7$.

[f] $J_{PC} = 5.9$.

[g] $J_{PC} = 5.9$.

was obtained almost quantitatively. In the cases of the Ge, Sn and Pb derivatives the reactions were complete in five minutes or less. The reaction with $[(CH_3)_3C](CH_3)_2SiCl$ required 20 to 30 minutes to reach completion. No carbene intermediates were detected in any of these reactions.

Reactions of $W(CO)_4L[C(SR_2)]$ with Primary Amines

The tungsten dithiocarbene complexes IIa, i and IIIb were found to undergo reactions with primary amines at room temperature in hexanes to form tungsten isocyanide derivatives (eq. 6):

$$W(CO)_4L[C(SR)_2] + NH_2R' \longrightarrow \underset{\text{Va-f}}{W(CO)_4L(CNR')} + 2\ HSR \qquad (6)$$

L=CO $R=R'=CH_3$ (Va)
L=CO $\widehat{R\,R}=(CH_2)_3$ $R'=CH_3$ (Va)
L=CO $R=CH_3$ $R'=(CH_2)_2CH_3$ (Vb)
L=CO $R=CH_3$ $R'=CH_2Ph$ (Vc)
L=CO $\widehat{R\,R}=(CH_2)_3$ $R'=CH_2Ph$ (Vc)
L=CO $R=CH_3$ $R'=C_6H_{11}$ (Vd)
L=CO $R=CH_3$ $R'=(CH_2)_2N(CH_3)_2$ (Ve)
L=CO $\widehat{R\,R}=(CH_2)_3$ $R'=(CH_2)_2N(CH_3)_2$ (Ve)
L=$P(OPh)_3$ $R=CH_3$ $R'=CH_2Ph$ (Vf)

The formation of the isocyanide presumably proceeds by nucleophilic attack of the amine on the p_z orbital of the carbene carbon to form an adduct which then splits off two mercaptans to form the product. The reactions of the six-membered cyclic dithiocarbene complex (IIIc) with primary amines are slower than those of either the substituted (IIh) or the unsubstituted (IIa) dimethyldithiocarbene complexes. This slower reactivity of the cyclic dithiocarbenes was also observed in the $CpFe(CO)_2[C(SR)_2]^+$ system.[9] This is probably due to the poorer leaving group ability of the dithiols and the stability of six-membered rings. Methylamine was also found to react with IV to form Va and a carbonyl containing product whose infrared spectrum contained one band in the carbonyl stretching region ($\nu(CO)=1933$ cm^{-1}). The infrared spectrum of this product is very similar to those of <u>trans</u> $[CpFe(CO)SR]_2$ complexes ($R=CH_3$, C_2H_5, Ph; (CO)=1929, 1929, 1938 respectively),[26] and may indicate the formation of trans $[CpFe(CO)SH]_2$.

Attempts to react IIa with NH_2Ph, $NH_2C(=O)CH_3$ and $NH_2C(CH_3)_3$ resulted in no reaction. This is probably due to the lower nucleophilic character of NH_2Ph and $NH_2C(=O)CH_3$, and to steric hindrance in the case of $NH_2C(CH_3)_3$.

Reactions of $W(CO)_5[C(SR_2)]$ with Secondary Amines

When IIa is reacted with secondary amines at room temperature, one equivalent of methyl mercaptan in evolved with the formation of an amino-thio carbene complex (eq 7):

$$\underset{\text{IIa}}{W(CO)_5[C(SCH_3)_2]} + HNR_2 \longrightarrow \underset{\text{VI}}{W(CO)_5[C(SCH_3)(NR_2)]} + HSCH_3 \qquad (7)$$

$R=CH_3$ VIa
$\overset{\frown}{R\,R}$=piperidine VIb
$\overset{\frown}{R\,R}$=morpholine VIc

Steric hindrance seems to exert a large influence over the reactions of IIa with secondary amines. The yields of amino-thiocarbenes decrease as the steric bulk of the amine increases; $HN(CH_3)_2$>piperdine≥morpholine> $HN(C_2H_5)_2$. No amino-thiocarbene is formed with $HN(i\text{-}C_3H_7)_2$. Even with a large excess of the amines, $HN(CH_3)_2$, piperidine, morpholine, or $HN(C_2H_5)_2$, there is no evidence for the replacement of two thiomethoxy groups to form diaminocarbene complexes $W(CO)_5\{C[N(CH_3)_2]\}$. When IIIa is reacted with $HN(CH_3)_2$ or piperidine, no reaction occurs. Presumably the barrier to ring opening prevents formation of the amino-thiocarbene.

The yellow amino-thiocarbenes, VIb and c, show no noticeable decomposition upon exposure to air at room temperature for a period of months in the solid state. However, VIa starts to decompose slowly after a week at these conditions. It, VIa, may be stored in the solid state at -20° C. The amino-thiocarbenes are soluble in most common organic solvents.

The spectral characteristics of VIa-c are in general very similar. The IR spectra of VIa-c show two ν(CO) absorptions at 2059-2064w cm^{-1} and 1923-1929s cm^{-1} (Table I). The greater tendency for nitrogen to donate electron density to the carbene carbon atom,[10,27,28] as compared to sulfur, is reflected in the lower ν(CO) frequencies of the amino-thiocarbene as compared to $W(CO)_5[C(SCH_3)_2]$ (2066, 1983, 1949, 1940 cm^{-1}). The ^1H NMR spectra of VIa-c contain a singlet at τ 7.01-7.06 for the thiomethoxy group (Table II). The amine methyl group of VIa and the four methylene groups of VIc are nonequivalent at room temperature. Nonequivalance of the amine methyl groups is also observed in $\{CpFe(CO)_2[C(SCH_3)[N(CH_3)_2]\}PF_6$,[8,29] and is consistent with a large donation of π-electron density from nitrogen to the carbene carbon atom, which causes restricted rotation around the C(carbene)-N bond.

The ^{13}C NMR chemical shift of the carbene carbon, δ(carbene), is very sensitive to changes in the electronic environment[30] at the carbene carbon atom. An upfield shift of approximately 70 ppm for the δ(carbene) is observed when an alkoxy group is substituted for by an amine group in complexes of the type $Cr(CO)_5C(YR)R$.[30] An upfield shift of at least 50 ppm is observed when a thiomethoxy group of IIa is replaced with an amine group to form complexes VIa-c (Table III). Upfield shifts of about 70 ppm are also observed upon replacing a SCH_3 group with piperidine in $CpFe(CO)L[C(SCH_3)_2]^+$ (L=CO or CH_3CN).[9,10]

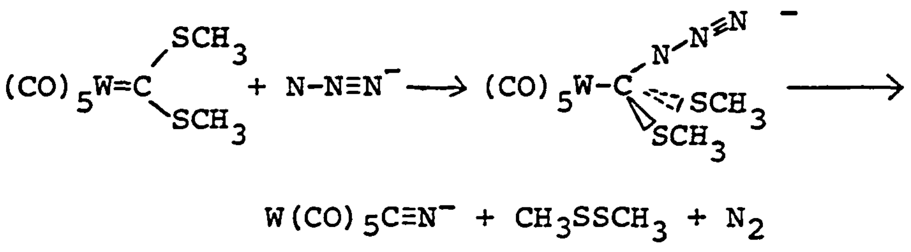
Reactions of $W(CO)_5[C(SR)_2]$ with Diamines It has been previously reported that $\{CpFe(CO)_2[C(SCH_3)_2]^+\}PF_6$ reacts with diamines to form cyclic diaminocarbene complexes (eq 1). However, when IIa and h are reacted with 1,3-diaminopropane no cyclic diaminocarbene complex is formed. Instead only the monomeric isocyanides, $W(CO)_4(L)CN(CH_2)_3NH_2$ (VIIa,b) result. This reaction is similar to that of IIa with primary amines (eq 6). Cyclic dithiocarbene tungsten complexes of the type $W(CO)_5\overline{CN(R)(CH_2)_2N}(R)$[31] ($R=CH_3$ and C_2H_5) are known, and it is not clear why the reactions of the Fe and W dithiocarbenes give different products with 1,3-diaminopropane.

The ^1H NMR spectra of VIIa and b show three absorptions in a 1:1:1 ratio, for the three different methylene groups. The proton of the NH_2 groups are not observed, presumably due to quadrupolar broadening by the nitrogen atom.

Reactions of $W(CO)_5[C(SR)_2]$ with Azide Anion The product obtained when IIa is reacted with $[N(C_2H_5)_4^+]$-$[N_3^-]$ at room temperature is $[N(C_2H_5)_4^+][W(CO)_5CN^-]$ (eq 8):

$$W(CO)_5[C(SCH_3)_2] + N_3^- \longrightarrow \underset{\text{VIII}}{W(CO)_5CN^-} + N_2 + CH_3SSCH_3 \qquad (8)$$

A similar reaction occurs between $CpFe(CO)_2[C(SCH_3)_2]^+$ and NaN_3. It yields $CpFe(CO)_2CN$ as one of several products.[8] Dimethyl disulfide was identified as a product formed from the reaction of IIa with N_3^- by comparing its ^1H NMR spectrum with that of an authentic sample. Evolution of a gas, presumably N_2, was also observed during the reaction. A possible mechanism for this reaction is shown in equation 9.



(9)

Other nucleophiles which did not react with IIa are: $[N(C_4H_9)^+][I^-]$, $N(C_2H_5)_3$ 1,4-diazabicyclo[2.2.2.]octane, $CNCH_3$ and $S(CH_3)_2$.

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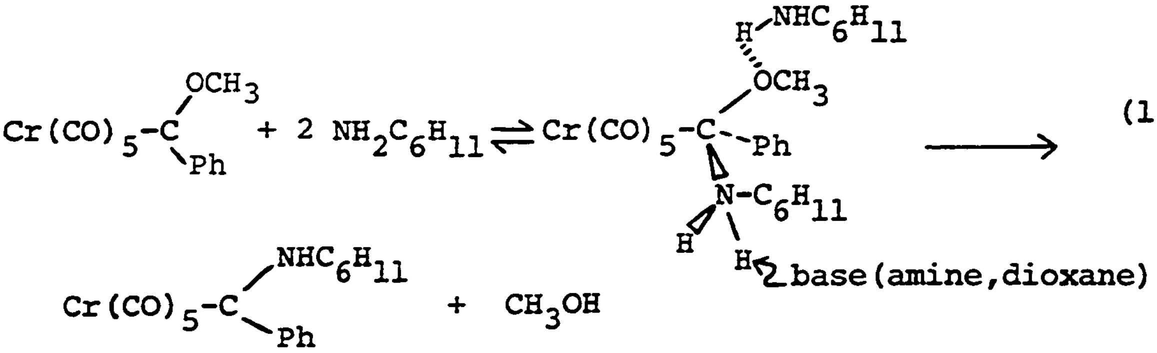
SECTION III. KINETIC STUDY OF THE REACTION OF $W(CO)_5[C(SCH_3)_2]$ WITH PHOSPHINES TO FORM PHOSPHORANE COMPLEXES $W(CO)_5[(CH_3S)_2C{=}PR_3]$ AND THE SYNTHESIS OF SOME CYCLIC PHOSPHORANE COMPLEXES

INTRODUCTION

Transition metal carbene complexes are very reactive species,[1-4] undergoing reactions at the carbene ligand as well as at the metal center. In spite of numerous synthetic investigations of carbene complexes, only a few kinetic studies of their reactions have been reported.[5-13] It has been found that the reaction of cyclohexylamine with $Cr(CO)_5[C(OCH_3)Ph]$ in decane to form $Cr(CO)_5[C(NHC_6H_{11})Ph]$ and CH_3OH is first order in the complex and third order in amine, whereas in dioxane it is still first order in the complex but only second order in amine.[5,6] The kinetic order difference in the different solvents is thought to occur because of the different abilities of the solvents to participate in hydrogen bonding. The reaction was suggested to proceed by formation of a hydrogen bond between an amine H and the O of the OCH_3 group. An activated amine (HNRH···B) then attacks the carbene carbon forming an adduct which undergoes loss of CH_3OH (eq 1):



(1)

In a related study, $Cr(CO)_5[C(OCH_3)R]$ ($R=CH_3$ or Ph) was found to react with phosphines ($P(C_6H_{11})_3$, $P(\underline{p}\text{-}CH_3C_6H_4)_3$, PPh_3, $PPh_2(C_2H_5)$, $PPh(C_2H_5)_2$, $P(C_2H_5)_3$ and $P(\underline{n}\text{-}C_4H_9)_3$)[7-10] to form $Cr(CO)_4L[C(OCH_3)R]$ and $Cr(CO)_{6-n}L_n$ (n=1 or 2) by a two term rate law (eq 2):

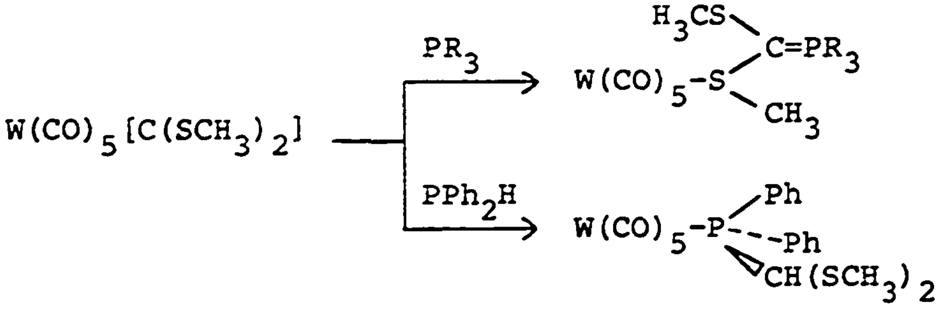
$$-d[Cr(carbene)]/dt = k_1[Cr(carbene)] + k_2[Cr(carbene)][L] \tag{2}$$

The second order term was assumed to indicate an associative pathway, and is important only for the nucleophilic trialkylphosphines ($P(C_2H_5)_3$ and $P(\underline{n}\text{-}C_4H_9)_3$). It is unclear whether nucleophilic attack of the phosphine is on the metal center or on the carbene carbon. However, Kreissl et al.[14] have isolated $Cr(CO)_5[C(OCH_3)(CH_3)P(\underline{n}\text{-}C_4H_9)_3]$,[15] and found it to rearrange to the products observed by Werner,[7,9] $Cr(CO)_4L[C(OCH_3)R]$ and $Cr(CO)_{6-n}L_n$ (n=1 or 2). This result, as well as the much smaller equilibrium constants for the formation of the carbene-phosphine adduct for the mixed alkyl-aryl or triaryl phosphines as compared to those for the trialkylphosphines, is strong evidence for nucleophilic attack at the carbene carbon (eq 3):

$$Cr(CO)_5[C(OCH_3)R'] + PR_3 \rightleftharpoons Cr(CO)_5[C(OCH_3)R'(PR_3)]$$

$$\begin{cases} \rightarrow Cr(CO)_5PR_3 + [C(OCH_3)R'] \\ \rightarrow \underline{cis}\text{-}Cr(CO)_4(PR_3)[C(OCH_3)R'] \end{cases} \tag{3}$$

In a previous paper[16] we reported the unusual reactions of the dithiocarbene complex $W(CO)_5[C(SCH_3)_2]$ with tertiary phosphines to form the phosphorane complexes $W(CO)_5[(CH_3S)_2\text{-}C{=}PR_3]$ and with the secondary phosphine, PPh_2H, to form the phosphine complex $W(CO)_5\{PPh_2[CH(SCH_3)_2]\}$ (eq 4):



(4)

Kinetic studies of the reactions of $W(CO)_5[C(SCH_3)_2]$ with $P(C_2H_5)_3$, $PPh(CH_3)_2$, $PPh_2(CH_3)$, PPh_2H and $P(OCH_3)_3$ were carried out in order to elucidate the mechanisms of these reactions and the factors which affect their rates. These kinetic results, as well as the preparation of some cyclic phosphorane pentacarbonyl tungsten complexes, are reported herein.

EXPERIMENTAL

General Kinetic and synthetic reactions were performed under argon and nitrogen respectively, using Schlenk ware and standard inert atomsphere techniques. Cyclohexane was distilled from $CaSO_4$ under N_2 onto 4A molecular sieves. All tertiary phosphines and phosphites were fractionally distilled under N_2. The dithiocarbene complexes $W(CO)_5[C(SCH_3)_2]$[16] and $W(CO)_5[\overline{CS(CH_2)_nS}]$,[17] where n=2, 3 or 4, were prepared as reported previously. All other chemicals were reagent grade and used without further purification.

Determination of Reaction Rates The rates of reaction were determined by following the disappearance of the $W(CO)_5[C(SCH_3)_2]$ absorption at 446 nm ($\varepsilon=1.63 \times 10^4$ M^{-1} cm^{-1}). The products, at the concentration used for the kinetic reactions, did not absorb in this region. A stock solution of 4.00×10^{-5} M $W(CO)_5[C(SCH_3)_2]$ in cyclohexane was prepared and UV cuvettes of 1 cm pathlength were used. The $W(CO)_5[C(SCH_3)_2]$ stock solution (2 mL) was syringed into the cuvette through a septum. The cuvette and solution were then flushed with a slow stream of argon. The cuvette was submerged in a H_2O bath and allowed to reach thermal equilibrium. The cuvette was transferred to the thermostatted cell compartment of the spectrophotometer and again allowed to reach thermal equilibrium. The thermostatted neat ligand was added, by syringe, through the septum, and the solution was mixed well. The Cary 219 spectrophotometer was programmed to automatically take absorption measurements at specific time intervals. The slopes of plots of ln $(A_\infty - A_\infty)$ *versus* time where A is the absorbance at time t and A_∞ is the absorbance at the completion of the reaction, gave pseudo-first-order rate constants k_{obsd}. The plots were linear for at least the first 80% of reaction.

Product Identification Although the products were never isolated from kinetic reaction mixtures, an infrared spectrophotometric study of the reaction of $W(CO)_5[C(SCH_3)_2]$ with $P(C_2H_5)_3$, under conditions of the kinetic reactions, showed formation of $W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ as the only product. No replacement of the phosphorane ligand of $W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ by 100 fold excess $P(C_2H_5)_3$ occurred even after 24 hours at room temperature. Total replacement of the phosphorane ligand by $P(C_2H_5)_3$ was achieved by heating a solution of $W(CO)_5[(CH_3S)_2C{=}P(C_2H_5)_3]$ with 100 fold excess of $P(C_2H_5)_3$ at approximately 60° C for 32 hours.

$W(CO)_5\{\overline{S(CH_2)_2SC}{=}[P(CH_3)Ph_2]\}$ (IVa) A solution of $W(CO)_5[\overline{CS(CH_2)_2S}]$ (0.055 g, 0.13 mmol) and $P(CH_3)Ph_2$ (0.051 g, 0.25 mmol) in 8 mL of cyclohexane was heated to 60° C for 24 hr. The product IVa was obtained as an oil.

$W(CO)_5\{\overline{S(CH_2)_3SC}{=}[P(CH_3)Ph_2]\}$ (IVb) To a solution of $W(CO)_5[\overline{CS(CH_2)_3S}]$ (0.0666 g, 0.151 mmol) in 10 mL of hexane was added $P(CH_3)Ph_2$ (0.060 g, 0.30 mmol). The solution was allowed to stir at room temperature for about 1.5 hr. During this time a yellow precipitate had started to form. Yellow crystals of IVb (0.042 g, 43%) were obtained from the supernatant liquid upon cooling it to -20° C. The yellow precipitate was recrystallized from CH_2Cl_2 and hexanes at -20° C yielding 0.022 g (23%) of IVb: mp 112-117° C(dec); ^1H NMR($CDCl_3$) τ 2.48(m, phenyl), 7.06(t, SCH_2), 7.15(t, SCH_2), 7.47(bm, CH_2), 7.84(d, J=13 Hz, PCH_3); Anal. Calcd for $C_{22}H_{19}O_5PS_2W$: C, 41.13; H, 2.99. Found: C, 40.78; H, 2.93.

$\underline{W(CO)_5\{\overline{S(CH_2)_4SC}=[PPh_2(CH_3)]\}\text{ (IVc)}}$ A solution of $W(CO)_5[\overline{CS(CH_2)_4S}]$ (0.0523 g, 0.115 mmol) and $PPh_2(CH_3)$ (0.023 g, 0.11 mmol) in 10 mL of hexane was stirred at room temperature for about 1.5 hr. The resulting yellow solution was concentrated to approximately 2 mL. The product was crystallized in 52% yield (0.039 g), from the concentrated solution at -20° C: mp 103-109° C(dec); ^1H NMR($CDCl_3$) τ 2.42(m, phenyl), 7.40(m, SCH_2), 7.59(m, SCH_2), 7.80(d, J=12 Hz, PCH_3), 8.14(m, CH_2), 8.34(m, CH_2); Anal. Calcd for $C_{23}H_{21}O_5PS_2W$: C, 42.08; H, 3.23. Found: C, 42.32; H, 3.28.

$\underline{W(CO)_5[PPh_2\overline{C(H)S(CH_2)_3S}]\text{ (Va)}}$ The complex Va was prepared by heating a solution of $W(CO)_5[\overline{CS(CH_2)_3S}]$ (0.025 g, 0.056 mmol) and PPh_2H (0.022 g, 0.12 mmol) in 8 mL of cyclohexane to 60° C for approximately 12 hr, after which the solution was reduced to dryness and taken up in hexane. Crystallization from hexane at -20° C yields 0.015 g (42%) of Va as a yellow solid: mp 94° C (begins to decompose); Anal. Calcd for $C_{21}H_{17}O_5PS_2W$: C, 40.14; H, 2.73. Found: C, 41.02; H, 2.85.

$W(CO)_5[PPh_2\overline{C(H)S(CH_2)_4S}]$ (Vb) The complex, Vb, was prepared by a route similar to the one used for preparing IVc, starting with $W(CO)_5[CS(CH_2)_4S]$ (0.054 g, 0.12 mmol) and PPh_2H (0.022 g, 0.12 mmol). The product, Vb, was crystallized from hexanes at -20° C yielding 0.056 g (73%); mp 95-99° C; ^1H NMR($CDCl_3$) τ 2.50(m, phenyl), 4.82(d, J=3 Hz, PCH), 7.22(m, SCH_2), 8.10(m, CH_2); Anal. Calcd for $C_{22}H_{19}O_5PS_2W$: C, 41.13; H, 2.99. Found: C, 41.48; H, 3.06.

Spectra Data Proton NMR spectra were recorded at room temperature on a Varian HA-100 spectrometer in $CDCl_3$ with $CHCl_3$ or TMS as the internal reference and TMS as the internal lock. The ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer; $Cr(acac)_3$ (~0.1M) was added to the solutions to reduce data collection time. Infrared spectra were taken on a Perkin-Elmer 281 spectrophotometer.

RESULTS

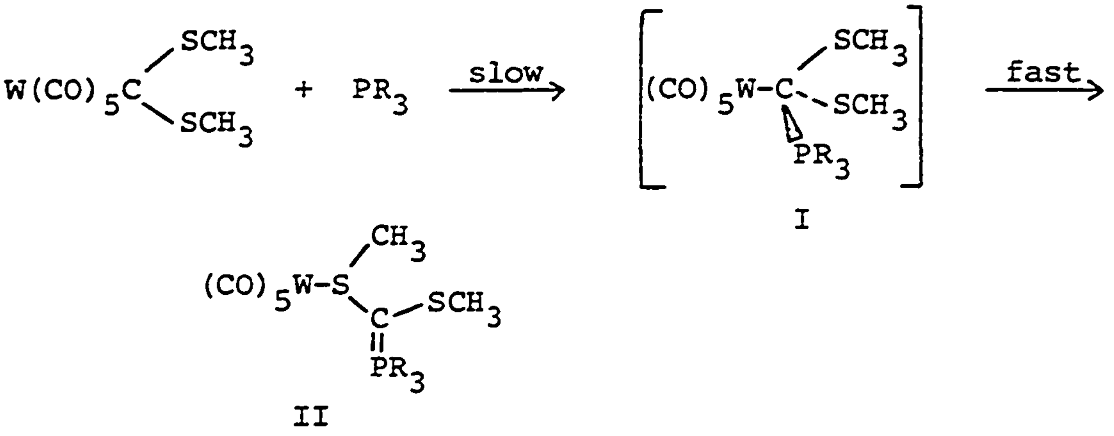
Determination of the Rates of Reactions of $W(CO)_5$-$[C(SCH_3)_2]$ with Phosphines The rates of reaction (eq 4) were determined using pseudo first order conditions (an excess of at least 40 fold of ligand was used in each case), and were found to follow the rate law (eq 5):

$$-d[W(CO)_5[C(SCH_3)_2]]/dt=k_{obsd}[W(CO)_5[C(SCH_3)_2]]=k[W(CO)_5\text{-}[C(SCH_3)_2]][L] \quad (5)$$

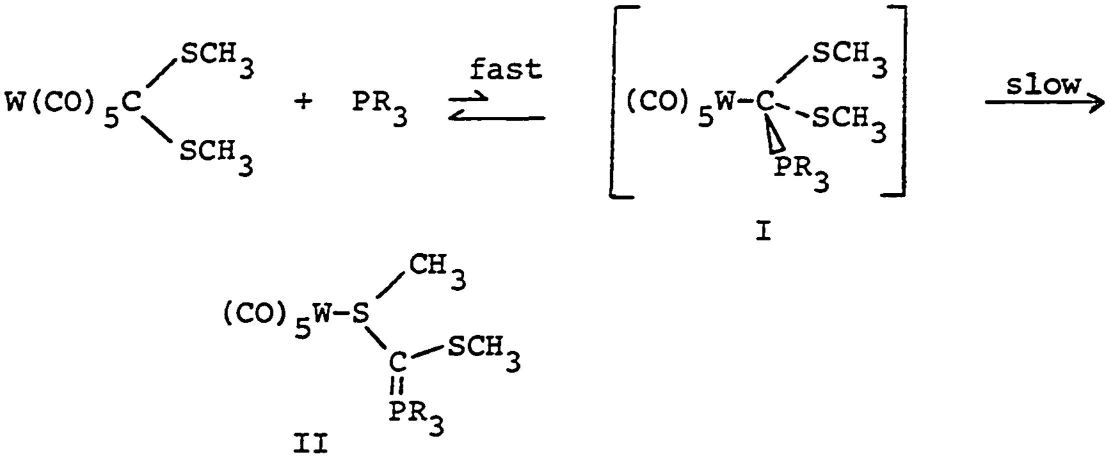
Each of the k_{obsd} values listed in Table I is an average of values from 3 or 4 runs; they are dependent on the ligand concentration and follow the expression, $k_{obsd}=k[L]$. Values of k for the same reaction at a specific temperature were constant, to within 10%, over a range of ligand concentrations. Average values of the second order rate constant, k, are given in Table II. Activation parameters and their associated standard deviations (Table III) were determined from a least-squares evaluation of the slope and intercept of a plot of ln(k/T) versus 1/T.

DISCUSSION

Mechanism of the Reaction of $W(CO)_5[C(SCH_3)_2]$ with PR_3 and PPh_2H The second order rate law which has been observed for the reaction of $W(CO)_5[C(SCH_3)_2]$ with phosphines is consistent with the following two mechanisms (eq 6 and 7):



(6)

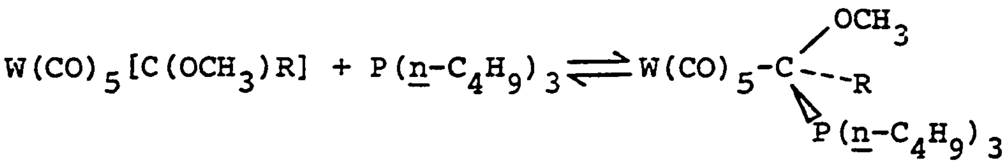


(7)

In mechanism (6), nucleophilic attack of the phosphine is the rate determining step, which is followed by a rapid rearrangement to produce the phosphorane product. In mechanism (7), the first step is a rapid equilibrium which lies far to the left, and the rate determining step is the rearrangement from the carbene-phosphine adduct to the phosphorane. Although mechanism (7) cannot be eliminated unequivocally, we believe the results best fit mechanism (6).

Mechanism (7) would suggest that intermediate I might be observable at high concentrations; however, infrared spectra of the ν(CO) region show no evidence of any intermediate in the reaction at dithiocarbene concentrations of approximately 50 times greater than those used in the kinetic runs. It should be noted however, that other carbene-phosphine adduct complexes have been well-characterized by others.[14] The fact that they are not observed here seems to indicate that once formed they rapidly rearrange to the phosphorane product or they are in such low concentration in the reaction mixture that they cannot be observed, which is consistent with either of the proposed mechanisms.

From equilibrium constants[8,10] of the reaction of oxo-alkyl and oxo-aryl carbene tungsten complexes with $P(\underline{n}\text{-}C_4H_9)_3$ to form carbene-phosphine adducts (eq 8)



$$W(CO)_5[C(OCH_3)R] + P(\underline{n}\text{-}C_4H_9)_3 \rightleftharpoons W(CO)_5\text{-}C(OCH_3)(R)(P(\underline{n}\text{-}C_4H_9)_3) \qquad (8)$$

$R = CH_3$ and $\underline{p}\text{-}C_6H_4(CF_3)$

it may be determined that adduct formation with the oxocarbenes, $W(CO)_5[C(OCH_3)R]$ is more favorable than with $W(CO)_5[C(SCH_3)_2]$. At 20° C and concentrations similar to those used in the kinetic experiments about 20% of $W(CO)_5$-$\{C(OCH_3)[\underline{p}\text{-}C_6H_4(CF_3)]\}$ and 80% of $W(CO)_5[C(OCH_3)(CH_3)]$ would be converted to the carbene-phosphine adducts. The smaller amount of adduct formation in the dithiocarbene may be due to the better electron donating ability of the S atoms, as compared to the O atom of the oxocarbene, into the p_z orbital of the carbene carbon making it less susceptible to nucleophilic attack.[18-20]

Support for the nucleophilic attack of the phosphines as being the slow step (eq 6) may be found in the trend of k values. These values (Table II) decrease with decreasing basicities and nucleophilicities of the phosphine ligand: $P(C_2H_5)_3 > PPh_2(CH_3) > PPh(CH_3)_2 > PPh_2H > P(OCH_3)_3$.[21-24] (Although, the nucleophilicity of PPh_2H is not known exactly, Ellgen and Gerlach[24] found that nucleophilic attack of phosphorus ligands of $Fe_2(CO)_5S_2C_6H_3CH_3$ decreases in the following order: $P(\underline{n}\text{-}C_4H_9)_3 > PPh_2H > P(OCH_3)_3$.) The one exception is $PPh_2(CH_3)$ whose k is slightly greater than that of $PPh(CH_3)_2$. It should be noted that the PPh_2H reaction, which leads to an entirely different product proceeds at a rate which is consistent with the

Table I. Average rate constants for the reaction (eq 3) of $W(CO)_5[C(SCH_3)_2]$ with L in cyclohexane solvent

L	Temp °C	[L]M	$10^4 k_{obsd}$, s^{-1}	$10^4 k$, $M^{-1}s^{-1}$
$P(C_2H_5)_3$	20.1	1.69×10^{-3}	57.3	33,900
	20.1	3.39×10^{-3}	114	33,500
	20.1	6.78×10^{-3}	235	34,600
	29.6	1.69×10^{-3}	86.6	51,200
	29.6	3.39×10^{-3}	17.7	52,200
	39.3	1.69×10^{-3}	133	78,900
$PPh(CH_3)_2$	20.1	5.79×10^{-2}	26.9	464
	20.1	1.16×10^{-1}	50.6	483
	20.1	2.28×10^{-1}	99.6	437
	29.6	2.81×10^{-2}	23.1	821
	29.6	5.79×10^{-2}	45.4	785
	29.6	1.16×10^{-1}	89.3	770
	39.3	2.81×10^{-2}	39.6	1,300

Table I. (continued)

L	Temp °C	[L]M	10^4k_{obsd}, s^{-1}	10^4k, $M^{-1}s^{-1}$
	39.3	5.79×10^{-2}	82.0	1,420
	39.3	1.16×10^{-1}	160	1,380
$PPh_2(CH_3)$	20.1	4.39×10^{-2}	24.4	555
	20.1	8.77×10^{-2}	45.7	521
	20.1	1.73×10^{-1}	87.9	509
	30.3	1.06×10^{-2}	10.4	981
	30.2	2.13×10^{-2}	21.4	1,000
	30.3	4.39×10^{-2}	42.5	968
	40.6	1.06×10^{-2}	18.5	1,740
	40.6	2.13×10^{-2}	37.8	1,780
	40.6	4.39×10^{-2}	74.8	1,710
PPh_2H	20.1	3.91×10^{-1}	5.12	13.1
	29.1	3.91×10^{-1}	10.5	26.9
	39.6	1.93×10^{-1}	10.6	54.9
	39.6	3.91×10^{-1}	21.9	56.0

Table I. (continued)

L	Temp °C	[L]M	10^4k_{obsd}, s^{-1}	10^4k, $M^{-1}s^{-1}$
$P(OCH_3)_3$	20.1	6.46×10^{-1}	4.77	7.38
	20.1	1.20	8.75	7.29
	30.3	6.46×10^{-1}	10.4	16.1
	30.3	1.20	19.3	16.1
	40.4	6.46×10^{-1}	21.2	32.8
	40.4	1.20	41.4	34.5

Table II. Average rate constants k for the reaction (eq 3) of $W(CO)_5[C(SCH_3)_2]$ with L in cyclohexane solvent

L	Temp °C	10^4k M^{-1} sec^{-1}
$P(C_2H_5)_3$	20.12	34,000
	29.60	51,700
	39.26	78,900
$PPh(CH_3)_2$	20.08	461
	29.58	792
	39.25	1,370
$PPh_2(CH_3)$	20.05	528
	30.28	983
	40.58	1,740
PPh_2H	20.08	13.1
	29.12	26.9
	39.62	55.5
$P(OCH_3)_3$	20.05	7.34
	30.33	16.1
	40.43	33.7

Table III. Activation parameters[a] for the reaction (eq 3) of $W(CO)_5[C(SCH_3)_2]$ with L in cyclohexane solvent

	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}
$P(C_2H_5)_3$	7.4(1)	-30.9(5)
$PPh(CH_3)_2$	9.7(3)	-31.6(10)
$PPh_2(CH_3)$	10.0(2)	-30.1(7)
PPh_2H	12.8(2)	-28.0(7)
$P(OCH_3)_3$	13.0(2)	-28.4(6)

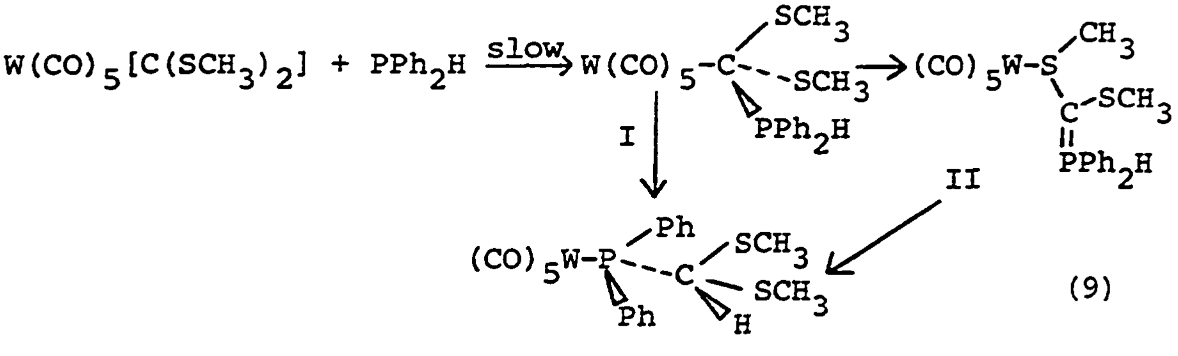
[a] Standard deviations (in parentheses).

nucleophilicity of PPh_2H. If rearrangement of the intermediate to the product were rate-determining, one might expect the rate of this reaction to be quite different than those which lead to the phosphorane products (eq 4).

The $\Delta H^{\ddagger}$ values for reaction 4 increase with decreasing nucleophilic strength of the phosphines (Table III): $P(C_2H_5)_3 < PPh(CH_3)_2 < PPh_2(CH_3) < PPh_2H < P(OCH_3)_3$.

Neither the nucleophilicities of the phosphines nor the type of product has an effect on the $\Delta S^{\ddagger}$ (Table III). They remain essentially constant for all of the phosphines used in this study. The negative values of $\Delta S^{\ddagger}$ (approximately -30 e.u.) support an associative type of mechanism, but they are somewhat less negative than those of -40 e.u. found for equation 8. This difference may reflect the greater disorder in the activated complex leading to intermediate I as compared to an isolable carbene-phosphine adduct (eq 8).

In the reaction of the secondary phosphine PPh_2H with $W(CO)_5[C(SCH_3)_2]$, there are two possible routes for the formation of the phosphine product from the carbene-phosphine adduct (eq 9):



(9)

It could rearrange to a phosphorane intermediate (II) (as in the case of the tertiary phosphines) which could then convert to the phosphine product by migration of the H atom from the P to the basic carbon atom followed by migration of the P atom to the W. Alternatively, intermediate I could rearrange directly by H atom migration to the C and P migration to the W. From our kinetic information it is impossible to distinguish between these routes. Even though we have not observed I during the course of these kinetic studies, its formation is supported by the work of Fischer et al.[8] They have isolated carbene-phosphine adduct $(CO)_5$-$Cr\{C(OCH_3)(Ph)[P(CH_3)_2H]\}$ and found that upon stirring in acetone for 8 hours at 25° C, it rearranges to the phosphine complex $(CO)_5Cr\{P(CH_3)_2[C(OCH_3)(Ph)H]\}$.

Reactions of Phosphines with $W(CO)_5[\overline{CS(CH_2)_nS}]$ As for $W(CO)_5[C(SCH_3)_2]$ (eq 4)[16], the 5, 6 and 7 membered cyclic dithiocarbene tungsten complexes react with $PPh_2(CH_3)$ to form cyclic phosphorane complexes (eq 10)

$$\underset{\text{III}}{W(CO)_5[\overline{CS(CH_2)_nS}]} + PPh_2CH_3 \longrightarrow \underset{\text{IV}}{(CO)_5W[\overline{S(CH_2)_nSC}{=}PPh_2(CH_3)]} \qquad (10)$$

n=2(IVa), 3(IVb), 4(IVc)

The spectral characteristics of IVa-c are very similar to those of the phosphorane complexes, $W(CO)_5[(CH_3S)_2C{=}PR_3]$, reported earlier.[16] Their infrared spectra (Table IV) contain three ν(CO) absorptions consistent with the pseudo C_{4V} symmetry of the molecule. Their ^1H and ^{13}C NMR spectra (Table V) of IVb and c show separate resonances for the two different methylene groups on the sulfur atoms.

The complexes, IVb and c, are yellow crystalline solids, (IVa has only been isolated as an oil). In the solid state, the complexes are stable at -20° C. They are soluble in $CHCl_3$ and CH_2Cl_2, but when exposed to air their solutions show evidence of decomposition within 2 to 4 hours.

The reactivities of the cyclic dithiocarbene tungsten complexes increase as the ring size increases. The 7- and 6-membered cyclic dithiocarbenes react in approximately 1.5 hours at room temperature with one or two equivalents of phosphine ligand respectively. However, to obtain complete reaction of the 5-membered cyclic dithiocarbene it must be heated with two equivalents of phosphine at 60° C in cyclohexane for at least 12 hours. The difference in reactivity may be explained on the basis of steric hindrance. The five-membered ring is fairly inflexible and allows for little movement to reduce steric hindrance as the $PPh_2(CH_3)$ ligand approaches. Although the 6-membered ring allows for some rearrangement to relieve steric problems, the 7-membered ring has even more flexibility.

Table IV. Infrared spectra of carbene and phosphorane complexes

Complex		$\nu(CO)\,cm^{-1}$
$W(CO)_5[CS(CH_2)_2S]$[a,b]	(IIIa)	2069(w), 1950(s)
$W(CO)_5[CS(CH_2)_3S]$[a,b]	(IIIb)	2067(w), 1944(s)
$W(CO)_5[CS(CH_2)_4S]$[a,b]	(IIIc)	2067(w), 1950(sh), 1944(s)
$W(CO)_5[S(CH_2)_2SC{=}PPh_2(CH_3)]$[c]	(IVa)	2072(w), 1946(sh), 1938(s)
$W(CO)_5[S(CH_2)_3SC{=}PPh_2(CH_3)]$[c]	(IVb)	2066(w), 1938(s), 1915(m)
$W(CO)_5[S(CH_2)_4SC{=}PPh_2(CH_3)]$[b]	(IVc)	2069(w), 1934(s), 1917(m)
$W(CO)_5[PPh_2C(H)S(CH_2)_3S]$[c]	(Va)	2071(w), 1942(s)
$W(CO)_5[PPh_2C(H)S(CH_2)_4S]$[b]	(Vb)	2072(w), 1947(sh), 1942(s)

[a] Reference 17.

[b] In hexanes.

[c] In cyclohexane.

Table V. ^{13}C NMR spectra of carbene and phosphorane complexes in $CDCl_3$[a](ppm)

Complex	Carbene	trans-CO	cis-CO	Others
IIIa[b]	282.2	204.6	196.0	47.8(SCH_2)
IIIb[b]	277.5	204.3	196.7	36.3(SCH_2); 17.4(CH_2)
IIIc[b]	291.1	205.3	197.5	44.3(SCH_2); 26.7(CH_2)
IVb[c]		204.1	200.3	133.9, 133.5, 130.9, 130.4, 129.6(Ph); 39.0, 27.3(SCH_2); 34.7(d, PCS_2)[d], 14.9(d, PCH_3)[e]
IVc		20.17	198.5	131.7, 131.2, 129.0, 128.5, 127.9(Ph); 50.5, 37.2(SCH_2); 28.4, 27.9(CH_2); 20.3(d, PCS_2)[f]; 13.2(d, PCH_3)[g]
Vb		198.7(d)[h]	196.6(d)[i]	134.4, 133.0, 132.4, 130.2, 128.0, 127.6(Ph); 52.1(PCS_2)[j]; 32.6(d, SCH_2)[k]; 30.9(CH_2)

[a] All resonances are singlets unless otherwise stated.

[b] Reference 17.

[c] Solvent CD_3CN.

[d] J_{PC}=78.2 Hz.

[e] J_{PC}=65.4 Hz.

[f] J_{PC}=124.8 Hz.

[g] J_{PC}=64.6 Hz.

[h] J_{PWC}=23.5 Hz.

[i] J_{PWC}=5.9 Hz.

[j] J_{PC}=11.7 Hz.

[k] J_{PC}=5.9 Hz.

Like $W(CO)_5[C(SCH_3)_2]$ (eq 4),[16] the 6- and 7-membered cyclic dithiocarbenes also react with PPh_2H to form phosphine products (eq 11):

$$W(CO)_5[\overline{CS(CH_2)_nS}] + PPh_2H \longrightarrow W(CO)_5\{PPh_2[\overline{CS(CH_2)_nS}(H)]\} \qquad (11)$$

III $\qquad$ V

n=3 (Va) or 4 (Vb)

The PPh_2H reacts slower than $PPh_2(CH_3)$ as would be expected on the basis of their nucleophilicities. Ring size again determines the rate of reaction since the 7-membered ring reacts much more rapidly than the six-membered ring. The phosphine products are yellow solids which may be stored at -20° C for months. They are soluble in organic solvents ranging in polarity from hexane to CH_2Cl_2. Like $W(CO)_5\{PPh_2[C(H)(SCH_3)_2]\}$,[16] the structural assignment of Vb was based on its ^1H and ^{13}C NMR spectra (Table V). Consistent with the structure are the equivalence of both SCH_2 groups in both the ^1H and ^{13}C spectra of the complex, IVb. The J_{PWC} values for the cis and trans CO groups (6 and 24 Hz, respectively) are very similar to those in related PR_3 complexes.[16,25,26] The small J_{PH} value (3 Hz) is consistent with the hydrogen atom being bound to the carbon atom rather than remaining on the phosphorus.[27]

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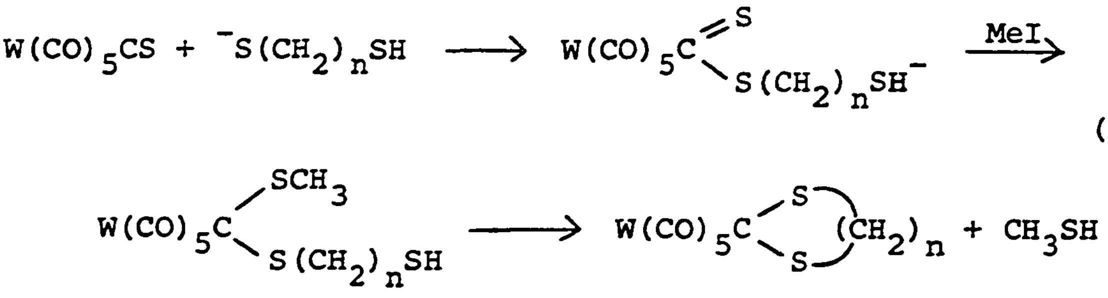
SUMMARY

In an effort to develop a general method for the preparation of tungsten ditniocarbene complexes and to better understand the reactivity of the carbene ligand, a series of tungsten dithiocarbene complexes, $W(CO)_5[C(SR)(SR')]$ was prepared by reacting $W(CO)_5CS$ with SR^- ($R=CH_3$, C_2H_5, *i*-C_3H_2, *n*-C_4H_9, *t*-C_4H_9) forming the dithioester anion which is then alkylated with CH_3I or C_2H_5I (eq 1):

$$W(CO)_5CS + SR^- \longrightarrow W(CO)_5[C(=S)(SR)]^- \xrightarrow{R'I} W(CO)_5[C(SR)(SR')] \qquad (1)$$

The substituted dithiocarbene complexes *cis*-$W(CO)_4(L)[C(SCH_3)_2]$ ($L=P(OCH_3)_3$ or $P(OPh)_3$) are prepared in a similar manner using *cis*-$W(CO)_4L(CS)$. However, if $\nu(CS)$ for the starting thiocarbonyl complex is less than 1247 cm^{-1} initial attack of the mercaptide anion does not occur. Cyclic dithiocarbene complexes may be made by an analogous route starting with dimercaptans (eq 2):



(2)

Five, six and seven membered cyclic dithiocarbene complexes have been prepared in this way.

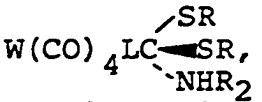
The carbene complexes $\mathrm{W(CO)_4L[C(SCH_3)_2]}$ (L=CO or $\mathrm{P(OPh)_3}$) and $\mathrm{W(CO)_5[\overline{CS(CH_2)_3S}]}$ reacted with primary amines to give isocyanides (eq 3):

$$\mathrm{W(CO)_4L[C(SR)_2]} \; + \; \mathrm{H_2NR} \longrightarrow \mathrm{W(CO)_4L(CNR)} + 2\ \mathrm{HSR} \qquad (3)$$

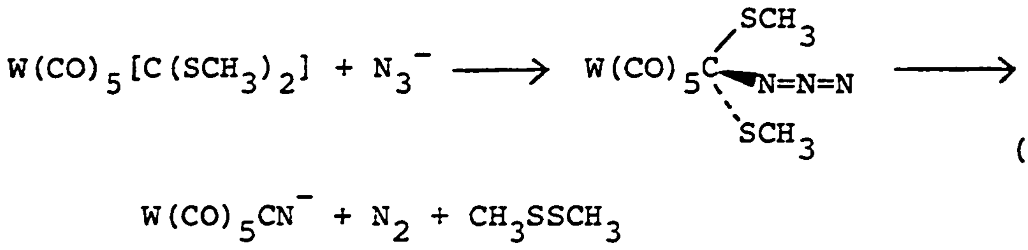
The dimethyldithicarbene complexes were found to react more rapidly then the cyclic dithiocarbenes. This is presumably caused by the better leaving group ability of $\mathrm{SCH_3}$ as compared to that of $\mathrm{S(CH_2)_3S}$. The isocyanide complexes, $\mathrm{W(CO)_4L[CN(CH_2)_3NH_2]}$, where L=CO or $\mathrm{P(OPh)_3}$ were also formed when $\mathrm{W(CO)_4L[C(SCH_3)_2]}$ complexes were reacted with 1,3-diaminopropane. The carbene complex $\mathrm{W(CO)_5[C(SCH_3)_2]}$ was found to react with secondary amines, $\mathrm{HN(CH_3)_2}$, $\mathrm{H\overline{N(CH_2)_4C}H_2}$ and $\mathrm{\overline{HN(CH_2)_2OCH_2C}H_2}$, to form amino-thiocarbene complexes (eq 4):

$$\mathrm{W(CO)_5[C(SCH_3)_2]} + \mathrm{HNR_2} \longrightarrow \mathrm{W(CO)_5[C(SCH_3)(NR_2)]} + \mathrm{HSCH_3} \qquad (4)$$

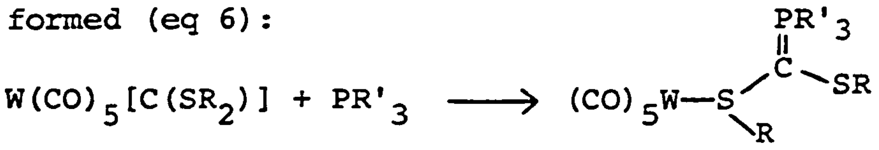
No reaction was observed when the 5-membered cyclic carbene was stirred with $\mathrm{HN(CH_3)_2}$ or piperdine;

presumably the barrier to ring opening prevents formation of the amino-thiocarbene. The first step in all of the amine reactions is thought to be the formation of an amino-carbene adduct,  $W(CO)_4LC(SR)_2(NHR_2)$, which then collapse to the isocyanide or amino-thiocarbene with the loss of HSR.

The reaction of N_3^- with $W(CO)_5[C(SCH_3)_2]$ to form $W(CO)_5CN^-$ and CH_3SSCH_3 is thought to proceed through the same type of adduct as the amine reactions. However the subsequent collapse of this adduct to form CH_3SSCH_3 appears to be quite different (eq 5):


(5)

When the dithiocarbene complexes, $W(CO)_5[C(SCH_3)_2]$ and $W(CO)_5[\overline{CS(CH_2)_nS}]$ (n=2, 3 or 4) are reacted with tertiary phosphines and phosphites, $P(C_2H_5)_3$, $PPh(CH_3)_2$, $PPh_2(CH_3)$, PPh_3 and $P(OCH_3)_3$, phosphorane complexes $W(CO)_5[(CH_3S)_2C{=}PR_3]$ and $W(CO)_5[\overline{S(CH_2)_nSC}{=}PR_3]$ are formed (eq 6):


(6)

In contrast, these carbene complexes react with the secondary phosphine, PPh_2H, to form phosphine complexes, $W(CO)_5PPh_2[C(SCH_3)_2H]$ or $W(CO)_5PPh_2$-$[\overline{C(H)S(CH_2)_nS}]$, (eq 7).

Kinetic studies of the reaction of $W(CO)_5[C(SCH_3)_2]$ with both secondary and tertiary phosphines show these reactions to be first order in both the carbene complex and the phosphorus ligand. The mechanism for the reactions presumably involves rate determining phosphorus ligand attack on the carbene-carbon followed by rapid rearrangement to the products. This type of mechanism is consistent with the observed trends in the values of k and $\Delta H^{\ddagger}$. The values of the rates constants, k, for attack of the phosphorus ligand increase with increasing nucleophilicities of the ligands: $P(OCH_3)_3 < PPh_2H < PPh(CH_3)_2 \simeq PPh_2(CH_3) < P(C_2H_5)_3$. The $\Delta H^{\ddagger}$ values for the reactions in equations 6 and 7 decrease as the nucleophilicities of the phosphorus ligand increase: $P(C_2H_5)_3 < PPh(CH_3)_2 < PPh_2(CH_3) < PPh_2H < P(OCH_3)_3$. The $\Delta S^{\ddagger}$ values (-30 e.u.) remain essentially constant over the entire series.

The present study poses several questions 1) is mercaptide attack on a thiocarbonyl ligand followed by alkylation of the dithioester a means for the preparation of dithiocarbene complexes in other systems and 2) how would the reactivity of dithiocarbene complexes of other metal systems compare with the known tungsten, $W(CO)_4L[C(SR)_2]$, and iron, $CpFe(CO)L[C(SR)_2]^+$, systems. The first question could be addressed by studying the reactivity of known thiocarbonyl complexes[41,42] whose $\nu(CS) > 1247\ cm^{-1}$ with mercaptide anions. This could lead not only to dithiocarbene complexes but to some other very interesting carbene complexes. For example, if $[Ir(CO)_2(CS)(PPh_3)_2{}^+]$ reacts with ^-SR in the same manner in which it reacts with $^-OCH_3$,[43] the product obtained would be $Ir(CO)[C(=O)(SR)](CS)(PPh_3)_2$ rather than the dithioester. Methylation of $Ir(CO)$-$[C(=O)(SR)](CS)(PPh_3)_2$ could give a carbene complex containing a thiocarbonyl ligand, $\{Ir(CO)[C(OCH_3)(SR)]$-$(CS)(PPh_3)_2{}^+\}$. It would then be interesting to see if the carbene on the CS ligand reacted preferentially with amines and other nucleophilics. The second question could easily be answered after the dithiocarbene complexes are prepared by studying their reactivity with nucleophilics.

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