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THIOCARBONYL ANIONS: PREPARATION AND REACTIONS OF $CpW(CO)_2CS^-$ AND $HB(pz)_3W(CO)_2CS^-$ *

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Summary

The anionic thiocarbonyl complexes $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ may be prepared by reaction of *trans*-$IW(CO)_4CS^-$ with NaC_5H_5 or potassium hydrotris(1-pyrazolyl)borate, The nucleophilic $CpW(CO)_2CS^-$ reacts with $ClSnPh_3$, $ClPbPh_3$, HgI_2 and BrSePh to give *cis*-$CpW(CO)_2(CS)SnPh_3$, *cis*-$CpW(CO)_2(CS)PbPh_3$, *cis*- and *trans*-$CpW(CO)_2(CS)HgI$, and *cis*- and *trans*-$CpW(CO)_2(CS)SePh$, respectively. Both $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ react with I_2 to yield the iodo complexes, *trans*-$CpW(CO)_2(CS)I$ and *trans*-$HB(pz)_3W(CO)_2(CS)I$. Refluxing *trans*-$CpW(CO)_2(CS)I$ with PMe_2Ph, PPh_3, $P(OPh)_3$, $P(NMe_2)_3$, or CNMe in toluene results in substitution of CO and yields the complexes CpW(CO)(CS)(L)I in which the CS group is *trans* to the iodide. At lower temperatures *trans*-$CpW(CO)_2(CS)I$ reacts with PMe_2Ph to give the ionic product [*trans*-$CpW(CO)(CS)(PMe_2Ph)_2$]I. Proposed structures for all of the complexes are based upon their IR, ^1H NMR, and ^{13}C NMR spectra.

Introduction

The sulfur atoms in electron-rich tungsten thiocarbonyl complexes such as $W(diphos)_2(CO)(CS)$ and *trans*-$IW(CO)_4CS^-$ act as nucleophiles, or Lewis bases, toward a variety of electrophiles, or Lewis acids [1]. They react to form various sulfur-acid adducts, e.g., eq. 1. The sulfur atoms in complexes that contain

$$IW(CO)_4CS^- + CH_3OSO_2F \rightarrow IW(CO)_4CS{-}CH_3 + SO_3F^- \quad (1)$$

less strongly electron-donating ligands, and thus have CS frequencies above 1200 cm^{-1}, do not react in this fashion [1]. Thiocarbonyl complexes with the electron-donating η^5-cyclopentadienyl, Cp^-, or hydrotris(1-pyrazolyl)borate,

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* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday on May 30, 1980.
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$HB(pz)_3^-$, ligands would be expected to have an especially nucleophilic sulfur. However, these ligands would also increase the nucleophilicity of the metal atoms, which could lead to reactions at the metal.

In this paper, we report the preparations of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ and their reactions with electrophiles which add to the metal. Their chemistries are compared and contrasted with those of the well-known carbonyl analogs, $CpW(CO)_3^-$ and $HB(pz)_3W(CO)_3^-$.

Results and discussion

A. Preparation of $Bu_4N[CpW(CO)_2CS]$ *and* $Bu_4N[HB(pz)_3W(CO)_2CS]$

Addition of $Na[C_5H_5]$ to a cold, anhydrous solution of $Bu_4N[IW(CO)_4CS]$ [2,3] in THF followed by heating to 60°C gives $Bu_4N[CpW(CO)_2CS]$. If the presence of I^- interferes with any subsequent reactions, the solution of $Bu_4N[IW(CO)_4CS]$ is treated with $AgBF_4$ and filtered before the $Na[C_5H_5]$ is added. After the reaction is complete, any remaining $Na[C_5H_5]$ is protonated with isopropyl alcohol.

The formation of $Bu_4N[CpW(CO)_2CS]$ from $Na[C_5H_5]$ and $Bu_4N[IW(CO)_4CS]$ probably occurs by replacement of the iodide ligand by cyclopentadienide, forming a η^1-C_5H_5 ligand, which subsequently displaces two CO ligands (eq. 2).

$$IW(CO)_4CS^- + C_5H_5^- \xrightarrow{THF} I^- + (\eta^1\text{-}C_5H_5)\,W(CO)_4CS^- \xrightarrow{\Delta} CpW(CO)_2CS^- + 2\,CO \qquad (2)$$

The infrared spectrum of $Bu_4N[CpW(CO)_2CS]$ (Table 1) in CH_2Cl_2 shows two terminal ν(CO) bands at 1890 and 1804 cm^{-1}. These absorptions occur in the same region as the CO band of $W(CO)(CS)(diphos)_2$, 1838 cm^{-1} [2], and

TABLE 1

IR STRETCHING FREQUENCIES OF VARIOUS TUNGSTEN THIOCARBONYL COMPLEXES [a]

Compound	Solvent	$\nu(CO)(cm^{-1})$	$\nu(CS)(cm^{-1})$
$W(CO)_5CS$ [b]	hexane	2096w, 2007m, 1989vs	1258 [c]
$Bu_4N[CpW(CO)_2CS]$	CH_2Cl_2	1890s, 1804s	unrecorded
$Bu_4N[HB(pz)_3W(CO)_2CS]$	CH_2Cl_2	1884s, 1787s	1149
cis-$CpW(CO)_2(CS)SnPh_3$	CS_2	1988s, 1924m	1238s
cis-$CpW(CO)_2(CS)PbPh_3$	CS_2	1985s, 1926m	1237s
$[CpW(CO)_2CS]_2Hg$	CS_2	1980(sh), 1975s, 1920m, 1900(sh)	1198m(br)
cis-/trans-$CpW(CO)_2(CS)HgI$	CS_2	1990s, 1945s	1268m, 1234s
cis-/trans-$CpW(CO)_2(CS)SePh$	CS_2	2008(sh), 2000m, 1958s	1262s
trans-$CpW(CO)_2(CS)I$	CS_2	2025m, 1972s	1267s
trans-$HB(pz)_3W(CO)_2(CS)I$	CS_2	2017m, 1961s	1243s
$CpW(CO)(CS)(PPh_3)I$	CS_2	1964s	1225s
$CpW(CO)(CS)(P[OPh]_3)I$	CS_2	1974s	1240s
$CpW(CO)(CS)(P[NMe_2]_3)I$	CS_2	1958s	1221s
$CpW(CO)(CS)(CNMe)I$	CS_2	1969s	1241s
$CpW(CO)(CS)(PMe_2Ph)I$	CS_2	1967s	1220s
trans-$[CpW(CO)(CS)(PMe_2Ph)_2]PF_6$	CH_3CN	1932s	1234s

[a] Abbreviations: s = strong, m = medium, w = weak, sh = shoulder, br = broad, v = very. [b] See ref. 2. [c] Recorded in CS_2.

indicate a relatively high electron density at the CS group. The CS absorption is obscured by the solvent.

The pyrazolylborate thiocarbonyl anion, $HB(pz)_3W(CO)_2CS^-$, can be prepared in a manner similar to that of $[CpW(CO)_2CS]^-$. An acetone solution of $Bu_4N[IW(CO)_4CS]$ which has been treated with $AgBF_4$ is refluxed with one equivalent of $K[HB(pz)_3]$ until the IR spectrum (Table 1) of the sample shows that $HB(pz)_3W(CO)_2CS^-$ is the only complex present. The ν(CO) absorptions of the pyrazolylborate anion are slightly lower in energy than those of $CpW(CO)_2CS^-$ (Table 1); this is consistent with the stronger electron donor properties of the pyrazolylborate ligand [4,5]. The ν(CS) absorption of $HB(pz)_3W(CO)_2CS^-$ occurs at 1149 cm^{-1}.

Both thiocarbonyl anions dissolve in most polar organic solvents but are insoluble in water. Solutions of these complexes may be handled in the air for short periods; however, prolonged contact with air results in decomposition. Because attempts to precipitate the anions as the Et_4N^+ or PPN^+ salts resulted in oils, their subsequent reactions were performed in situ.

B. Preparation of $CpW(CO)_2(CS)MPh_3$ where M = Sn or Pb

A common reaction of $CpW(CO)_3^-$ is nucleophilic displacement of a halide ion from electrophiles yielding products with an additional ligand on the metal [6—8]. Like its carbonyl analog, $[CpW(CO)_2(CS)]^-$ displaces halide from Ph_3MX (M = Sn and Pb) to produce metal—metal bonded derivatives, *cis*-$CpW(CO)_2(CS)MPh_3$ (eq. 3). For the carbonyl complexes, the germanium and tin derivatives are reportedly more stable than the lead compound; but for the thiocarbonyl analogues, the lead derivative appears more air stable than the tin.

$$[CpW(CO)_2CS]^- + Ph_3MCl \xrightarrow{THF} cis\text{-}CpW(CO)_2(CS)\,MPh_3 + Cl^- \qquad (3)$$

With the thiocarbonyl ligand present in $CpW(CO)_2CS^-$, addition at the metal could produce either a *cis* isomer, a *trans* isomer, or a mixture of both. The assignment of a *cis* configuration to the $CpW(CO)_2(CS)MPh_3$ complexes was based on the relative intensities of the two carbonyl infrared stretching bands, ν_{sym} and ν_{as}, because these intensities are directly related to the angle between the carbonyl ligands [9—12]. The ^{13}C NMR spectra (Table 2) of the complexes show two ^{13}CO resonances, which establishes the *cis* geometry.

The ν(CS) absorption in the IR spectrum of these complexes occurs at about 1238 cm^{-1}. Further results from this investigation suggest that a thiocarbonyl absorption near 1235 cm^{-1} is characteristic of *cis*-thiocarbonyl complexes of this type, whereas an absorption about 1265 cm^{-1} indicates a *trans* geometry. The higher frequency of the CS absorption in *trans*-complexes is unexpected and is the reverse of what is commonly found in carbonyl systems. A possible explanation would involve consideration of π-bonding from the CS π-bonding orbitals to the W. If this bonding were more important than the familiar π-bonding from W to the π^* orbitals of CS, the ν(CS) frequency of a CS *trans* to I^- would be expected to be higher than that *cis* to I^-. This explanation was proposed previously to account for infrared data for octahedral *cis*- and *trans*-$W(CO)_4(L)(CS)$ complexes [13].

C. Preparation of $CpW(CO)_2(CS)HgI$ and $[CpW(CO)_2CS]_2Hg$

Mercuric halides react with complexes containing terminal and bridged thio-

TABLE 2

^{13}C NMR CHEMICAL SHIFTS OF Cp, CO, AND CS LIGANDS FOR VARIOUS TUNGSTEN THIOCARBONYL COMPLEXES IN $CDCl_3$ SOLUTION [a]

Compounds	δCp (ppm)	δCO (ppm)	δCS (ppm)
$W(CO)_5CS$ [b]	—	−192.4(*cis*), −189.3(*trans*)	−298.7
cis-$CpW(CO)_2(CS)SnPh_3$	−89.0(s)	−201.3(s), −199.9(s)	−283.3(s)
cis-$CpW(CO)_2(CS)PbPh_3$ [c]	−88.8(s)	−215.3(s), −218.0(s)	−311.7(s)
trans-$CpW(CO)_2(CS)I$	−93.5(s)	−195.0(s)	−310.5(s)
trans-$HB(pz)_3W(CO)_2(CS)I$	—	−224.0(s)	−300.0(s)
$CpW(CO)(CS)(PPh_3)I$	−94.6(s)	−224.5(d) [d]	−353.1(d) [d]
$CpW(CO)(CS)(P[OPh]_3)I$	−94.1(s)	−218.9(d) [e]	−348.4(d) [e]
$CpW(CO)(CS)(P[NMe_2]_3)I$	−94.7(s)	−227.3(d) [f]	−355.9(d) [f]
$CpW(CO)(CS)(CNMe)I$	−93.9(s)	−222.9(s)	−353.6(s)
$CpW(CO)(CS)(PMe_2Ph)I$	−93.8(s)	−224.1(d) [g]	−352.8(d) [g]
trans-$[CpW(CO)(CS)(PMe_2Ph)_2]PF_6$ [h]	−95.5(d) [i]	−229.8(t) [i]	−338.1(t) [i]

[a] Abbreviations: s = singlet, d = doublet, t = triplet. [b] See ref. 2. [c] Recorded in CD_2Cl_2 solution. [d] *J*(P—CO) 10.0 Hz; *J*(P—CS) 23.8 Hz. [e] *J*(P—CO) 10.4 Hz; *J*(P—CS) 37.2 Hz. [f] *J*(P—CO) 10.4 Hz; *J*(P—CS) 29.8 Hz. [g] *J*(P—CO) 10.0 Hz; *J*(P—CS) 24.0 Hz. [h] Recorded in CD_3CN solution. [i] *J*(P—Cp) 28.0 Hz; *J*(P—CO) 21.0 Hz; *J*(P—CS) 21.0 Hz.

carbonyl ligands to form mercuric halide adducts, e.g. $(diphos)_2W(CO)(CS\text{-}HgX_2)$ [1,14,15]. In contrast, addition of HgI_2 to two equivalents of Bu_4N-$[CpW(CO)_2CS]$ in THF gives an orange substance which has been tentatively identified as $[CpW(CO)_2CS]_2Hg$ by its IR and ^{1}H NMR spectra (Tables 1 and 3). Unfortunately this compound was not soluble enough in common organic solvents to obtain a ^{13}C NMR spectrum, and it was not sufficiently stable in solution to crystallize an analytical sample. When excess HgI_2 is added to Bu_4N-$[CpW(CO)_2CS]$, an IR spectrum of the solution shows that $[CpW(CO)_2CS]_2Hg$ is formed as above. However, elution of the reaction mixture on a Florisil column with CH_2Cl_2 gives a different orange product, identified by its spectra (Tables 1 and 3) and elemental analyses as $CpW(CO)_2(CS)HgI$. From the above observations, the reaction scheme shown in eq. 4 is postulated.

$$2\ CpW(CO)_2CS^- + HgI_2 \rightarrow [CpW(CO)_2CS]_2Hg + 2\ I^- \xrightarrow[\text{Florisil}]{HgI_2} 2\ \textit{cis-/trans-}CpW(CO)_2(CS)\ HgI + 2\ I^- \tag{4}$$

Obviously, the elution of the reaction mixture is crucial to the formation of $CpW(CO)_2(CS)HgI$, but its function remains obscure because addition of Florisil to the reaction mixture causes no change. This behavior of the thiocarbonyl mercury compound is the reverse of the behavior exhibited by its carbonyl analogs. In solution, $[CpW(CO)_3]_2Hg$ reacts rapidly with excess HgX_2 to produce two equivalents of $CpW(CO)_3HgX$; and when a solution of $CpMo(CO)_3$-HgX is passed through an alumina column, $[CpMo(CO)_3]_2Hg$ is eluted and HgX_2 is left behind [16]. The reason for this difference is not evident.

The $CpW(CO)_2(CS)HgI$ derivative is a crystalline solid that is air stable indefinitely at room temperature; in solution it is susceptible to air oxidation and thermal decomposition. The spectral evidence (Tables 1 and 3) suggests that $CpW(CO)_2(CS)HgI$ exists in solution as a mixture of *cis* and *trans* isomers with identical CO absorption frequencies but different ν(CS) values.

TABLE 3

^{1}H NMR CHEMICAL SHIFTS OF VARIOUS CYCLOPENTADIENYL TUNGSTEN THIOCARBONYL COMPOUNDS IN $CDCl_3$ SOLUTION [a]

Compounds	δCp (ppm)	δR (ppm)
cis-$CpW(CO)_2(CS)SnPh_3$	5.31(s)	7.25(m, Ph)
cis-$CpW(CO)_2(CS)PbPh_3$	5.47(s)	7.44(m, Ph)
$[CpW(CO)_2CS]_2Hg$	5.83	—
cis-/trans-$CpW(CO)_2(CS)HgI$	5.76(s)	—
cis-/trans-$CpW(CO)_2(CS)SePh$	5.67(s) [b], 5.73(s) [c]	7.18(m, Ph), 7.48(m, Ph)
trans-$CpW(CO)_2(CS)I$	5.84(s)	—
trans-$HB(pz)_3W(CO)_2(CS)I$	—	6.23(t, pz) [d], 7.61(d, pz) [e], 8.45(d, pz) [f]
$CpW(CO)(CS)(PPh_3)I$	5.62(s)	7.52(m, Ph)
$CpW(CO)(CS)(P[OPh]_3)I$	5.30(s)	7.42(m, Ph)
$CpW(CO)(CS)(P[NMe_2]_3)I$	5.60(s)	2.68(d, Me) [g]
$CpW(CO)(CS)(CNMe)I$	5.74(s)	3.95(s, Me)
$CpW(CO)(CS)(PMe_2Ph)I$	5.52(s)	2.21(d, Me) [h], 7.55(m, Ph)
trans-$[CpW(CO)(CS)(PMe_2Ph)_2]PF_6$ [i]	5.40(t) [j]	2.18(dd, Me) [k], 7.52(m, Ph)

[a] Abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = complex multiplet, br = broad. [b] *cis* isomer. [c] *trans* isomer. [d] J 2 Hz. [e] J 2 Hz. [f] J 2 Hz. [g] $J(P—CH_3)$ 8 Hz. [h] $J(P—CH_3)$ 9.5 Hz. [i] Recorded in CD_3CN solution. [j] $J(P—Cp)$ 3 Hz. [k] $J(P—CH_3)$ 10 Hz, $J'(P—CH_3)$ 3 Hz.

D. Preparation of $CpW(CO)_2(CS)SePh$

Sodium mercaptides, NaSR (R = Me or Ph), react with $CpW(CO)_3Cl$ to produce complexes of the type $CpW(CO)_3SR$ [17]. These compounds evolve CO in solution, forming $[CpW(CO)_2SR]_2$, and they undergo CS_2 insertion, producing $CpW(CO)_2(S_2CSR)$ derivatives. The thiocarbonyl anion acts on PhSeBr to give $CpW(CO)_2(CS)SePh$. This compound readily decomposes in solution to $(PhSe)_2$ and other unidentified products. No reaction between $CpW(CO)_2(CS)SePh$ and CS_2 has been observed either. The relative intensities of the $\nu(CO)$ absorptions at 2000m and 1958s cm^{-1} of $CpW(CO)_2(CS)SePh$ indicate that the complex exists predominantly as the *trans* isomer. However, the presence of a shoulder at 2008 cm^{-1} suggests the presence of a small amount of the *cis* isomer. This is supported by the compound's ^{1}H NMR spectrum (Table 3), which shows a weak Cp resonance 0.06 ppm upfield from the major peak.

E. Preparation of $CpW(CO)_2(CS)I$

The thiocarbonyl anion reacts directly with I_2 to give $CpW(CO)_2(CS)I$ (eq. 5).

$$CpW(CO)_2CS^- + I_2 \xrightarrow{THF} trans\text{-}CpW(CO)_2(CS)I + I^- \qquad (5)$$

This complex has IR, ^{1}H NMR, and ^{13}C NMR spectra consistent with a *trans* configuration (Tables 1—3). Similarly, the addition of I_2 to a solution of $HB(pz)_3W(CO)_2CS^-$ gives *trans*-$HB(pz)_3W(CO)_2(CS)I$, whose spectra (Tables 1—3) are also consistent with this geometry. The lower $\nu(CS)$ frequency of this complex as compared with that of *trans*-$CpW(CO)_2(CS)I$ is attributed to the strong electron donor properties of the pyrazolylborate ligand [4,5]. Both iodide derivatives are air-stable, crystalline complexes.

In an attempt to prepare $CpW(CO)_2(CS)H$, a possible precursor to $[CpW(CO)_2(CS)]_2$, $CpW(CO)_2(CS)I$ was reacted with Ph_3SnH. Unexpectedly, the reaction gives *cis*-$CpW(CO)_2(CS)SnPh_3$ in about 60% yield.

F. *Substitution Reactions of trans-CpW(CO)$_2$(CS)I*

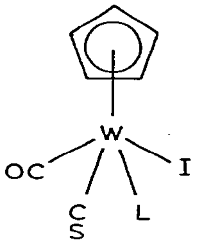
The thiocarbonyl complex *trans*-CpW(CO)$_2$(CS)I undergoes thermal carbonyl substitution by PMe$_2$Ph, P(NMe$_2$)$_3$, P(OPh)$_3$, PPh$_3$, and CNMe to give the monosubstituted complexes CpW(CO)(CS)(L)I (eq. 6). The reactions are slow, and

$$\textit{trans}\text{-CpW(CO)}_2\text{(CS) I} + \text{PR}_3 \xrightarrow[110^\circ\text{C}]{\text{toluene}} \text{CpW(CO)(CS)(PR}_3\text{) I} + \text{CO} \qquad (6)$$

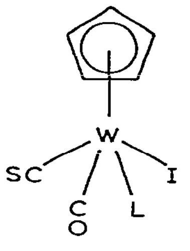
the yields poor, in refluxing THF and CH$_3$CN; in the case of PMe$_2$Ph and CNMe, reaction in these solvents led to a mixture of products. In refluxing toluene, substitution proceeds rapidly and with little decomposition. Dimethylphenylphosphine and methylisocyanide react faster than P(NMe$_2$)$_3$, P(OPh)$_3$, and PPh$_3$.

Carbonyl substitution in CpW(CO)$_3$X has been accomplished with a variety of ligands [9,18—21]. The reaction of CpW(CO)$_3$Cl with PPh$_3$ in benzene requires 20 h to give a 60% yield [18], whereas the iodide complex takes longer than 12 days to react completely with PPh$_3$ in the same solvent [22]. The carbonyl ligands of *trans*-CpW(CO)$_2$(CS)I are much more labile; the reaction with 20% excess PPh$_3$ in refluxing benzene is virtually complete in 3—4 h. This labilizing effect of the CS ligand has been observed in other thiocarbonyl complexes [2,23,24]. Minute quantities of thiocarbonyl-substituted product, CpW(CO)$_2$(L)I, are always isolated from the reaction of *trans*-CpW(CO)$_2$(CS)I with ligands.

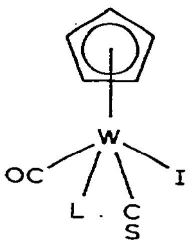
Three different configurations are possible for CpW(CO)(CS)(L)I, as shown below:



(A)



(B)



(C)

The similarity of their spectral data (Tables 1—3) indicate that all of the derivatives have the same configuration in solution. In an effort to establish this geometry, ^{13}C NMR spectra of the complexes were recorded and coupling constants between the ^{31}P atom of the ligand and the ^{13}C of the CO and CS groups were measured. A recent report [25] concludes that in the ^{13}C NMR spectra of *cis*-CpMo(CO)$_2$(PPh$_3$)X compounds, the J(P—C) value for CO *cis* to PPh$_3$ is larger than for CO *trans* to PPh$_3$. In the ^{13}C NMR spectra of the CpW(CO)(CS)(PR$_3$)I complexes, the J(P—C) values for the CS ligand are larger than for the CO ligands (Table 2). Assuming that ^{31}P coupling will be larger to *cis* CO or CS groups as described in the above-cited report [25], the phosphine and phosphite derivatives will have structure A; This conclusion is supported by the coupling constants in *trans*-CpW(CO)(CS)(PMe$_2$Ph)$_2$$^+$. Both the CO ligand and the CS ligand in this complex are *cis* to the PMe$_2$Ph ligands, and both the J(P—CO) value and the J(P—CS) value are 21.0 Hz (Table 2). This value is close to 24.0 Hz, the value of J(P—CS) in CpW(CO)(CS)(PMe_2Ph)I, indicating that the PMe_2-Ph and CS ligands in CpW(CO)(CS)(PMe_2Ph)I are *cis* to each other, and the complex has structure A.

When equal amounts of *trans*-$CpW(CO)_2(CS)I$ and PMe_2Ph are stirred in toluene below 100°C the yield of CpW(CO)(CS)(PMe_2Ph)I is low, some *trans*-CpW-$(CO)_2(CS)I$ remains, and $[CpW(CO)(CS)(PMe_2Ph)_2]I$ precipitates from solution. As the temperature of the reaction is increased the amount of precipitate decreases until, above 105°C, no precipitate forms and CpW(CO)(CS)(PMe_2Ph)I is the major product. Although the mechanisms for formation of these two products are not known, clearly CpW(CO)(CS)(PMe_2Ph)I is favored at high temperature while $[CpW(CO)(CS)(PMe_2Ph)_2]I$ is favored below 100°C. Addition of two equivalents of PMe_2Ph to a solution of *trans*-$CpW(CO)_2(CS)I$ at 100°C gives close to a 90% yield of $[CpW(CO)(CS)(PMe_2Ph)_2]I$, which can be crystallized as the PF_6^- salt. A singlet phosphine resonance at 8.89 ppm upfield from H_3PO_4 in the ^{31}P NMR plus other spectroscopic evidence (Tables 1—3) are consistent with a *trans* configuration for $[CpW(CO)(CS)(PMe_2Ph)_2]PF_6$, the same as observed for $[CpMo(CO)_2(PEt_3)_2]I$ [20].

Others have shown [19] that $CpW(CO)_3Cl$ reacts similarly with PEt_3 to give a mixture of monosubstituted, $CpW(CO)_2(PEt_3)Cl$, and ionic, $[CpW(CO)_2(PEt_3)_2]Cl$, products.

Infrared spectra of reaction solutions containing CNMe and *trans*-$CpW(CO)_2(CS)I$ indicate that this reaction follows the pattern described for the reaction of PMe_2Ph; however, $[CpW(CO)(CS)(CNMe)_2]I$ is an oil, and exchanging the I^- for PF_6^- fails to induce crystallization. The only product isolated from the reaction between *trans*-$CpW(CO)_2(CS)I$ and two equivalents of PPh_3 in refluxing toluene is CpW(CO)(CS)(PPh_3)I, even when $AlCl_3$ or $AgPF_6$ is added to the reaction mixture as in the preparation of *trans*-$[CpW(CO)_2(PPh_3)_2]Cl$ [18].

Experimental

All reactions were performed under prepurified N_2 using standard inert atmosphere techniques; solution transfers were made by syringe. Tetrahydrofuran (THF) was distilled from $NaK_{2.8}$ [26] 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 [27], potassium hydrotris(1-pyrazolyl)borate [28], phenylselenenylbromide [29], phenylsulfenylchloride [30] and methylisocyanide [31] were prepared as reported in the literature. Cyclopentadiene was distilled twice under N_2 just before use. Phosphines and phosphites were fractionally distilled under N_2 or, when appropriate, recrystallized. All other reagents were commercial products of the highest purity available amd were used as received. Solutions of $AgBF_4$ in THF were maintained at 0°C under N_2.

Infrared spectra were recorded with a Perkin-Elmer 237B or 337 grating spectrophotometer, and the peak positions were determined 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; $Cr(acac)_3$ ($\sim$0.1 *M*) was added to each sample to reduce data collection time [32]. Tetramethylsilane (TMS) was the standard of reference for all ^1H and ^{13}C NMR spectra; chemical shifts are reported in δ, ppm downfield from TMS.

$Na[C_5H_5]$. Freshly distilled cyclopentadiene (3.0 ml, 36.0 mmol) was added in 1.0 ml portions to a slurry of crystalline NaH (0.85 g, 35 mmol) in anhydrous THF (67 ml) at 0° C. After the solution had stirred for 2 h, it was slowly warmed to room temperature. When the evolution of hydrogen was finished (usually after 12 h), the reaction vessel was purged with N_2, sealed, and stored at 0° C. Any impurity settled to the bottom, leaving a pale pink solution of $Na[C_5H_5]$. The concentration of the $Na[C_5H_5]$ solution was determined by titration of an accurately weighed sample of $Bu_4N[IW(CO)_4CS]$ in THF at 60° C; the disappearance of the carbonyl stretching band at 1947 cm^{-1} marked the end point (see below). This method of preparing $Na[C_5H_5]$ was less stringent than the published procedure [33].

$Bu_4N[CpW(CO)_2CS]$. Method 1: A solution of $Bu_4N[IW(CO)_4CS]$ (0.71 g, 1.0 mmol) in 50 ml of THF was stirred at 0° C while an equivalent of $Na[C_5H_5]$ (2.0 ml of a 0.50 *M* solution) was added. After stirring for 15 min at 0° C, the solution was heated to 60° C for 2 h. The mixture was then cooled again to 0° C, and a small amount of i-PrOH (0.5 to 1.0 ml) was added to destroy any remaining $Na[C_5H_5]$. Under anhydrous conditions, the IR spectrum showed complete conversion to the η^5-cyclopentadienyl complex. IR(CH_2Cl_2): 1890s and 1804vs cm^{-1}.

Method 2: Silver tetrafluoroborate (0.19 g, 1.0 mmol) in 20 ml of THF was added to a stirring solution of $Bu_4N[IW(CO)_4CS]$ (0.71 g, 1.0 mmol) in 40 ml of THF at 0° C. Silver iodide precipitated, and the reaction vessel was shielded from the light to prevent the formation of Ag^0. After 40 min at 0° C the suspension was filtered. Addition of $Na[C_5H_5]$ (2.0 ml of a 0.5 *M* solution, 1.0 mmol) followed by heating the reaction mixture to 60° C for 2 h, gave a solution of $[CpW(CO)_2CS]^-$. The reaction mixture was cooled to 0° C, and i-PrOH (0.5 ml to 1.0 ml) was added to destroy any residual $Na[C_5H_5]$ before further reaction.

$Bu_4N[HB(pz)_3W(CO)_2CS]$. A solution of $Bu_4N[IW(CO)_4CS]$ (0.71 g, 1.0 mmol) in 40 ml of acetone was stirred at 0° C while $AgBF_4$ (2.0 ml of a 0.5 *M* solution) was added slowly. After stirring an hour, the suspension was filtered. The filtrate was treated with $K[HB(pz)_3]$ (0.25 g, 1.0 mmol) and stirred at reflux until the IR spectrum showed only the CO bands corresponding to $Bu_4N[HB(pz)_3W(CO)_2CS]$. IR(CH_2Cl_2): 1884s and 1787s cm^{-1}. The solution was cooled to 0° C, and usually filtered through Celite, before further reaction.

cis-$CpW(CO)_2(CS)MPh_3$ ($M = Sn$ and Pb). A solution of $Bu_4N[CpW(CO)_2CS]$ (1.0 mmol, method 1) was cooled to 0° C, and Ph_3SnCl (0.39 g, 1.0 mmol) was added. After 10 min the solution was filtered through Celite and evaporated under reduced pressure. The residue was slurried in CH_2Cl_2 and placed on a 2 × 40 cm column of Florisil; elution with CH_2Cl_2 gave a yellow solution. The solution was concentrated to 30 ml, diluted with 30 ml of hexane, and evaporated under reduced pressure to 10 ml. Yellow crystals of *cis*-$CpW(CO)_2(CS)SnPh_3$ were filtered from solution (0.41 g, 61%). An analytical sample was recrystallized from CH_2Cl_2 with hexane at —20° C. (Found: C, 44.13; H, 2.56.

$C_{26}H_{20}O_2SSnW$ calcd.: C, 44.66; H, 2.88%).

The analogous reaction with Ph_3PbCl gave *cis*-$CpW(CO)_2(CS)PbPh_3$ in 51% yield. (Found: C, 39.59; H, 2.52. $C_{26}H_{20}O_2PbSW$ calcd.: C, 39.64; H, 2.56%).

$CpW(CO)_2(CS)HgI$. An excess of HgI_2 (0.60 g, 1.3 mmol) was added to a solution of $Bu_4N[CpW(CO)_2CS]$ (0.1 mmol, method 1) at 0° C, and the mixture was stirred for 30 min. At this point, an IR spectrum of the solution showed carbonyl bands at 1980, 1975, 1920, and 1900 cm^{-1} and a thiocarbonyl band at 1198 cm^{-1}, suggesting that the species in solution was $Hg[CpW(CO)_2CS]_2$ (Table 1). The solution was warmed to room temperature, and the solvent was evaporated under reduced pressure. The residue was slurried in CH_2Cl_2 and placed on a 2 × 40 cm column of Florisil. Elution with CH_2Cl_2 gave a yellow solution that was diluted with 30 ml of hexane and evaporated under reduced pressure to give $CpW(CO)_2(CS)HgI$ (0.49 g, 73%). The analytical sample was recrystallized from CH_2Cl_2 with hexane at —20° C. (Found: C, 14.29; H, 0.89. $C_8H_5HgIO_2SW$ calcd.: C, 14.20; H, 0.74%).

$CpW(CO)_2(CS)SePh$. Addition of PhSeBr (0.24 g, 1.0 mmol) to a solution of $Bu_4N[CpW(CO)_2CS]$ (1.0 mmol, method 1) at 0° C gave a purple solution. The solution was filtered through Celite and evaporated to dryness under reduced pressure. The residue was dissolved in a minimum of CH_2Cl_2 and eluted through a 2 × 40 cm Florisil column with CH_2Cl_2. The purple eluate was collected and evaporated to dryness. The product was re-dissolved in CS_2 and eluted through a 2.5 × 60 cm silica gel column with CS_2. The product separated into three components: a yellow band ($(PhSe)_2$), a purple band (*trans*-$CpW(CO)_2(CS)Br$), and a red band ($CpW(CO)_2(CS)SePh$). The solution of $CpW(CO)_2(CS)SePh$ was evaporated, and large, red crystals were obtained by crystallization from CH_2Cl_2 with hexane at —20° C (0.18 g, 35%). (Found: C, 33.50; H, 2.10. $C_{14}H_{10}O_2SSeW$ calcd.: C, 33.29; H, 1.99%).

trans-$CpW(CO)_2(CS)I$. Solid I_2 (0.25 g, 1.0 mmol) was added to a solution of $Bu_4N[CpW(CO)_2CS]$ (1.0 mmol, method 1) at 0° C, causing an immediate color change. The solution was stirred for 10 min, filtered through Celite, and then evaporated under reduced pressure. Dissolving the residue in a minimum of CH_2Cl_2 and rapidly eluting the solution on a 2 × 40 cm Florisil column with the same solvent separated a purple solution. Hexane (30 ml) was added to the fraction containing the product, and the solution was evaporated slowly under reduced pressure to yield shiny, purple crystals of *trans*-$CpW(CO)_2(CS)I$. A typical yield was 0.37 g (77%). The analytical sample was recrystallized from CH_2Cl_2 with hexane at —20° C. (Found: C, 20.21; H, 1.11. $C_8H_5IO_2SW$: C, 20.18; H, 1.06%).

A similar reaction with $Bu_4N[HB(pz)_3W(CO)_2CS]$ gave the dark red *trans*-$HB(pz)_3W(CO)_2(CS)I$ (0.22 g, 33%). (Found: C, 23.17; H, 1.57. $C_{12}H_{10}BIN_6O_2SW$ calcd.: C, 23.09; H, 1.61.)

$CpW(CO)(CS)(L)I$ ($L = PPh_3$, $P(OPh)_3$, $P(NMe_2)_3$, PMe_2Ph, and CNMe). In a typical reaction, a solution of *trans*-$CpW(CO)_2(CS)I$ (0.53 g, 1.1 mmol) and PPh_3 (0.29 g, 1.1 mmol) in 50 ml of dry toluene was refluxed for 2.5 h. The resultant dark red solution was cooled to room temperature, filtered through Celite, and evaporated to dryness under reduced pressure at 50° C. The residue was slurried in 10 ml of CS_2 and placed on top of a 2 × 40 cm silica gel column. Careful development with CS_2 resolved the product into 3 bands: purple, yel-

low, and dark red. The purple and yellow bands were eluted with CS_2, and they contained *trans*-$CpW(CO)_2(CS)I$ and *trans*-$CpW(CO)_2(PPh_3)I$, respectively. Elution of the last band with CH_2Cl_2 gave a red solution, which was diluted with hexane until crystallization began. Slow evaporation under reduced pressure resulted in dark red crystals of $CpW(CO)(CS)(PPh_3)I$ (0.56 g, 78%). The analytical sample was obtained from CH_2Cl_2 with hexane at —20° C. (Found: C, 42.53; H, 2.87. $C_{25}H_{20}IOPSW$ calcd.: C, 42.28; H, 2.84%).

The above procedure, using *trans*-$CpW(CO)_2(CS)I$ (0.24 g, 0.5 mmol) and $P(OPh)_3$ (0.17 g, 0.55 mmol), produced a 65% yield of $CpW(CO)(CS)$-$(P[OPh]_3)I$ (0.49 g). (Found: C, 39.82; H, 2.75. $C_{25}H_{20}IO_4PSW$ calcd.: C, 39.59; H, 2.66%).

Reaction of PMe_2Ph (0.048 g, 0.34 mmol) and the thiocarbonyl (0.16 g; 0.33 mmol) gave $CpW(CO)(CS)(PMe_2Ph)I$ (0.37 g, 63%). The toluene solution of *trans*-$CpW(CO)_2(CS)I$ was heated to 105° C before addition of PMe_2Ph to avoid the formation of significant amounts of $[CpW(CO)(CS)(PMe_2Ph)_2]I$. Elution of the crude product mixture on a 2 X 40 cm Florisil column with CH_2Cl_2 separated the product from any residual starting material. The analytical sample was obtained from CH_2Cl_2 with hexane at —80° C. (Found: C, 30.90; H, 2.95. $C_{15}H_{16}IOPSW$ calcd.: C, 30.74; H, 2.76%).

Addition of $P(NMe_2)_3$ (0.11 g, 0.6 mmol) to a toluene solution of *trans*-CpW-$(CO)_2(CS)I$ (0.25 g, 0.5 mmol) at 105° C led to $CpW(CO)(CS)(P[NMe_2]_3)I$ (0.12 g, 19%). In this case, after heating 3 h, the solution was cooled and evaporated to dryness under reduced pressure. The residue was extracted with three 10 ml portions of pentane, and the remaining solid was crystallized from CH_2-Cl_2 with hexane at —20° C.

To a refluxing solution of *trans*-$CpW(CO)_2(CS)I$ (0.24 g, 0.50 mmol) in toluene, CNMe (0.021 g, 0.50 mmol) was added. After 40 min the reaction mixture was cooled and evaporated to dryness under reduced pressure. The residue was extracted with a minimum of benzene, and the extract was eluted on a column of Grade III Woelm alumina (2 X 40 cm) with the same solvent. Two bands were resolved, purple (starting material) and red (product). The red eluate was collected, diluted with 30 ml of hexane, and evaporated under reduced pressure to give an 83% yield of $CpW(CO)(CS)(CNMe)I$ (0.41 g). (Found: C, 22.04; H, 1.71. C_9H_8INOSW: C, 22.10; H, 1.65%).

trans-*[CpW(CO)(CS)(PMe₂Ph)₂]PF₆*. A solution of *trans*-$CpW(CO)_2(CS)I$ (0.12 g, 0.25 mmol) and PMe_2Ph (0.068 g, 0.50 mmol) in 30 ml of toluene was heated to 80° C for 2 h. The reaction mixture was filtered through a fritted-glass funnel, and the orange precipitate was washed with CS_2. The powder was dissolved in acetone, and the solution was passed through a column of Amberlite IRA-400 anion exchange resin in the PF_6^- form. The volume of the yellow eluate was reduced to about 5 ml under reduced pressure; a layer of diethyl ether (10 ml) was carefully placed on top of the eluate; and the mixture was cooled to —20° C for 48 h. Small, translucent crystals of *trans*-$[CpW(CO)(CS)$-$(PMe_2Ph)_2]PF_6$ were obtained (0.52 g, 70%). ^{31}P NMR (CD_3CN): singlet 8.89 ppm downfield from 85% H_3PO_4 external standard. (Found: C, 37.16; H, 3.78. $C_{23}H_{27}F_6OP_3SW$ calcd.: C, 37.21; H, 3.67%).

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