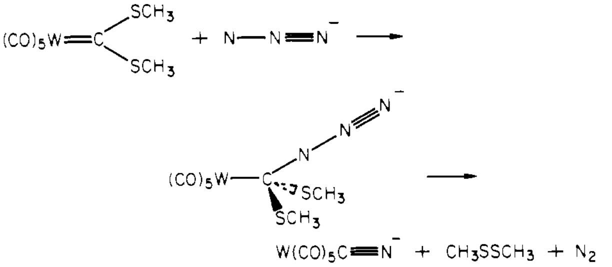
presumably N_2, was also observed during the reaction. A possible mechanism for this reaction is shown in eq 9.



(9)

Other nucleophiles that did not react with IIa are $[N(C_4H_9)_4^+]I^-$, $N(C_2H_5)_3$, 1,4-diazabicyclo[2.2.2]octane, $CNCH_3$, and $S(CH_3)_2$.

Registry No. IIa, 76262-42-5; IIb, 77826-89-2; IIc, 77826-90-5; IId, 77826-91-6; IIe, 77826-92-7; IIf, 67517-56-0; IIg, 77846-65-2; IIh, 77826-93-8; IIIa, 77826-94-9; IIIb, 77826-95-0; IIIc, 77826-96-1; IV, 77826-97-2; Va, 50298-27-6; Vb, 77826-98-3; Vc, 77826-99-4; Vd, 15603-77-7; Ve, 77827-00-0; Vf, 77827-01-1; VIa, 77827-02-2; VIb, 77827-03-3; VIc, 77827-04-4; VIIa, 77827-05-5; VIIb, 77827-06-6; VIII, 77827-07-7; $W(CO)_5CS$, 50358-92-4; *cis*-$W(CO)_4(CS)[P(OCH_3)_3]$, 66007-60-1; *cis*-$W(CO)_4(CS)[P(OPh)_3]$, 65969-60-0; $Na[W(CO)_5C(S)(SCH_3)^-]$, 77846-66-3; $[CpFe(CO)_2(THF)][BF_4]$, 63313-71-3; HSC_2H_5, 75-08-1; $HSCH(CH_3)_2$, 75-33-2; $HS(CH_2)_3CH_3$, 109-79-5; $HSC(CH_3)_3$, 513-44-0; $HSCH_3$, 74-93-1; $HS(CH_2)_2SH$, 540-63-6; $HS(CH_2)_3SH$, 109-80-8; $HS(CH_2)_4SH$, 1191-08-8; CH_3I, 74-88-4; C_2H_5I, 75-03-6; H_2NCH_3, 74-89-5; $H_2N(CH_2)_2CH_3$, 107-10-8; H_2NCH_2Ph, 100-46-9; $H_2NC_6H_{11}$, 108-91-8; $H_2N(CH_2)_2N(CH_3)_2$, 108-00-9; $HN(CH_3)_2$, 124-40-3; $HN(CH_2)_4CH_2$, 110-89-4; $HN(CH_2)_2OCH_2CH_2$, 110-91-8; $H_2N(CH_2)_3NH_2$, 109-76-2; $[N(C_2H_5)_4^+][N_3^-]$, 993-20-4.

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Thiocarbonyl Complexes of Cyclopentadienyltungsten and [Hydrotris(1-pyrazolyl)borato]tungsten. Reactions at the CS Ligand Leading to Mercaptocarbyne and Isocyanide Complexes

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Received December 22, 1980

The anionic thiocarbonyl complexes $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ reacted with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and acid or with $NOPF_6$ to give $CpW(CO)(CS)NO$ and $HB(pz)_3W(CO)(CS)NO$. The $CpW(CO)_2CS^-$ complex reacted with chloro-2,4-dinitrobenzene (DNP-Cl) to yield the mercaptocarbyne $Cp(CO)_2W\equiv C—S—DNP$. Analogous reactions of $CpW(CO)_2CS^-$ with MeI and EtI gave spectroscopic evidence for the formation of the less stable $CpW(CO)_2CS–R$ mercaptocarbyne complexes. The hydrotris(1-pyrazolyl)borate complex $HB(pz)_3W(CO)_2CS^-$ reacted with MeI, EtI, and DNP-Cl to give the stable mercaptocarbyne derivatives $HB(pz)_3W(CO)_2CS–R$. These reactions of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ with alkyl halides contrast with those of $CpW(CO)_3^-$ and $HB(pz)_3W(CO)_3^-$, which give σ-bonded W–R complexes. Unexpectedly, $CpW(CO)(CS)(PPh_3)I$ reacted with LiPh to give the mercaptocarbyne $CpW(CO)(PPh_3)CS–Ph$, whose structure was established by an X-ray crystallographic determination. Evidence for the formation of $CpW(CO)_2CS–R$ complexes was also found in the reactions of *trans*-$CpW(CO)_2(CS)I$ with LiMe and LiPh. A stable mercaptocarbyne, $HB(pz)_3W(CO)_2CS–Me$, was isolated from the reaction of *trans*-$HB(pz)_3W(CO)_2(CS)I$ with LiMe. Possible mechanisms for the reactions of LiR with W(CS)I-containing complexes to give $W\equiv C—S—R$ and I^- are considered; a radical mechanism appears most likely. The conversion of CS groups to mercaptocarbynes involves the reduction of CS multiple bonds to C—S single bonds, a transformation that may have relevance for the catalytic cleavage of $C\equiv O$ bonds in carbon monoxide. Finally, reactions of $CpW(CO)(CS)NO$, $HB(pz)_3W(CO)(CS)NO$, *cis*-$CpW(CO)_2(CS)SnPh_3$, and *cis*-$CpW(CO)_2(CS)PbPh_3$ with H_2NMe smoothly transform the CS to the $C\equiv N—Me$ ligand in the products $CpW(CO)(CNMe)NO$, $HB(pz)_3W(CO)(CNMe)NO$, *cis*- and *trans*-$CpW(CO)_2(CNMe)SnPh_3$, and *cis*- and *trans*-$CpW(CO)_2(CNMe)PbPh_3$. Trends in the ν(CO) frequencies, the ^1H and ^{13}C NMR spectra, and the reactivities of the complexes are discussed.

Introduction

Recently, we reported[2] the preparation of the nucleophilic cyclopentadienyl and hydrotris(1-pyrazolyl)borate complexes $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$. They were observed to react with a series of electrophiles E–X, where E = I, SePh, HgI, $SnPh_3$, or $PbPh_3$ and X = Cl, Br, or I, to yield products in which the E group was coordinated to the tungsten atom.

$$CpW(CO)_2CS^- \text{ or } HB(pz)_3W(CO)_2CS^- + E–X \rightarrow CpW(CO)_2(CS)E \text{ or } HB(pz)_3W(CO)_2(CS)E + X^- \quad (1)$$

In other electron-rich thiocarbonyl complexes, however, the sulfur atom of the CS group can act as the nucleophile. Thus, the reaction

$$IW(CO)_4CS^- + CH_3OSO_2F \rightarrow IW(CO)_4CS–CH_3 + SO_3F^- \quad (2)$$

yields the *S*-methyl product.[3] In the study reported here, we performed reactions of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ with more electrophiles to determine whether addition occurs at the W or S atom. Also reported are reactions of the CS group in some complexes with the nucleophiles LiR and CH_3NH_2. Some of these results were communicated previously.[4]

Results and Discussion

Reactions at the Tungsten Atom. CpW(CO)(CS)NO and HB(pz)₃W(CO)(CS)NO. As in the procedure for the synthesis

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[1] To whom correspondence should be addressed.

[2] Greaves, W. W.; Angelici, R. J. *J. Organomet. Chem.* **1980**, *191*, 49.

[3] Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2397.

[4] Greaves, W. W.; Angelici, R. J.; Helland, B. J.; Klima, R.; Jacobson, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7618.

0020-1669/81/1320-2983$01.25/0

Table I. IR Stretching Frequencies of Various Tungsten Complexes in CS_2 Solution[a]

compd	ν(CO), cm^{-1}	ν(CS), cm^{-1}
CpW(CO)(CS)NO	1990 s, 1680 s[b]	1260 s
$CpW(CO)_2NO$[h]	2012, 1933, 1682[b,e]	
$HB(pz)_3W(CO)(CS)NO$	1982 s, 1670 s[b]	1252 s
$HB(pz)_3W(CO)_2NO$[8]	2010, 1910, 1651[b,d]	
trans-$IW(CO)_4CS$-Me[3]	2115 w, 2033 vs[c]	1118 m[c]
$[(diphos)_2W(CO)CS$-Me]FSO_3[3]	1898 s[d]	
$CpW(CO)_2CPh$[15]	1991 s, 1922 s	
$CpW(CO)_2CNEt_2$[15]	1958 s, 1880 s[e]	
$CpW(CO)_2CSiPh_3$[16]	2003 s, 1926 vs[d]	
$CpW(CO)_2CS$-DNP	2001 s, 1930 s	
$CpW(CO)(PPh_3)CS$-Ph	1886 s	
$HB(pz)_3W(CO)_2CS$-Me	1979 s, 1893 s	
$HB(pz)_3W(CO)_2CS$-Et	1979 s, 1892 s	
$HB(pz)_3W(CO)_2CS$-DNP	1999 s, 1914 s	
CpW(CO)(CNMe)NO	2141 m,[f] 1911 s, 1601 s[b,d]	
$HB(pz)_3W(CO)(CNMe)NO$	2140 m,[f] 1906 s, 1607[b]	
cis- and *trans*-$CpW(CO)_2$-(CNMe)$SnPh_3$[g]	2105 m,[f] 1947 vs, 1932 w,[g] 1888 vs, 1875 s	
cis- and *trans*-$CpW(CO)_2$-(CNMe)$PbPh_3$[g]	2112 m,[f] 1950 s, 1936 w,[g] 1892 s, 1882 m	

[a] Abbreviations: s = strong, m = medium, w = weak, v = very. [b] ν(NO). [c] Pentane solution. [d] CH_2Cl_2 solution. [e] Hexane solution. [f] ν(CN). [g] Cyclohexane solution. [h] Fischer, E. O.; Beck, H.-J. *Chem. Ber.* 1971, *104*, 3101.

Table II. ^1H NMR Chemical Shifts of Various Tungsten Compounds in $CDCl_3$ Solution[a]

compd	δ(Cp)[b]	δ(R)[b]
CpW(CO)(CS)NO	5.87 (s)	
trans-$IW(CO)_4CS$-Me[3]		2.60 (s, Me)
$CpW(CO)_3CH_3$[17]	5.40 (s)[c]	0.40 (s, Me)[c]
$CpW(CO)_2CPh$[15]	5.80 (s)[d]	7.51 (m, Ph)[d]
$CpW(CO)_2CNEt_2$[15]	5.66 (s)[d]	1.28 (t, CH_3), 3.33 (q, CH_2)[d]
$CpW(CO)_2CSiPh_3$[16]	5.89 (s)[e]	7.53 (m, Ph)[e]
$CpW(CO)_2CS$-DNP	5.80 (s)	8.50 (dd, Ph), 9.05 (d, Ph), 9.05 (d, Ph)[f]
$CpW(CO)(PPh_3)CS$-Ph	5.24 (d)[g]	7.32 (m, Ph)
$HB(pz)_3W(CO)_2CS$-Me		2.59 (s, Me)
$HB(pz)_3W(CO)_2CS$-Et		1.45 (t, CH_3), 2.97 (q, CH_2)[h]
$HB(pz)_3W(CO)_2$(CS-DNP)[i]		8.35 (dd, Ph), 9.02 (d, Ph), 9.06 (d, Ph)[j]
CpW(CO)(CNMe)NO	5.60 (s)	3.77 (s, Me)
$HB(pz)_3W(CO)(CNMe)NO$		3.75 (s, Me)
cis- and *trans*-$CpW(CO)_2$-(CNMe)$SnPh_3$	5.21 (s, trans), 5.35 (s, cis)	2.94 (s, cis Me),[k] 3.68 (s, trans Me),[k] 7.58 (m, Ph)
cis- and *trans*-$CpW(CO)_2$-(CNMe)$PbPh_3$	5.16 (s, trans),[k] 5.34 (s, cis)[k]	2.96 (s, cis Me),[k] 3.61 (s, trans Me),[k] 7.41 (m, Ph)

[a] Pyrazolyl resonances have been omitted for clarity; see Experimental Section. H-B resonance not observed. [b] Abbreviations: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = complex multiplet. [c] CCl_4 solution. [d] CD_2Cl_2 solution. [e] Acetone-d_6 solution. [f] dd $J = 9$ Hz, $J' = 2$ Hz; d $J = 9$ Hz; d $J = 2$ Hz. [g] $J_{P-Cp} = 0.8$ Hz. [h] $J = 7$ Hz. [i] Recorded at −60 °C. [j] dd $J = 9$ Hz, $J' = 3$ Hz; d $J = 3$ Hz; d $J = 9$ Hz. [k] There are also small satellites due to proton coupling with isotopes of Sn or Pb.

Table III. ^{13}C NMR Chemical Shifts of Various Tungsten Complexes in $CDCl_3$ Solution[a]

compd	δ(Cp)	δ(CO)	δ(W-C-R)
CpW(CO)(CS)NO	−94.4 (s)	−215.1 (s)[b]	
$HB(pz)_3W(CO)(CS)NO$	...	−217.9 (s)[c]	
trans-$IW(CO)_4CS$-Me[3]	...	−188.8 (s)	−252.7 (s)
$CpW(CO)_2CPh$[15]	−92.1 (s)[d]	−221.3 (s)[d]	−299.0 (s)[d]
$CpW(CO)_2CSiPh_3$[16]	−92.6 (s)[d]	−222.2 (s)[d]	−354.3 (s)[d]
$CpW(CO)_2CS$-DNP	−92.5 (s)	−219.3 (s)	−261.7 (s)
$CpW(CO)(PPh_3)CS$-Ph	−91.5 (s)	−237.7 (d)[e]	−254.9 (d)[e]
$HB(pz)_3W(CO)_2CS$-Me	...	−224.7 (s)	−264.4 (s)

[a] Abbreviations: s = singlet, d = doublet. [b] δ(CS) = −329.7 (s). [c] δ(CS) = −319.2 (s). [d] CH_2Cl_2 solution. [e] $J_{P-CO} = 7$ Hz; $J_{P-WCS} = 12$ Hz.

of $CpW(CO)_2NO$,[5] *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and acetic acid were added to a THF solution of $CpW(CO)_2CS^-$. This reaction yielded a mixture of CpW(CO)(CS)NO (57% yield) and $CpW(CO)_2NO$ that could be separated chromatographically. The infrared, ^1H, and ^{13}C NMR spectra (Tables I–III) are consistent with the CpW(CO)(CS)NO formulation and are very similar to those of the recently reported analogue CpCr(CO)(CS)NO, which was prepared by an entirely different route.[6]

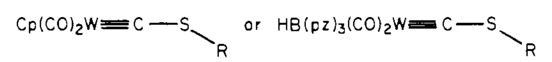
The formation of CpW(CO)(CS)NO may proceed through the hydride $CpW(CO)_2(CS)H$, as implied by the reaction of $CpW(CO)_3H$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to form $CpW(CO)_2NO$.[7] Although addition of CH_3CO_2H or CF_3SO_3H to a solution of $CpW(CO)_2CS^-$ caused a color change and a shift of the ν(CO) bands to higher frequency, suggesting the possible formation of $CpW(CO)_2(CS)H$, the product was unstable and was not characterized further.

The reaction of $HB(pz)_3W(CO)_2CS^-$ with $NO^+PF_6^-$ yielded a mixture of $HB(pz)_3W(CO)(CS)NO$ and $HB(pz)_3W(CO)_2NO$[8], which could not be completely separated, even by repeated chromatography. The $HB(pz)_3W(CO)(CS)NO$ complex is air stable and exhibits the expected IR and NMR spectral characteristics.

Although carbonyl–thiocarbonyl complexes frequently undergo only CO substitution by phosphine and phosphite ligands,[9] both the CO and CS groups in $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ are replaced by NO^+ in the above reactions. Different mechanisms of reaction in these cases may account for their different substitution behaviors.

A comparison of ν(NO) values of CpW(CO)(CS)(NO) and $HB(pz)_3W(CO)(CS)NO$ with their dicarbonyl analogues (Table I) leads to the conclusion that the CS group has about the same, or somewhat higher, π-acceptor/σ-donor ratio as CO. This conclusion is consistent with the results of a variety of other studies.[10]

Reactions at the Sulfur Atom. (a) Reactions of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$. In contrast to the reactions of $CpW(CO)_3^-$[11] and $HB(pz)_3W(CO)_3^-$[12] with alkyl halides to give σ-alkyl complexes, the analogous thiocarbonyl anions yield *S*-alkyl or -aryl (i.e., mercaptocarbyne) complexes according to the equation



(3)

where R = 2,4-dinitrophenyl, Me, or Et and X = Cl or I. The alkylation of the CS sulfur atom in electron-rich thiocarbonyl

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(5) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1967**, *6*, 469.
(6) Herberhold, M.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 631.
(7) Stewart, R. P.; Moore, G. W. *Inorg. Chem.* **1975**, *14*, 2699.
(8) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 2675.
(9) Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 1089. Wnuk, T. A.; Angelici, R. J. *Ibid.* **1977**, *16*, 1173. Pickering, R. A.; Angelici, R. J. *Ibid.* **1978**, *17*, 2035.
(10) Butler, I. S. *Acc. Chem. Res.* **1977**, *10*, 359.
(11) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.
(12) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588.

complexes, those with ν(CS) frequencies below approximately 1200 cm^{-1}, has been reported previously for $W(diphos)_2(CO)CS$ and $IW(CO)_4CS^-$.[3] However, the carbonyl analogues of those compounds do not have the well-established metal-alkylation pattern that is known for $CpW(CO)_3^-$ and $HB(pz)_3W(CO)_3^-$. Although our results indicate that the sulfur is the preferred site of alkylation in the reactions of eq 3, it is not clear why the electrophiles Ph_3SnCl, Ph_3PbCl, and PhSeBr react at the metal.

The products of eq 3 are assigned a mercaptocarbyne structure, in which there is a formal W≡C triple bond and a C—S single bond. This assignment is based on the recent X-ray structure determination[4] of $Cp(CO)(PPh_3)W{\equiv}C{-}S{-}Ph$, which shows that the W≡C—S—Ph unit is best represented as a mercaptocarbyne group.

The orange $CpW(CO)_2CS$–DNP (DNP = 2,4-dinitrophenyl) was obtained in 40% yield from the reaction at 0 °C of $CpW(CO)_2CS^-$ and chloro-2,4-dinitrobenzene. The compound is somewhat air sensitive but can be handled for short periods in air without significant decomposition. It is insoluble in aliphatic hydrocarbons but soluble in more polar organic solvents.

Consistent with its formulation as a mercaptocarbyne complex are the lack of a ν(CS) absorption and the presence of two ν(CO) absorptions. Its ^{13}C NMR spectrum (Table III) exhibits single resonances for the Cp and CO groups; the carbyne carbon resonance at −261.7 ppm is similar to those of other tungsten carbyne complexes listed in Table III. The phenyl resonance at −138.5 ppm is comparable to reported values of a phenyl carbon attached to sulfur.[13]

Fischer and co-workers[14–16] have prepared a series of related $CpW(CO)_2C$–Y carbyne complexes. In the infrared spectra of $CpW(CO)_2CS$–DNP and Fischer's compounds (Table I), the ν(CO) values decrease as the Y group changes: S–DNP ~ $SiPh_3$ > Ph > NEt_2. This trend follows the expected increasing electron-donating ability of the Y groups.

Whereas $CpW(CO)_2CS$–DNP was isolated and fully characterized, alkyl derivaties of the type $CpW(CO)_2CS$–R were not isolated because of their instability. Addition of MeI or $MeOSO_2F$ to a THF solution of $CpW(CO)_2CS^-$ gives an orange compound whose IR spectrum in CS_2 exhibits two strong ν(CO) bands at 1985 and 1911 cm^{-1} but no CS absorption. Its ^1H NMR spectrum has a Cp resonance at δ 5.65 and an Me resonance at δ 2.58 in a ratio of 5:3. The position of the latter resonance is very similar to those of the Me groups[8] in *trans*-$IW(CO)_4CS$–Me and $(diphos)_2W(CO)CS$–Me^+ and quite different from that of the σ-bound Me (0.4 ppm, Table II) in $CpW(CO)_3Me$. It therefore appears that $CpW(CO)_2CS$–Me forms but, like the product from analogous reactions with EtI and $PhCH_2Br$, is an air-sensitive oil. In an attempt to isolate a solid substituted product, $CpW(CO)_2CS$–Me was refluxed with PPh_3 in THF, but no reaction occurred. Spectroscopic evidence to suggest the formation of mercaptocarbyne complexes was also obtained in reactions of $CpW(CO)_2CS^-$ with *i*-PrI, MeC(O)Cl, PhC(O)Cl, Ph_2PCl, and $(Ph_3P)AuCl$, but the products were not isolated owing to their instability.

The reactions of $HB(pz)_3W(CO)_2CS^-$ with DNP-Cl, MeI, and EtI yield stable $HB(pz)_3W(CO)_2CS$–R products. These orange, crystalline solids may be recrystallized many times with little decomposition. Their ν(CO) values (Table I) are lower than those of the corresponding $CpW(CO)_2CS$–R derivatives, reflecting the stronger electron-donor properties of the $HB(pz)_3^-$ ligands.[8,12] The ^{13}C chemical shift (−264.4 ppm) of the carbyne carbon atom in $HB(pz)_3W(CO)_2CS$–Me is very similar to those of other tungsten mercaptocarbyne complexes (Table III), which supports the formulation of these derivatives as carbynes.

(b) Reactions of $CpW(CO)(CS)(PPh_3)I$, *trans*-$CpW(CO)_2(CS)I$, and *trans*-$HB(pz)_3W(CO)_2(CS)I$. Although halo complexes normally react with alkyl- and aryllithium and alkyl and aryl Grignard reagents to give σ-bonded metal–alkyl or –aryl organometallic derivatives, treatment of $CpW(CO)(CS)(PPh_3)I$[2] with LiPh gives the mercaptocarbyne $CpW(CO)(PPh_3)CS$–Ph:

$$CpW(CO)(CS)(PPh_3)I + LiPh \rightarrow CpW(CO)(PPh_3)CS\text{–}Ph + LiI \quad (4)$$

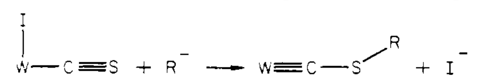
The X-ray analysis[4] of this product supports the formulation of the W≡C—S—Ph unit as a mercaptocarbyne group on the basis of the following results: (1) the W–C(carbyne) bond distance (1.807 Å) is very short and almost identical with that found in other types of carbyne complexes,[15,16] (2) the S–C(carbyne) distance (1.716 Å) is that expected for a S–C(sp) single bond, (3) the W≡C—S bond is nearly linear (174.2°), and (4) the Ph–S–C(carbyne) bond angle is essentially tetrahedral (106.2°). Consistent with this structure are the absence of a ν(C≡S) absorption in the IR region and a doublet Cp resonance caused by ^{31}P coupling in the ^1H NMR spectrum. Also, a doublet for the mercaptocarbyne carbon is observed at −254.9 ppm in the ^{13}C NMR spectrum, which is in the region where other mercaptocarbyne carbons resonate (Table III).

Although $CpW(CO)(CS)(PPh_3)I$ reacted with LiMe at −78 °C in THF to give a compound with a ν(CO) absorption at 1890 cm^{-1}, suggesting the formation of $CpW(CO)(PPh_3)CS$–Me, the product decomposed before it could be isolated.

In a reaction similar to that in eq 4, *trans*-$CpW(CO)_2(CS)I$ reacted with LiMe in THF at −78 °C to give an orange product with IR and ^1H NMR spectra that are identical with those of the unstable $CpW(CO)_2CS$–Me produced from $CpW(CO)_2CS^-$ and MeI. Low-temperature reactions of *trans*-$CpW(CO)_2(CS)I$ with LiPh, *p*-$Me_2NC_6H_4Li$, and LiC_6F_5 give spectroscopic evidence for the formation of mercaptocarbyne complexes, but like $CpW(CO)_2CS$–Me, these compounds are unstable oils. The dimethyl malonate anion is not sufficiently nucleophilic to react with *trans*-$CpW(CO)_2(CS)I$ under these conditions.

Reaction of *trans*-$HB(pz)_3W(CO)_2(CS)I$ with LiMe produces $HB(pz)_3W(CO)_2CS$–Me in 83% yield. This product, identified by its IR and ^1H NMR spectra (Tables I and II) and elemental analyses, is identical with the compound produced from the reaction of $HB(pz)_3W(CO)_2CS^-$ and MeI. In the only reaction of this type that did not yield a mercaptocarbyne complex, *trans*-$HB(pz)_3W(CO)_2(CS)I$ and LiPh gave a reaction mixture with ν(CO) bands at 1885 (s) and 1785 (s) cm^{-1} characteristic[2] of $HB(pz)_3W(CO)_2CS^-$. Apparently, in this case, *trans*-$HB(pz)_3W(CO)_2(CS)I$ was reduced.

These reactions of $CpW(CO)(CS)(PPh_3)I$, *trans*-$CpW(CO)_2(CS)I$, and *trans*-$HB(pz)_3W(CO)_2(CS)I$ with carbanions reveal a new route to mercaptocarbyne complexes:



$$\overset{I}{\overset{|}{W}}{-}C{\equiv}S + R^- \longrightarrow W{\equiv}C{-}S{-}R + I^- \quad (5)$$

The mechanism of this reaction is unlikely to involve nucleophilic attack of R^- on the sulfur atom. Initial attack at the W atom or the CS carbon atom would seem possible, but those reactions might be expected to yield isolable interme-

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(13) Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra"; Wiley-Interscience: New York, 1972; p 164.

(14) Fischer, E. O.; Lindner, T. L.; Kreissl, F. R. *J. Organomet. Chem.* **1976**, *112*, C27.

(15) Fischer, E. O.; Lindner, T. L.; Huttner, G.; Friedrich, P.; Kreissl, R. F.; Besenhard, J. O. *Chem. Ber.* **1977**, *110*, 3397.

(16) Fischer, E. O.; Hollfelder, H.; Friedrich, P.; Kreissl, F. R.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 401.

(17) Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133.

diates of the types W–R or W–C(S)R (coordinated through either C or C and S).

The reaction of organic thioketones, $R_2C{=}S$, with LiPh to give *S*-phenyl products, R_2CHSPh, suggests a charge-transfer radical mechanism in which an electron is transferred from R^- to the thioketone, followed by combination of the radicals to yield the product.[18-21] That electron transfer is possible in reaction 5 is suggested by the reaction of $CpMo(CO)_3I$ with PhMgBr to give $[CpMo(CO)_3]_2$ and biphenyl[11] and reactions of $CpM(CO)_4^+$, where M = Mo or W, with LiPh to yield $[CpM(CO)_3]_2$ and biphenyl.[22] Although a radical mechanism appears possible for reaction 5, further studies are required.

The overall effect of converting a terminal CS ligand to a mercaptocarbyne, either by reaction 3 or 5, is to reduce the multiple CS bond to a single bond. Such a reduction in CO bond strength has been suggested to account for catalytic reactions that lead to cleavage of the C≡O bond.[23,24] Thus mercaptocarbyne complexes may serve as stable analogues of M≡C—O—R or M≡C—O—M′ intermediates postulated in such catalytic reactions.

Reactions at the CS Carbon Atom. Since the original report of the reaction of $W(CO)_5CS$ with primary amines (H_2NR) to form isocyanide complexes, $W(CO)_5C{\equiv}N{-}R$,[25] the CS group in several other complexes with ν(CS) values higher than $\sim$1250 cm^{-1} have been reported to undergo analogous reactions.[26] We have found that the following compounds, with their ν(CS) frequencies indicated in parentheses, also react with H_2NMe in this manner: CpW(CO)(CS)NO (1260 cm^{-1}), $HB(pz)_3W(CO)(CS)NO$ (1252 cm^{-1}), *cis*-$CpW(CO)_2(CS)SnPh_3$ (1238 cm^{-1}),[2] *cis*-$CpW(CO)_2(CS)PbPh_3$ (1237 cm^{-1}).[2] In all cases, the reactions resulted in the conversion of the CS into a C≡N—Me ligand:

$$W{-}C{\equiv}S + H_2N{-}Me \rightarrow W{-}C{\equiv}N{-}Me + H_2S \qquad (6)$$

The reactions of the nitrosyl complexes, which had the higher ν(CS) values, were complete in 20 min at room temperature, whereas the Sn and Pb complexes, with lower ν(CS) values, required 20 h. If these reactions proceed by hydrogen-bonded amine attack at the CS carbon atom as proposed[25] for the reactions of $W(CO)_5CS$, one would expect the more electron-rich complexes with the lower ν(CS) values to react more slowly.

Infrared and ^{1}H NMR spectra (Tables I and II) of the CpW(CO)(CNMe)NO and $HB(pz)_3W(CO)(CNMe)NO$ complexes are consistent with the expected products from reaction 6. In the carbonyl region, the IR spectra of the $CpW(CO)_2(CNMe)MPh_3$ complexes show a marked dependence on the solvent (Figure 1). In cyclohexane, four ν(CO) bands are observed, which suggests the presence of cis and trans isomers. The closely related $CpMo(CO)_2(CNMe)SnMe_3$ and $CpMo(CO)_2(CNMe)PbPh_3$ had previously[27] been observed to exist as a cis–trans mixture in solution. The changes in relative intensities from solvent to solvent suggest that the 1947- and 1888-cm^{-1} bands may be assigned to the ν_{sym} and ν_{asym} modes of the cis isomer, and the 1932 (m) and 1875 (s) cm^{-1} bands may be assigned to the trans isomer. The relative intensities of the ν(CO) bands of this latter isomer allow it to be assigned a trans structure.[28] The cis/trans ratio in a particular solvent is established immediately upon dissolving the compound and does not change with time.

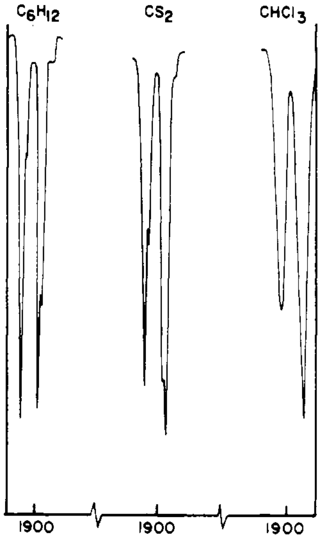

Figure 1. Carbonyl absorptions of $CpW(CO)_2(CNMe)SnPh_3$ in various solvents.

Proton NMR spectra of the $CpW(CO)_2(CNMe)MPh_3$ complexes (Table II) in $CDCl_3$ show two sharp Cp resonances and two methyl absorptions. Since the IR spectra indicated that the trans isomer predominates in $CHCl_3$, the more intense peaks were assigned to that isomer. Thus, the higher field Cp resonance and the lower field Me resonance are ascribed to the trans isomer; the same relative positions of the Cp and Me resonances were found in the cis and trans isomers of $CpMo(CO)_2(CNMe)SnMe_3$ and $CpMo(CO)_2(CNMe)PbPh_3$.[27] The singlet at −219.5 ppm observed for the CO groups in the ^{13}C NMR spectrum of $CpW(CO)_2(CNMe)PbPh_3$ in CD_2Cl_2 further supports the conclusion that the trans isomer is favored in polar solvents.

Experimental Section

All reactions were performed under prepurified N_2. Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$ under N_2 immediately before use. Acetone was stored over $CaSO_4$, and other commercial, reagent grade solvents were stored over type 4A molecular sieves; all these solvents were purged with N_2 and maintained under an N_2 atmosphere. All thiocarbonyl complexes[2,29] and potassium hydrotris(1-pyrazolyl)borate[12] were prepared as reported in the literature. Cyclopentadiene was distilled twice under N_2 just before use. Triphenylphosphine was recrystallized from diethyl ether, and chloro-2,4-dinitrobenzene was recrystallized from ethanol. The lithium reagents *p*-lithio-*N*,*N*-dimethylaniline[30] and (pentafluorophenyl)lithium[31,32] were prepared by reacting *n*-butyllithium with ether solutions of the corresponding aryl halides at −78 °C; all lithium reagents were transferred to reaction vessels by syringe. Solutions of $AgBF_4$ in THF were maintained at 0 °C under N_2. All other reagents were commercial products of the highest purity available and were used as received.

Infrared spectra were recorded with a Perkin-Elmer 237B or 337 grating spectrophotometer, and the band positions were determined

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(18) Beak, P.; Worley, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 4142.
(19) Beak, P.; Worley, J. W. *J. Am. Chem. Soc.* **1972**, *94*, 597.
(20) Ohno, A.; Nakamura, K.; Uohama, M.; Oka, S.; Yamabe, T.; Nagata, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3718.
(21) Ohno, A.; Nakamura, K.; Schizume, Y.; Oka, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1003.
(22) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328.
(23) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.
(24) Wong, A.; Harris, M.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 4529.
(25) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7516. Dombek, B. D.; Angelici, R. J. *Inorg. Chem.* **1976**, *15*, 2403.
(26) Quick, M. H.; Angelici, R. J. *J. Organomet. Chem.* **1978**, *160*, 231. Busetto, L.; Palazzi, A. *Inorg. Chim. Acta* **1976**, *19*, 233. Faraone, F.; Piraino, P.; Marsala, V.; Sergi, S. *J. Chem. Soc., Dalton Trans.* **1977**, 859.
(27) Adams, R. D. *Inorg. Chem.* **1976**, *15*, 169.
(28) Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 2672 and references therein.
(29) Dombek, B. D.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 183.
(30) Cook, J. D.; Wakefield, B. J. *J. Chem. Soc. C* **1969**, 2376.
(31) Coe, P. L.; Tatlow, J. C. *J. Chem. Soc.* **1962**, 3227.
(32) Schmeisser, M.; Wessel, N.; Weidenbruch, M. *Chem. Ber.* **1968**, *101*, 1897.

on an expanded-scale recorder with a CO (carbonyl region) or polystyrene (CS region) reference. Proton NMR spectra were recorded with Varian A-60 and Varian HA-100 spectrometers. All ^{13}C NMR spectra were measured with a Bruker HX-90 spectrometer operating in the Fourier transform mode at 22.64 MHz; $\mathrm{Cr(acac)_3}$ (~0.1 M) was added to each sample to reduce the data collection time.[33] Tetramethylsilane ($\mathrm{Me_4Si}$) was the standard of reference for all NMR spectra; chemical shifts are reported in δ downfield from $\mathrm{Me_4Si}$.

CpW(CO)(CS)NO. Glacial acetic acid (0.02 mL) was added to a solution of $\mathrm{Bu_4N[CpW(CO)_2CS]}$ (1.0 mmol, method 2 in ref 2) in THF, followed by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, 0.22 g, 1.0 mmol) and then more glacial acetic acid (0.10 mL). The solution was heated to 40 °C for 2 h; it was then cooled to 0 °C, filtered through Celite, and evaporated under reduced pressure. The residue was dissolved in 5 mL of $\mathrm{CH_2Cl_2}$ and chromatographed on a Florisil column (2 × 40 cm) with $\mathrm{CH_2Cl_2}$. The green-brown solution that eluted was evaporated under reduced pressure; the residue was extracted with 10 mL of $\mathrm{CS_2}$, and the solution was chromatographed on a silica gel column (2.5 × 65 cm). Elution with $\mathrm{CS_2}$ gave three bands: green (CpW(CO)(CS)NO), yellow ($\mathrm{CpW(CO)_2NO}$), and pink (unidentified). The green band was collected, and the eluate was evaporated slowly under reduced pressure to give a solid. Recrystallization from $\mathrm{CH_2Cl_2}$ with hexane at -20 °C gave olive needles of CpW(CO)(CS)NO, yield 0.20 g (0.57 mmol, 57%). Anal. Calcd for $\mathrm{C_7H_5NO_2SW}$: C, 23.94; H, 1.43. Found: C, 23.81; H 1.50. The parent ion in the mass spectrum was at *m/e* 350.

HB(pz)$_3$W(CO)(CS)NO. An acetone solution of $\mathrm{Bu_4N[HB(pz)_3W(CO)_2CS]}$ (1.0 mmol), prepared as described previously,[2] was evaporated under reduced pressure, and the residue was dissolved in 20 mL of $\mathrm{CH_2Cl_2}$. Solid $\mathrm{NOPF_6}$ (0.17 g 1.0 mmol) was added, and the solution was stirred until gas evolution ceased (~6 h). The reaction mixture was then evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of $\mathrm{CS_2}$ and eluted on a silica gel column (2.5 × 60 cm) with the same solvent. Two bands, green and yellow, developed but never completely separated. The green solution was collected and evaporated to dryness. Crystallization from $\mathrm{CH_2Cl_2}$ with hexane at -20 °C gave green crystals of $\mathrm{HB(pz)_3W(CO)(CS)NO}$ (0.24 g, 49%). The thiocarbonyl complex was always contaminated with some $\mathrm{HB(pz)_3W(CO)_2NO}$; neither recrystallization nor repeated chromatography separated the two completely. Anal. Calcd for $\mathrm{C_{11}H_{10}BN_7O_2SW}$: C, 26.47; H, 2.02; N, 19.64. Found: C, 29.73; H, 3.00; N, 17.97. The parent ion in the mass spectrum was at *m/e* 499. ^{13}C NMR ($\mathrm{CDCl_3}$): -106.0, -135.8, -143.9 (pz).

CpW(CO)$_2$CS–DNP. Addition of chloro-2,4-dinitrobenzene (0.20 g, 1.0 mmol) to a solution of $\mathrm{Bu_4N[CpW(CO)_2CS]}$ (1.0 mmol, method 1 in ref 2) in 50 mL of THF at 0 °C produced a red solution that continued to darken until it was black. After 15 min the solution was filtered through Celite. Evaporation of the filtrate under reduced pressure gave a black residue that was extracted with 50-mL portions of $\mathrm{Et_2O}$ until the extract was colorless. The ether extracts were combined and evaporated to a dark red solid. The solid was dissolved in a minimum of $\mathrm{CH_2Cl_2}$ and eluted through a Florisil column (2 × 40 cm) with the same solvent. A purple band eluted first (*trans*-$\mathrm{CpW(CO)_2(CS)Cl}$) followed by a deep red band ($\mathrm{CpW(CO)_2CS}$–DNP). The red band was collected, and any red material remaining on the column was eluted with $\mathrm{Et_2O}$. The red eluates were combined and evaporated to a solid. Orange crystals of $\mathrm{CpW(CO)_2CS}$–DNP were obtained by recrystallizing the solid from $\mathrm{CH_2Cl_2}$ with hexane at -20 °C (0.20 g, 40%). Anal. Calcd for $\mathrm{C_{14}H_8N_2O_6SW}$: C, 32.57; H, 1.56. Found: C, 32.40; H, 1.49. ^{13}C NMR ($\mathrm{CDCl_3}$): -121.2, -127.1, -128.2, -138.5 (DNP). The carbon atoms attached to the $\mathrm{NO_2}$ groups were not observed.

HB(pz)$_3$W(CO)$_2$CS–Me. Iodomethane (0.14 g, 1.0 mmol) was added to an acetone solution of $\mathrm{Bu_4N[HB(pz)_3W(CO)_2CS]}$ (1.0 mmol).[2] After 30 min, the solution was evaporated to dryness under reduced pressure, and the residue was dissolved in a minimum amount of $\mathrm{CH_2Cl_2}$. This solution was eluted from a 2 × 40 cm column of Florisil with $\mathrm{CH_2Cl_2}$, and the single orange band was collected. The eluate was concentrated, diluted with hexane, and cooled to -20 °C. Orange crystals of $\mathrm{HB(pz)_3W(CO)_2CS}$–Me resulted (0.41 g, 80%). Anal. Calcd for $\mathrm{C_{13}H_{13}BN_6O_2SW}$: C, 30.42; H, 2.73; N, 16.48. Found: C, 30.14; H, 2.61; N, 16.66. ^{1}H NMR ($\mathrm{CS_2}$): 6.17 t, 7.55 m, br, 7.75 m, br (pz). ^{13}C NMR ($\mathrm{CDCl_3}$): -17.4 (S–$\mathrm{CH_3}$); -105.7, -144.9, -135.2 (pz). The parent ion in the mass spectrum was *m/e* 509.

HB(pz)$_3$W(CO)$_2$CS–Et. In a procedure similar to the one above, $\mathrm{Bu_4N[HB(pz)_3W(CO)_2CS]}$ (1.0 mmol) was reacted with EtI (0.16 g, 1.0 mmol). The reaction required heating the solution to 40 °C for 30 min. The product was chromatographed on a silica gel column (2 × 40 cm) in $\mathrm{CS_2}$. The orange solid (0.28 g, 54%) was recrystallized from hexane at -20 °C. Anal. Calcd. for $\mathrm{C_{14}H_{15}BN_6O_2SW}$: C, 31.96; H, 2.87; N, 15.97. Found: C, 31.89; H, 1.20; N, 15.69. ^{1}H NMR ($\mathrm{CDCl_3}$): 6.12 t, 7.50 d, 7.54 m (pz).

HB(pz)$_3$W(CO)$_2$CS–DNP. To a solution of $\mathrm{Bu_4N[HB(pz)_3W(CO)_2CS]}$ (1.0 mmol)[2] at room temperature was added chloro-2,4-dinitrobenzene (0.21 g, 1.0 mmol). After being stirred for 1 h, the solution was filtered through Celite and evaporated to dryness under reduced pressure. The product was eluted through a 2 × 40 cm column of Florisil in $\mathrm{CH_2Cl_2}$ with the same solvent; any red material remaining on the column was eluted with $\mathrm{Et_2O}$. The red solutions were combined and evaporated to a dark powder; deep orange crystals of $\mathrm{HB(pz)_3W(CO)_2CS}$–DNP (0.41 g, 62%) were obtained from a 3:1 mixture of $\mathrm{CHCl_3}$ and hexane at -20 °C. Anal. Calcd for $\mathrm{C_{18}H_{13}BN_8O_6SW}$: C, 32.55; H, 1.97; N, 16.87. Found: C, 32.89; H, 2.00; N, 16.41. ^{1}H NMR ($\mathrm{CDCl_3}$) at -60 °C: 6.22 s, 6.38 s, 7.71 d, 7.78 d, 8.02 d (pz).

CpW(CO)(PPh$_3$)CS–Ph. When PhLi (0.25 mL of a 2 M solution) was added to $\mathrm{CpW(CO)(PPh_3)(CS)I}$ (0.35 g, 0.5 mmol)[2] in 40 mL of THF at 0 °C, the red solution faded to yellow. Isopropyl alcohol (0.10 mL) was added to destroy any remaining PhLi. After the solution was warmed to room temperature, the solvent was evaporated under reduced pressure. The residue was extracted with 15 mL of benzene and filtered through a fritted-glass funnel. Then the volume was reduced to 5 mL, and the solution was eluted on a 2 × 40 cm column of Grade II Woelm alumina with benzene. Three bands developed: yellow (product), red (starting material), and another yellow (unidentified, remained on column). The first band off the column was collected, and evaporation was carried out under reduced pressure. The orange residue was dissolved in a 2:1 pentane/$\mathrm{CS_2}$ mixture, and then the solution was diluted to 4:1 pentane/$\mathrm{CS_2}$. Cooling to -20 °C afforded orange needles of $\mathrm{CpW(CO)(PPh_3)CS}$–Ph (0.14 g, 43%). Anal. Calcd for $\mathrm{C_{31}H_{25}OPSW}$: C, 56.37; H, 3.82. Found: C, 56.19; H, 3.76.

Reaction of *trans*-HB(pz)$_3$W(CO)$_2$(CS)I with MeLi. A solution of *trans*-$\mathrm{HB(pz)_3W(CO)_2(CS)I}$ (0.31 g, 0.5 mmol) in 30 mL of THF was cooled to -78 °C, and MeLi (0.5 mL of a 1.0 M solution) was added by syringe. After the solution warmed to room temperature, 0.10 mL of *i*-PrOH was added. The solvent was evaporated under reduced pressure, and the residue was eluted on a Florisil column (2 × 40 cm) with $\mathrm{CH_2Cl_2}$. The single orange band was eluted, and the solution was diluted with hexane and slowly evaporated to give $\mathrm{HB(pz)_3W(CO)_2CS}$–Me (0.21 g, 83%). An analytical sample was obtained from $\mathrm{CH_2Cl_2}$ with hexane at -20 °C. Anal. Calcd for $\mathrm{C_{13}H_{13}BN_6O_2SW}$: C, 30.42; H, 2.73; N, 16.58. Found: C, 30.54, H, 2.66, N, 16.26. ^{1}H NMR ($\mathrm{CDCl_3}$): 6.17 t, 7.55 m, 7.75 m (pz).

CpW(CO)(CNMe)NO. A slow steam of $\mathrm{MeNH_2}$ was bubbled through a solution of CpW(CO)(CS)NO (0.19 g, 0.53 mmol) in 10 mL of THF for 20 min. The mixture was evaporated under reduced pressure, and the residue was eluted on a column of Grade III Woelm alumina (2 × 40 cm) with $\mathrm{CH_2Cl_2}$. The orange eluate was evaporated to a powder, and crystallization from $\mathrm{CH_2Cl_2}$ with hexane at -20 °C gave orange needles of CpW(CO)(CNMe)NO (0.11 g, 60%). Anal. Calcd for $\mathrm{C_8H_8N_2O_2W}$: C, 27.61; H, 2.32. Found: C, 27.52; H, 2.32. The parent ion in the mass spectrum was at *m/e* 348.

The same procedure with $\mathrm{HB(pz)_3W(CO)(CS)NO}$ rapidly produced $\mathrm{HB(pz)_3W(CO)(CNMe)NO}$ in nearly quantitative yield. Anal. Calcd for $\mathrm{C_{12}H_{13}BN_8O_2W}$: 29.06; H, 2.65. Found: C, 29.17; H, 2.47. ^{1}H NMR ($\mathrm{CDCl_3}$): 6.25 m, 7.70 m, 7.95 m (pz).

CpW(CO)$_2$(CNMe)MPh$_3$ (M = Sn and Pb). A sample of *cis*-$\mathrm{CpW(CO)_2(CS)SnPh_3}$ (0.24 g, 0.33 mmol) was placed in a 20-mL heavy-walled Pyrex tube with a magnetic stirring bar. The tube was tightly capped with a self-sealing rubber-lined cap, evacuated, and filled with $\mathrm{N_2}$. Tetrahydrofuran (10 mL) was injected from a syringe. After a mercury bubbler was connected to the tube by syringe, $\mathrm{MeNH_2}$ was introduced into the tube and allowed to bubble through the solution for 15 min. Then the bubbler was disconnected, and the reaction vessel was pressurized to ~2 atm with $\mathrm{MeNH_2}$. The solution was stirred

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(33) Gansow, O. A.; Burke, A. R.; LaMar, G. N. *J. Chem. Soc., Chem. Commun.* **1972**, 456.

for 20 h at 50 °C; afterward, it was cooled to room temperature and evaporated under reduced pressure. The residue was extracted with 5 mL of benzene, and the solution was eluted on a column of Grade III Woelm alumina (2 × 40 cm) with benzene. The eluate was collected in 50-mL portions; all portions showing a CN stretch in the IR spectrum were combined. Evaporation to a white powder and crystallization from CH_2Cl_2 with hexane at −20 °C gave colorless crystals of $CpW(CO)_2(CNMe)SnPh_3$ (0.14 g, 63%). Anal. Calcd for $C_{27}H_{23}NO_2SnW$: C, 46.59; H, 3.34. Found: C, 46.74; H, 3.50.

Repeating this procedure with *cis*-$CpW(CO)_2(CS)PbPh_3$ (0.27 g, 0.34 mmol) gave yellow needles of $CpW(CO)_2(CNMe)PbPh_3$ (0.08 g, 30%). Anal. Calcd for $C_{27}H_{23}NO_2PbW$: C, 41.33; H, 2.96. Found: C, 41.50; H, 3.04.

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Registry No. $CpW(CO)(CS)NO$, 77827-50-0; $HB(pz)_3W(CO)(CS)NO$, 77846-73-2; $CpW(CO)_2CS–DNP$, 77827-51-1; $CpW(CO)(PPh_3)CS–Ph$, 72303-52-7; $HB(pz)_3W(CO)_2CS–Me$, 77827-54-4; $HB(pz)_3W(CO)_2CS–Et$, 77846-72-1; $HB(pz)_3W(CO)_2CS–DNP$, 77827-55-5; $CpW(CO)(CNMe)NO$, 77827-52-2; $HB(pz)_3W(CO)(CNMe)NO$, 77827-53-3; *cis*-$CpW(CO)_2(CNMe)SnPh_3$, 77881-61-9; *trans*-$CpW(CO)_2(CNMe)SnPh_3$, 77827-56-6; *cis*-$CpW(CO)_2(CNMe)PbPh_3$, 77827-57-7; *trans*-$CpW(CO)_2(CNMe)PbPh_3$, 77880-85-4; $Bu_4N[CpW(CO)_2CS]$, 74989-73-4; $Bu_4N[HB(pz)_3W(CO)_2CS]$, 75008-92-3; $CpW(CO)(PPh_3)(CS)I$, 72303-51-6; *trans*-$HB(pz)_3W(CO)_2(CS)I$, 77827-58-8; *cis*-$CpW(CO)_2(CS)SnPh_3$, 77880-86-5; *cis*-$CpW(CO)_2(CS)PbPh_3$, 74989-75-6; *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 80-11-5; $NOPF_6$, 16921-91-8; DNP–Cl, 97-00-7; MeI, 74-88-4; EtI, 75-03-6; PhLi, 591-51-5; MeLi, 917-54-4; $MeNH_2$, 74-89-5.

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Reactions of (η^5-Cyclopentadienyl)cobalt(III) Alkyls with Cobalt(I) Phosphines and Iron Carbonyls. Evidence for Direct η^5-Cyclopentadienyl and Trimethylphosphine Group Transfer between Metal Centers

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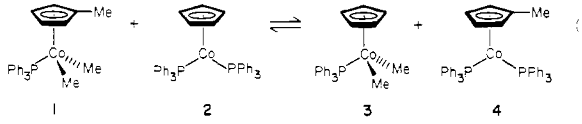
We have found that (η^5-methylcyclopentadienyl)(triphenylphosphine)dimethylcobalt(III) (**1**) undergoes intermolecular cyclopentadienyl ligand exchange with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt(I) (**2**). The unsubstituted cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (**3**) reacts in two different types of processes, with both $Fe_2(CO)_9$ and $Fe(CO)_5$. The first involves electrophilic displacement of coordinated phosphine by unsaturated $Fe(CO)_4$, and the second takes place by abstraction of CO from $Fe(CO)_5$ by the unsaturated $CpCoMe_2$ fragment (generated by phosphine dissociation from the saturated starting material).

Introduction

Alkyl groups are easily transferred between many types of metal centers, apparently by a number of different mechanisms. The best understood of these processes are those in which a metal alkyl interacts with a second metal in a higher oxidation state and are usually thought of as involving electrophilic attack of the high-oxidation-state center upon the metal–carbon bond.[1]

A number of formally symmetrical alkyl-transfer reactions have also been uncovered recently. In the majority of these, alkyl transfer is assisted by transfer of halogen or another electronegative group in the opposite direction,[2] but cooperative transfer of two alkyl groups (as well as examples of stable dialkyls in which the alkyl groups bridge two metal centers) is now known.[3,4]

Transfer of an alkyl group from a metal center to a second center in a *lower* oxidation state (i.e., attack at metal-bound carbon by a second, nucleophilic, metal center) is less common.[5] During a recent study of pairwise exchange of methyl groups between the Co(III) centers in $CpCoLR_2$ complexes,[4] we considered the possibility that traces of a cobalt(I) complex, $CpCo(PPh_3)_2$, might contribute to the alkyl-transfer reactivity of the system. We have now examined that possibility directly and have found reactions such as that shown in eq 1 occur with relative ease. However, the mechanism surprisingly involves *cyclopentadienyl* rather than alkyl transfer. We report here the details of this study, as well as some observations on reactions of cobalt(III) dimethyl complexes with several other low-valent metal complexes.



(1)

Results and Discussion

Reaction of $MeCpCo(PPh_3)Me_2$ (1) with $CpCo(PPh_3)_2$ (2). When a solution of **1** and $CpCo(PPh_3)_2$ (**2**) in THF-d_8 was heated in a sealed NMR tube at 62 °C, new methyl resonances arising from the unsubstituted methyl analogue **3** were observed in the ^1H NMR spectrum; AA′BB′ Cp resonances corresponding to $MeCpCo(PPh_3)_2$ (**4**) were also seen (cf. eq 1). After 48 h the reaction had apparently reached equilibrium, with NMR observations showing a 67:33 ratio of **1** and **3**. The cobalt(III) complexes could be removed from this mixture by chromatography under air-free conditions and recrystallized together from benzene/hexane solvent. Because

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(1) See, for example: (a) Leslie, J. P.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4839. (b) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57 and references cited there. (c) Jawad, J. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1977**, 892.

(2) (a) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1975**, 1811. (b) Puddephatt, R. J.; Thompson, P. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1219. (c) Thompson, P. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1975**, 841.

(3) (a) Jolly, P. W.; Jonas, K.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1970**, *33*, 109. (b) Kruger, C.; Sekutowski, J. C.; Berke, H.; Hoffman, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1110. (c) Holton, J. H.; Lappert, M. F.; Ballard, D. G. H.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45, 54.

(4) Bryndza, H. E.; Bergman, R. G.; Evitt, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 4948.

(5) (a) Dodd, D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1971**, 1371. (b) Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664. (c) Magnuson, R. H.; Halpern, J. H.; Levitin, I. Ya.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1978**, 44.

0020-1669/81/1320-2988$01.25/0