due to the trans isomer. Perhaps the magnetic influence of the benzyl substituent is sufficiently different from that of a phenyl substituent in the cis isomer to account for the opposite pattern observed for the cis and trans methyl resonances of the complexes **6** and Co(bzac)$_3$. If this assignment is correct, 18.5% of complex **6** is present as the cis isomer at +36 °C at equilibrium.

The prochiral methylene groups of complexes **5** and **6** should contain additional information regarding the geometrical isomerization of these compounds. Unfortunately, the low solubility of these complexes prevents a detailed analysis of these highly split resonances.

The partial solution decomposition of complex **8** prevents any estimate as to geometrical isomerization. Complex **14** exhibits only one singlet for the resonance of the methyl substituent and a single doublet for the resonance of the methyl groups of the isopropyl substituent. This pattern is unexpected and seems to suggest that only the cis isomer is present. A more reasonable explanation is that since the Mn–Al complexes apparently reach cis–trans equilibration rapidly after dissolution at 25 °C, the Re–Ga complex, **14**, may be undergoing such rapid cis–trans isomerization at +36 °C that only the higher symmetry structure of the cis isomer is observed as a time-averaged spectrum. This may be quite probable since Ga(pmhd)$_3$ undergoes cis–trans isomerization ca. 80 000 times faster than Al(pmhd)$_3$,[18] and this isomerization is fast on the proton NMR time scale at only +85 °C affording only a single doublet for the methyl groups of the isopropyl substituents.[21] At present, we have no quantitative information regarding the lability of the metallo-β-diketonate ligand, although, if this explanation is correct, these metallo ligands should be slightly more labile than the nonmetallo β-diketonate ligands.

The interpretation of complex **7** existing in solution as predominantly the trans isomer and complexes **5** and **6** exhibiting some cis isomer is consistent with the larger steric bulk of an isopropyl group compared to either an ethyl or a benzyl group. Apparently the effect of the size of the ring substituents in nonmetallo tris(β-diketonate) complexes is not significant and cis–trans mixtures of nearly statistical proportions are observed.[24]

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Registry No. 1, 58034-11-0; **5**, 59839-89-3; *cis*-**6**, 59839-96-2; *trans*-**6**, 59839-85-9; **7**, 59839-92-8; **8**, 59839-91-7; **9**, 59839-94-0; **10**, 59839-95-1; **11**, 59839-90-6; **12**, 59839-87-1; **13**, 59839-88-2; **14**, 59839-93-9; isobutyrylpentacarbonylrhenium, 59831-00-4; propionylpentacarbonylmanganese, 15022-56-7; phenacetylpentacarbonylmanganese, 15022-57-8; isobutyrylpentacarbonylmanganese, 15022-36-3; acetylpentacarbonylmanganese, 13963-91-2; acetylpentacarbonylrhenium, 23319-44-0; carboethoxypentacarbonylmanganese, 28300-66-5.

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Electrophilic and Oxidative Addition Reactions of Tungsten Thiocarbonyl Complexes

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Electrophilic reagents react with tungsten(0) thiocarbonyl complexes to yield products which result from either oxidative addition to the metal atom or electrophilic addition to the thiocarbonyl sulfur atom. Thus, W(CO)$_5$(CS) reacts with Br$_2$ and PPh$_3$ to yield W(CO)$_2$(CS)(PPh$_3$)$_2$Br$_2$, but it does not undergo Lewis acid adduct formation at the thiocarbonyl sulfur. Proton addition to the metal atom in W(CO)(CS)(diphos)$_2$ [diphos = ethylenebis(diphenylphosphine)] is observed with CF$_3$SO$_3$H, to afford [HW(CO)(CS)(diphos)$_2$]CF$_3$SO$_3$. However, [(diphos)$_2$(CO)W(CS)HgX$_2$], [{(diphos)$_2$(CO)W(CS)}$_2$Ag]BF$_4$, [(diphos)$_2$(CO)W(CS)W(CO)$_5$], [(diphos)$_2$(CO)W(CSCH$_3$)]SO$_3$F, and [(diphos)$_2$(CO)W(CSC$_2$H$_5$)]BF$_4$ result from reactions of Lewis acids (HgX$_2$, AgBF$_4$, W(CO)$_5$(CH$_3$COCH$_3$), CH$_3$OSO$_2$F, or [(C$_2$H$_5$)$_3$O]BF$_4$, respectively) at the thiocarbonyl sulfur atom. Sulfur dioxide is absorbed reversibly by W(CO)(CS)(diphos)$_2$, and ir evidence suggests that this Lewis acid also coordinates to the thiocarbonyl sulfur atom. The Bu$_4$N[W(CO)$_4$(CS)(I)] complex is alkylated at sulfur by CH$_3$OSO$_2$F and [(C$_2$H$_5$)$_3$O]BF$_4$, to afford W(CO)$_4$(I)(CSR) products, and is acylated by carboxylic acid anhydrides to give W(CO)$_4$(I)(CSC(O)R) complexes. These reactions of thiocarbonyl complexes are contrasted with those of carbonyl analogues, which give different types of products with many of these reagents.

Introduction

The formal similarity of carbon monosulfide (CS) to CO has stimulated much recent interest in the reactivity of the CS ligand in its metal complexes.[1-6] Certain electron-rich metal carbonyl complexes have shown the capability of forming Lewis acid adducts at the oxygen atom of a terminal carbonyl ligand.[7-13] It was therefore expected that thiocarbonyl complexes might form sulfur-bound adducts with Lewis acids under suitable conditions. By analogy with the metal carbonyl adducts, thiocarbonyl complexes having high electron density, as evidenced by low infrared ν(CS) frequencies, would be the most likely to undergo electrophilic addition to the sulfur atom. Electrophilic reagents also have the capability of adding to the central metal atom or causing a simple oxidation of the complex. Thus, examples of both oxidative addition to the metal and electrophilic addition to the sulfur are observed with tungsten(0) thiocarbonyl complexes. Some of these results were reported in previous communications.[3,4]

Results and Discussion

Reactions of $W(CO)_5(CS)$. The unsubstituted $W(CO)_5(CS)$ complex (**1**) was found not to react with a variety of Lewis acids, including BF_3, B_2H_6, $HgCl_2$, $[(C_2H_5)_3O]BF_4$, CH_3OSO_2F, or HCl. The complex, however, is oxidized by Br_2 in a process which appears to be quite similar to that reported for $W(CO)_6$.[14] Carbon monoxide is evolved as a reactive intermediate presumed to have the formula $W(CO)_3(CS)Br_2$ is formed. No attempt was made to isolate this intermediate, but addition of PPh_3 to this mixture causes immediate CO evolution, and the substituted product, $W(CO)_2(CS)(PPh_3)_2Br_2$, can be isolated

$$\mathrm{W(CO)_5(CS)} \xrightarrow[\text{2. 2PPh}_3]{\text{1. Br}_2} \mathrm{W(CO)_2(CS)(PPh_3)_2Br_2} + 3\mathrm{CO} \qquad (1)$$

The analogous $W(CO)_3(PPh_3)_2Br_2$ complex, prepared similarly, has been reported to lose 1 mol of CO upon heating to 40 °C in CH_2Cl_2 for 2–3 h to form the $W(CO)_2(PPh_3)_2Br_2$ complex.[14] Presumably the steric bulk of the phosphine ligands causes this decarbonylation to occur. Thus, although it might be expected that $W(CO)_2(CS)(PPh_3)_2Br_2$ would also undergo carbonyl loss, this was never observed even upon heating in $CHCl_3$ at 60 °C for 4 h. The complex rather decomposed slowly to yield insoluble, non-carbonyl-containing products.

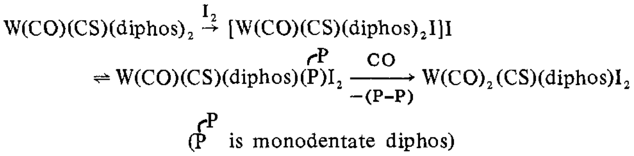
The stability of $W(CO)_2(CS)(PPh_3)_2Br_2$ to decarbonylation may be due to structural factors. If a carbonyl group in the tricarbonyl complex is lost specifically from one coordination site and if the CS ligand occupies that site in the thiocarbonyl complex, loss of the thiocarbonyl ligand would be expected to be much less favorable, as suggested by the generally stronger metal–carbon bonds formed by CS as compared to CO.[1,15]

Reaction of the presumed $W(CO)_3(CS)Br_2$ intermediate and the very bulky $P(2\text{-}CH_3C_6H_4)_3$ ligand in CH_2Cl_2 solution did not lead to a phosphine-substituted product. Instead, an ionic complex with high bromine content was isolated in 45% yield. This was shown by ir spectroscopy (ν(P–H) at 2350 cm^{-1} in KBr) and elemental analyses to be $[(2\text{-}CH_3C_6H_4)_3PH][W(CO)_3(CS)Br_3]$. The mechanism of formation of this product is unknown, but the CH_2Cl_2 solvent or water in this undried solvent may be the source of the proton. Similar reactions of molybdenum carbonyl complexes have previously been reported to give phosphonium salt products in this solvent.[16]

Reactions of Phosphine-Substituted Complexes. (a) Reactions at the Metal. Unsuccessful attempts were made to react $W(CO)_4(CS)(PPh_3)$[5] and *fac*-$W(CO)_3(CS)(diphos)$[5] with many of the Lewis acid reagents which were previously tried with **1**. The action of I_2 on $W(CO)_3(CS)(diphos)$ does cause CO evolution and formation of a product tentatively identified as $W(CO)_2(CS)(diphos)I_2$. The complex could not be crystallized but was always obtained as a powder which gave poor elemental analyses.

Iodine reacts with $W(CO)(CS)(diphos)_2$ (**2**)[5] without gas evolution. Reactions performed with varying molar ratios of the reactants showed that each mole of $W(CO)(CS)(diphos)_2$ required 1 mol of I_2 in order for all of the starting complex to react, thus suggesting that a W(II) complex is produced.

Scheme I



$$\mathrm{W(CO)(CS)(diphos)_2} \xrightarrow{I_2} \mathrm{[W(CO)(CS)(diphos)_2I]I} \rightleftharpoons \mathrm{W(CO)(CS)(diphos)(\overset{\frown}{P})I_2} \xrightarrow[-(P\text{–}P)]{CO} \mathrm{W(CO)_2(CS)(diphos)I_2}$$

($\overset{\frown}{P}$ is monodentate diphos)

The product initially formed in this reaction is quite unstable and is converted to other products upon standing in solution. Only in one reaction with excess iodine was it possible to isolate a few crystals of the initial product, which analyzed for C and H as $[W(CO)(CS)(diphos)_2I]I_3$ and exhibited one ν(CO) and one ν(CS) absorption in its infrared spectrum. Decomposition of this complex in CH_2Cl_2 solution gives a mixture containing mainly one product which has ir bands identical with those of $W(CO)_2(CS)(diphos)I_2$, prepared from $W(CO)_3(CS)(diphos)$ and I_2. Decomposition in solution may be the source of the CO which has been added to this complex. A possible reaction sequence which would lead to this product is shown in Scheme I. Carbonyl analogues of the two proposed intermediates, containing Br or I, are known.[17] This reaction of **2** with I_2 may be contrasted with the reported reaction of its carbonyl analogue, $W(CO)_2(diphos)_2$, with I_2,[18] which gives the stable W(I) complex, $[W(CO)_2(diphos)_2]I_3$, isolated in good yields as the only product.

The $W(CO)(CS)(diphos)_2$ complex also undergoes addition with a number of Lewis acids. Some of these reactions were also carried out with the dicarbonyl analogue, $W(CO)_2(diphos)_2$. Both complexes are protonated by strong acids to give tungsten(II) hydride complexes

$$\mathrm{W(CO)(CX)(diphos)_2} + \mathrm{CF_3SO_3H} \rightarrow \mathrm{[HW(CO)(CX)(diphos)_2]CF_3SO_3} \qquad (2)$$
$$\mathrm{X = O, S}$$

That the metal is the site of protonation is confirmed by the high frequencies of the ν(CO) and ν(CS) absorptions (Table I) and the Fourier-transform proton NMR spectra of the products, which both exhibit a high-field metal hydride resonance. In both spectra, the hydride resonance is split into a triplet of triplets by coupling to the diphos ligand phosphorus atoms through the metal. This AA′BB′ pattern suggests a molecular structure in which the phosphorus atoms occupy four coplanar coordination sites with the proton coordinating through an octahedral face, a structure which has recently been established for the isoelectronic $HTa(CO)_2(Me_2PCH_2CH_2PMe_2)_2$.[19] A similar protonated complex of molybdenum, $[HMo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]HCl_2$, has also been reported.[20] Proton NMR spectra of these latter complexes both exhibit high-field AA′BB′ metal hydride resonances. The tungsten complexes, which originally had cis structures, have thus isomerized to the trans isomers upon protonation. Similar rearrangements have been observed during the electrochemical oxidation of $W(CO)_2(diphos)_2$, and molecular orbital based arguments have been presented to rationalize the isomerization.[21]

(b) Reactions at the Sulfur. Reactions of **2** with mercuric halides give products of a different type

$$\mathrm{W(CO)(CS)(diphos)_2} + \mathrm{HgX_2} \rightarrow \mathrm{(diphos)_2(CO)W{-}CS{\rightarrow}HgX_2} \qquad (3)$$

The ν(CO) absorption in these products is also shifted to higher frequencies, but by less than 50 cm^{-1}. The ν(CS) absorption has apparently shifted to lower frequency. No new bands are detectable within 200 cm^{-1} above the 1161-cm^{-1} position of the original band, but a strong diphos ligand absorption at about 1095 cm^{-1} has become more intense, suggesting that the CS band overlaps at this position (Figure 1B). A shoulder is discernible on the high-frequency side of this composite band, which suggests that the CS stretching frequency of the mercuric halide adducts occurs at about 1100 cm^{-1}. This

Table I. ν(CO) and ν(CS) in the Infrared Region

Compd	ν(CO), cm^{-1}	ν(CS), cm^{-1}
$W(CO)_5(CS)$[a]	2096 w, 2007 m, 1989 vs[b]	1258 vs[c]
trans-$W(CO)_4(CS)(PPh_3)$[a]	2061 vw, 1956 vs[b]	1241 vs[c]
$W(CO)_3(CS)$(diphos)[a]	2013 w, 1925 vs[d]	1215 vs[c]
W(CO)(CS)(diphos)[a]	1838 s[d]	1161 s[d]
$W(CO)_2(diphos)_2$	1847 s, 1782 s[d]	
$W(CO)_2(CS)(PPh_3)_2Br_2$	2014 m, 1959 s[d]	1249 s[c]
$[(2\text{-}CH_3C_6H_4)_3PH][W(CO)_3(CS)Br_3]$	2078 w, 2028 s, 1992 s[e]	1260 s[e]
$W(CO)_2(CS)(diphos)I_2$	2036 s, 1972 s[d]	1245 s[c]
$[W(CO)(CS)(diphos)_2I]I_3$	1916 s[d]	1232 s[d]
$[HW(CO)(CS)(diphos)_2]CF_3SO_3$	1958 s[d]	1207 s[d]
$[HW(CO)_2(diphos)_2]CF_3SO_3$	1968 w, 1862 vs[d]	
$W(CO)(diphos)_2(CS\cdot HgCl_2)$	1885 s[d]	*f*
$W(CO)(diphos)_2(CS\cdot HgI_2)$	1872 s[d]	*f*
$[\{W(CO)(diphos)_2(CS)\}_2Ag]BF_4$	1869 s[d]	1106 m[d]
$W(CO)(diphos)_2(CS)W(CO)_5$	2062 w, 1925 vs, 1878 m[c]	*f*
$[W(CO)(diphos)_2(CSCH_3)]FSO_3$	1898 s[d]	*f*
$[W(CO)(diphos)_2(CSC_2H_5)]BF_4$	1898 s[d]	*f*
$[W(CO)_2(diphos)_2(C_2H_5)]BF_4$	1970 w, 1864 vs[d]	
Bu_4N[*trans*-$W(CO)_4(CS)(I)$]	2062 w, 1947 vs[d]	1195 vs[d]
$W(CO)_4(I)(CSCH_3)$	2115 w, 2033 vs[b]	1118 m[b]
$W(CO)_4(I)(CSC(O)CF_3)$[g]	2137 w, 2080 w, sh, 2057 vs, 2052 vs[b]	*f*
$W(CO)_4(I)(CSC(O)CH_3)$[h]	2124 w, 2065 w, sh, 2049 vs, 2040 vs[b]	1081 m[b]

[a] Reference 5. [b] Pentane solution. [c] CS_2 solution. [d] CH_2Cl_2 solution. [e] KBr disk. [f] Region obscured by other absorptions; see text. [g] ν(C=O) at 1737 cm^{-1}. [h] ν(C=O) at 1753 cm^{-1}.

represents a lowering by about 60 cm^{-1} from its position in **2** as a result of coordination through sulfur. Metal carbonyls which are adducted through oxygen to a Lewis acid also show decreases in their ν(CO) frequencies.[7-13]

Both the $HgCl_2$ and HgI_2 adducts are isolable in high yields as stable, crystalline solids. No decomposition to the starting complex is observed either in solution or in the solid state. However, removal of HgX_2 by the addition of PPh_3 to their solutions gives rapid regeneration of the starting complex, **2**. The adducts are poor conductors in nitrobenzene, indicating little or no ionic dissociation. Thus, all of the available evidence points to their formulation as $(diphos)_2(CO)W{-}C{\equiv}S{\rightarrow}HgX_2$ adducts. By way of contrast, the carbonyl complex $W(CO)_2(diphos)_2$ reacts with mercuric halides to form ionic $[W(CO)_2(diphos)_2HgX]HgX_3$ complexes.[22]

Silver ion also reacts with **2** to form an isolable complex

$$2W(CO)(CS)(diphos)_2 + Ag^+ \rightarrow [\{(diphos)_2(CO)W\text{-}CS\}_2Ag]^+ \qquad (4)$$

A stoichiometric study showed that only 0.5 mol of Ag^+ is required per mole of complex. The product is not the result of an oxidation, since no silver metal is produced, and addition of PPh_3 to the solution gives back the starting complex, **2**. Conversion to **2** is also observed within a few minutes when an infrared spectrum of a CH_2Cl_2 solution of the complex is recorded in an NaCl cell. These reactions apparently occur because of coordination of PPh_3 and chloride ion to the Ag^+. The crystalline product isolated from reaction 4 has an infrared spectrum similar to those of the mercuric halide adducts, with a peak at 1106 cm^{-1} which is assigned to ν(CS).

Reactions of **2** with more than 0.5 equiv of $AgBF_4$ give other products as well, which apparently result from oxidation, since silver metal is plated out. Although a pure product could not be isolated from these reactions, magnetic susceptibility measurements gave no evidence for any paramagnetic W(I) products. Again, a contrast may be drawn with the carbonyl analogue, $W(CO)_2(diphos)_2$, which was found to react with $AgBF_4$ in any proportions to yield the paramagnetic $[W(CO)_2(diphos)_2]BF_4$.[3,18]

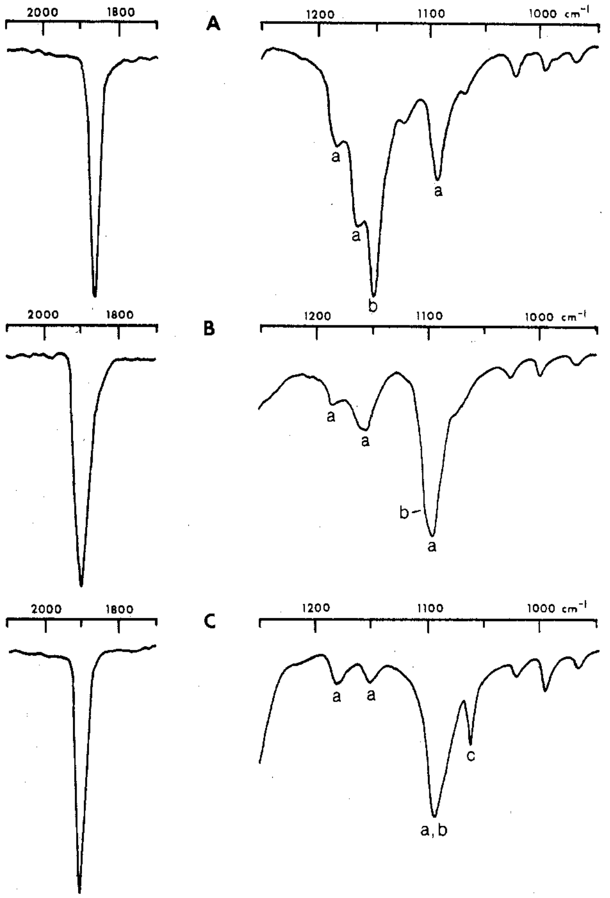


Figure 1. Carbonyl and thiocarbonyl regions of the infrared spectra of (A) $W(CO)(CS)(diphos)_2$, (B) $W(CO)(diphos)_2(CS\cdot HgCl_2)$, and (C) $[W(CO)(diphos)_2(CSCH_3)]FSO_3$. All spectra were recorded in KBr disks: a, diphos ligand absorption; b, ν(CS); c, FSO_3^- absorption.

A novel bridged complex, $(diphos)_2(CO)W\text{-}CS\text{-}W(CO)_5$, was synthesized by reacting **2** with $W(CO)_5(Me_2CO)$

$$W(CO)(CS)(diphos)_2 + W(CO)_5(Me_2CO) \rightarrow (diphos)_2(CO)W\text{-}CS\text{-}W(CO)_5 + Me_2CO \qquad (5)$$

The complex undergoes noticeable decomposition in the solid state after several days, and its reaction in solution with PPh_3 is quite rapid, yielding **2** and $W(CO)_5(PPh_3)$ within 30 min. Nevertheless, the complex can be isolated as a crystalline solid. It is anticipated that a number of other reactive transition metal species will also coordinate to the thiocarbonyl sulfur atom of **2**.

Organic electrophiles have also been found to bond to the sulfur atom of this complex. Both methyl fluorosulfonate and triethyloxonium tetrafluoroborate (eq 6) alkylate the complex,

$$W(CO)(CS)(diphos)_2 + [(C_2H_5)_3O]BF_4 \rightarrow [(diphos)_2(CO)W(CSC_2H_5)]BF_4 \qquad (6)$$

giving stable, crystalline *S*-alkylthiocarbonylium complexes (they may also be considered alkylthiocarbyne complexes), which are formally related to carbyne complexes prepared by Fischer et al.[23] The ν(CS) frequency in the ir spectra of these products is also lowered by more than 60 cm^{-1} (Figure 1C). Unlike the metal complex adducts, these derivatives do not react with PPh_3; they do, however, react very slowly with *n*-butylamine to regenerate **2**.

The carbonyl complex $W(CO)_2(diphos)_2$ was also found to react with CH_3OSO_2F and $[(C_2H_5)_3O]BF_4$. These reactions appear to give similar products, and only the latter was characterized (eq 7). A yellow, crystalline ethylated complex

$$W(CO)_2(diphos)_2 + [(C_2H_5)_3O]BF_4 \rightarrow [(C_2H_5)W(CO)_2(diphos)_2]BF_4 \qquad (7)$$

is produced which contains two carbonyl groups in a nearly trans arrangement, as suggested by the intensities of the ν(CO) absorptions in its ir spectrum (Table I). Therefore, the complex is formulated as a tungsten(II) alkyl complex, $[W(CO)_2(diphos)_2(C_2H_5)]BF_4$. A related molybdenum(II) alkyl complex, $[Mo(o\text{-phen})(PBu_3)_2(CO)_2(CH_3)]SO_3F$, has been reported.[24]

The exposure of **2** to SO_2, either in CH_2Cl_2 solution or in the solid state, causes a rapid color change from yellow to dark brown. Bubbling N_2 through the solution, subjecting the solid to a high vacuum, or allowing either to stand in air for several hours brings back the yellow color of the unchanged complex. The ir spectrum of an SO_2-saturated solution shows a large amount of **2**, but a shoulder is evident at 1950 cm^{-1} on the ν(CO) band, which represents a shift of about 10 cm^{-1} to higher frequency. This small shift is indicative of a weak interaction at the thiocarbonyl sulfur atom, which is consistent with the facile reversibility of SO_2 absorption. An attempt was made to trap the SO_2 adduct with CH_3OSO_2F, but only $[(diphos)_2(CO)W(CSCH_3)]SO_3F$ was isolated. Although SO_2 has been observed to bond to the metal atom in several organometallic complexes,[25] it seems unlikely that the metal is the site of coordination in this complex because of the small shift in the ν(CO) frequency. Furthermore, $W(CO)_2(diphos)_2$, which appears to have higher metal electron density, does not react with SO_2.

Reactions of $Bu_4N[$*trans*-$W(CO)_4(CS)(I)]$. Reactions at the Sulfur. The low ν(CS) frequency in the ir spectrum of $Bu_4N[$*trans*-$W(CO)_4(CS)(I)]$ (**3**) suggested that this complex might also undergo electrophilic attack at the thiocarbonyl sulfur atom. Addition of small amounts of $AgBF_4$ to solutions of the complex gives immediate precipitation of AgI. Thus silver ion adducts were not obtained. This process, however, provides a general method for the preparation of a variety of *trans*-$W(CO)_4(CS)(L)$ complexes.[5]

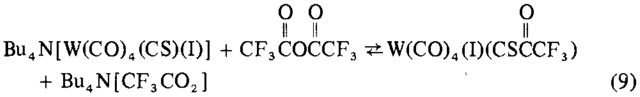
The action of $[(C_2H_5)_3O]BF_4$ on **3** in the presence of PPh_3 yields two products in approximately equal amounts. One is *trans*-$W(CO)_4(CS)(PPh_3)$,[5] apparently formed by the abstraction of I^- by $[(C_2H_5)_3O]^+$, similar to the Ag^+ reaction.[26] The second product, $W(CO)_4(I)(CSC_2H_5)$, is also formed by reaction with $[(C_2H_5)_3O]^+$ in the absence of PPh_3. A very similar complex is produced by addition of CH_3OSO_2F to **3** (eq 8) and this product was isolated in 15–20% crude yields.

$$W(CO)_4(I)(CS)^- + CH_3OSO_2F \rightarrow W(CO)_4(I)(CSCH_3) + SO_3F^- \qquad (8)$$

The complex is air sensitive in solution but is more stable in the solid state and was fully characterized. Only a singlet is observed in the proton NMR spectrum of the complex, and an abundant mass spectrum parent ion is observed which corresponds to $W(CO)_4(I)(CSCH_3)^+$.

Its ir spectrum establishes that alkylation has occurred at the sulfur, since the clearly visible ν(CS) absorption at 1118 cm^{-1} is nearly 80 cm^{-1} lower than in the starting complex, although the ν(CO) bands have shifted to higher frequencies. The ν(CO) region of its ir spectrum (Table I) and the ^{13}C NMR data show that the $W(CO)_4(I)(CSCH_3)$ complex has a trans geometry, as does the starting complex.

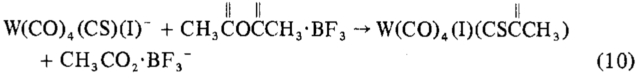
Trifluoroacetic anhydride also reacts with **3** to give a complex with a similar infrared spectrum in the ν(CO) region. The thiocarbonyl region is, unfortunately, obscured by C–F absorptions. All of the starting material is consumed when reacted in CH_2Cl_2 solution with $(CF_3CO)_2O$, as indicated by the ir spectrum. However, removal of the solvent under reduced pressure also causes regeneration of the starting complex, presumably by removal of the volatile trifluoroacetic anhydride



$$Bu_4N[W(CO)_4(CS)(I)] + CF_3\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CF_3 \rightleftarrows W(CO)_4(I)(CS\overset{\overset{O}{\|}}{C}CF_3) + Bu_4N[CF_3CO_2] \qquad (9)$$

The acylated complex *trans*-$W(CO)_4(I)(CSC(=O)CF_3)$ could be isolated when the reaction was performed in a pentane suspension, since the trifluoroacetate salt product is insoluble in this solvent. The complex is rather unstable, and the yellow crystals obtained by cooling a pentane solution to −80 °C darken even on standing in the mother liquor at this temperature. An elemental analysis was not attempted, but the exact mass of the parent ion in the high-resolution mass spectrum supports the assigned formula. Fragment ions were observed as a result of the loss of CF_3CO and $CF_3C(O)SC$, as well as those due to CO dissociation.

A similar reaction between **3** and acetic anhydride was attempted, but there was no evidence of reaction. However, in the presence of BF_3 a reaction does take place (eq 10), and

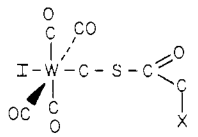


$$W(CO)_4(CS)(I)^- + CH_3\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CH_3\cdot BF_3 \rightarrow W(CO)_4(I)(CS\overset{\overset{O}{\|}}{C}CH_3) + CH_3CO_2\cdot BF_3^- \qquad (10)$$

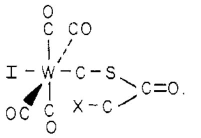
a 15–20% yield of the crude *S*-acetylthiocarbonylium (may also be called an acetylthiocarbyne) complex was isolated. This neutral complex has a ν(CS) which is more than 100 cm^{-1} lower than that of the starting complex. The use of BF_3 in this reaction presumably enhances the electrophilic character of the anhydride and prevents the reverse reaction from occurring. The compound is air sensitive both in solution and in the solid state.

Both $W(CO)_4(I)(CSC(O)CF_3)$ and $W(CO)_4(I)(CS\text{-}C(O)CH_3)$ have ir carbonyl spectra (Table I) characteristic of four CO groups in a C_{4v} structure, except that the strong E mode is split into a doublet and a weak B_1 absorption band appears. The ir spectrum of the ethylthiocarbyne complex, $W(CO)_4(I)(CSC_2H_5)$, also exhibits this splitting and the B_1 band, but the spectrum of the methyl analogue does not. These effects suggest that there is a distortion of the local C_{4v} symmetry of the carbonyl ligands caused by the thiocarbyne ligand. Similar effects have been observed in complexes of the type $R\text{–}Mn(CO)_5$, where R is a sterically large group.[27]

Based on the apparent distortion caused by steric interaction with the alkylated and acylated thiocarbonyl ligands, tentative structures of these ligands might be proposed. A linear C–S–R arrangement, I, would seem to prohibit such interaction by



I



II

placing the alkyl or acyl groups too far from the carbonyls. However, a bent C–S–R linkage, II, brings an atom separated from the sulfur by three bonds quite close to the carbonyl plane. The methylthiocarbonylium substituent has atoms no further than two bonds from the sulfur and would show no such interaction. Adducts of $W(CO)(CS)(diphos)_2$ with alkyl cations would presumably also have bent C–S–R structures, and the metal-containing Lewis acids probably bond in this fashion also. Metal carbonyl–Lewis acid adducts have been observed to form bent carbonyl–acid bonds; the angles reported are in the range of 140–160°.[7,12]

Conclusions

As for complexes of CO, high ligand electron density is required for thiocarbonyl adduct formation. Using a low ν(CS) frequency to indicate high electron density at a metal thiocarbonyl ligand, we expect to find that complexes with low ν(CS) frequencies form the most stable Lewis acid adducts. Thus, of the tungsten complexes examined, only those with ν(CS) frequencies below 1200 cm^{-1} gave isolable sulfur-bound adducts with Lewis acids.

The number and variety of Lewis acids which were found in this work to coordinate to the sulfur atom of certain thiocarbonyl ligands point out the relatively high nucleophilicity of this atom as compared to the oxygen atom of a CO ligand. The stability of the adducts thus formed is presumably a result of the greater polarizability and lower electronegativity of sulfur as compared to oxygen. These properties also allow the thiocarbonyl sulfur atom to coordinate to acids of large size and low positive charge, such as HgX_2, Ag^+, and $W(CO)_5$. Metal carbonyls, in contrast, form O-bound adducts with "hard" acids containing trivalent aluminum,[7-9] gallium,[9] and lanthanides,[10,11] or divalent magnesium.[12]

Strong protonic acids add to the metal atom of W(CO)(CS)(diphos)$_2$ rather than to the thiocarbonyl sulfur. Although it is not yet certain what factors are important in directing coordination at sulfur vs. the metal atom, it does appear that the larger Lewis acids with low charge prefer sulfur coordination.

Experimental Section

Unless otherwise noted, all reactions were performed under an atmosphere of dry N_2. Reagent grade solvents and chemicals were used without further purification. Thiocarbonyl complexes were synthesized as reported in the literature.[5,28] The W(CO)$_2$(diphos)$_2$ was prepared using a modification of the literature procedure.[29] A mixture of 1.5 g of $W(CO)_6$ and 4.0 g of diphos in 50 ml of decalin solvent was heated to reflux for 7 days and isolated as described previously.[29] Infrared spectra were recorded using a Perkin-Elmer 337 spectrometer with an expanded-scale recorder calibrated in the CO region with gaseous CO and DCl and in the CS region with polystyrene. Proton NMR spectra were recorded with a Perkin-Elmer Hitachi R-20B spectrometer or a Bruker HX-90 spectrometer operating in the Fourier-transform mode. ^{13}C NMR spectra were also obtained with the Bruker HX-90 instrument using solutions containing 0.05 M Cr(acac)$_3$.[30] Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., or Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Conductivity measurements were performed at 25 °C on solutions of approximately 10^{-3} M complex in nitrobenzene.

Preparation of W(CO)$_2$(CS)(PPh$_3$)$_2$Br$_2$. A solution of W(CO)$_5$(CS) (0.10 g, 0.27 mmol) in 3 ml of CH_2Cl_2 was cooled to −80 °C, and Br_2 (0.05 g, 0.31 mmol) in 1 ml of CH_2Cl_2 was added dropwise. The Schlenk reaction vessel was then removed from the cooling bath and allowed to warm to room temperature. A solution of PPh_3 (0.20 g, 0.76 mmol) in 2 ml of CH_2Cl_2 was added to this mixture, which caused immediate gas evolution. The solution was concentrated on a rotary evaporator and crystallized by the addition of hexane and cooling to −20 °C. A yield of 0.25 g (92%) of dark yellow crystals was obtained. Anal. Calcd for W(CO)$_2$(CS)(PPh$_3$)$_2$Br$_2$: C, 48.35; H, 3.10. Found: C, 47.48; H, 3.24.

Preparation of [(2-CH$_3$C$_6$H$_4$)$_3$PH][W(CO)$_3$(CS)Br$_3$]. A solution of 0.15 g of W(CO)$_5$(CS) (0.41 mmol) in 5 ml of CH_2Cl_2 was cooled to −80 °C and allowed to react with Br_2 (0.075 g, 0.47 mmol) as it warmed to room temperature. Then a solution of P(2-tol)$_3$ (0.28 g, 0.92 mmol) in 2 ml of CH_2Cl_2 was added, which caused immediate evolution of a gas. After standing 10 min, approximately 10 ml of hexane was added and the mixture was filtered. Addition of 10 ml more hexane and cooling to −20 °C gave crystals (0.15 g, 45%) having a metallic yellow appearance. The complex was recrystallized from CH_2Cl_2–hexane: NMR (DCCl$_3$) τ 2.50 (m, C_6H_4), 7.50 (s, CH_3); molar conductivity Λ = 20.0 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for [(2-CH$_3$C$_6$H$_4$)$_3$PH][W(CO)$_3$(CS)Br$_3$]: C, 34.97; H, 2.56; Br, 27.97. Found: C, 35.36; H, 2.88; Br, 28.50.

Reaction of W(CO)$_3$(CS)(diphos) with I$_2$. A solution of W(CO)$_3$(CS)(diphos) (0.07 g, 0.098 mmol) and I_2 (0.027 g, 0.106 mmol) in 10 ml of CH_2Cl_2 was stirred at room temperature for 4 h. The solution was then filtered, diluted with hexane, and cooled to −20 °C. The resulting powder was reprecipitated from CH_2Cl_2–hexane; however, crystals could not be obtained. The product (0.04 g) was dried for 12 h at 85 °C under high vacuum. Although the infrared spectrum (Table I) supports its formulation as W(CO)$_2$(CS)(diphos)I$_2$, satisfactory analyses could not be obtained. Anal. Calcd for W(CO)$_2$(CS)(diphos)I$_2$: C, 37.18; H, 2.56; I, 27.14. Found: C, 35.82; H, 2.51; I, 24.38.

Reaction of W(CO)(CS)(diphos)$_2$ with I$_2$. A mixture of W(CO)(CS)(diphos)$_2$ (0.073 g, 0.069 mmol) and I_2 (0.028 g, 0.11 mmol) in 10 ml of CH_2Cl_2 was stirred for approximately 30 min. The solution was filtered, diluted with hexane, and cooled to −20 °C to give dark yellow crystals (0.014 g, 13%) which were recrystallized from CH_2Cl_2–hexane and dried 1 h at 50 °C under high vacuum. Anal. Calcd for [W(CO)(CS)(diphos)$_2$I]I$_3$: C, 41.53; H, 3.08. Found: C, 40.66; H, 3.24.

Preparation of [HW(CO)(CS)(diphos)$_2$]CF$_3$SO$_3$. Trifluoromethanesulfonic acid (0.086 g, 0.57 mmol) in 2 ml of CH_2Cl_2 was added to a suspension of W(CO)(CS)(diphos)$_2$ (0.60 g, 0.57 mmol) in 20 ml of CH_2Cl_2. The solution was stirred for 10 min, filtered, diluted with 35 ml of ethyl ether, and cooled to 0 °C. Orange crystals of the CH_2Cl_2-solvated complex (0.64 g, 87%) were collected. After three recrystallizations from CH_2Cl_2–ether the crystals were dried at 100 °C under high vacuum for 5 h: NMR (DCCl$_3$) τ 2.67 (m, C_6H_5), 7.30 (m, CH_2CH_2), 12.79 (triplet of triplets, J_{PWH} = 72 Hz, $J_{P'WH}$ = 13 Hz); Λ = 19.8 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for [HW(CO)(CS)(diphos)$_2$]CF$_3$SO$_3$: C, 54.91; H, 4.08; P, 10.65. Found: C, 54.50; H, 4.03; P, 10.75.

Preparation of [HW(CO)$_2$(diphos)$_2$]CF$_3$SO$_3$. In a procedure similar to the previous one, W(CO)$_2$(diphos)$_2$ (1.0 g, 0.97 mmol) was reacted with CF_3SO_3H (0.16 g, 1.07 mmol) to yield 1.09 g (89%) of the CH_2Cl_2-solvated complex. The complex was recrystallized and dried at 100 °C under high vacuum: NMR (DCCl$_3$) τ 2.80 (m, C_6H_5), 7.35 (d, CH_2CH_2), 14.91 (triplet of triplets, J_{PWH} = 74 Hz, $J_{P'WH}$ = 13 Hz); Λ = 19.8 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for [HW(CO)$_2$(diphos)$_2$]CF$_3$SO$_3$: C, 56.07; H, 4.16; P, 10.88. Found: C, 55.40; H, 3.84; P, 10.64.

Preparation of (diphos)$_2$(CO)W(CS·HgCl$_2$). A suspension of W(CO)(CS)(diphos)$_2$ (0.10 g, 0.095 mmol) and $HgCl_2$ (0.026 g, 0.096 mmol) in 8 ml of CH_2Cl_2 was stirred (in air) for approximately 10 min. The solution was filtered, diluted with 7 ml of hexane, and cooled to −20 °C to complete the crystallization. The orange solid (0.11 g, 87%) was recrystallized from CH_2Cl_2–hexane; Λ = 5.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for W(CO)(CS)(diphos)$_2$·HgCl$_2$: C, 46.84; H, 3.55; S, 2.42. Found: C, 46.59; H, 3.44; S, 2.37.

Preparation of (diphos)$_2$(CO)W(CS·HgI$_2$). A suspension of W(CO)(CS)(diphos)$_2$ (0.10 g, 0.095 mmol) and HgI_2 (0.045 g, 0.099 mmol) in 10 ml of CH_2Cl_2 gave red crystals (0.14 g, ~93%) following the previous procedure. These were recrystallized from CH_2Cl_2–hexane. After drying the crystals under high vacuum, a proton NMR spectrum in DCCl$_3$ solution showed the presence of CH_2Cl_2; Λ = 5.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for W(CO)(CS)(diphos)$_2$·HgI$_2$·CH$_2$Cl$_2$: C, 41.45; H, 3.14; S, 2.05. Found: C, 40.98; H, 2.99; S, 1.91.

Preparation of [{(diphos)$_2$(CO)WCS}$_2$Ag]BF$_4$. A suspension of W(CO)(CS)(diphos)$_2$ (0.39 g, 0.37 mmol) in 30 ml of acetone was stirred while $AgBF_4$ (0.036 g, 0.185 mmol) in 2 ml of acetone was added dropwise. The mixture was stirred for 10 min, and the resulting clear yellow solution was filtered, concentrated, and diluted with 20 ml of ethyl ether. Cooling to −20 °C completed the precipitation. The yellow powder (0.38 g, 89%) was dissolved in 30 ml of CH_2Cl_2, filtered through Celite, and diluted with warm hexane. Crystals were obtained upon cooling the solution to −20 °C. A Gouy magnetic susceptibility measurement showed the complex to be diamagnetic; Λ = 26.4 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for [{W(CO)(CS)(diphos)$_2$}$_2$Ag]BF$_4$: C, 56.37; H, 4.17; P, 10.79. Found: C, 56.20; H, 4.39; P, 10.87.

Preparation of (diphos)$_2$(CO)W–CS–W(CO)$_5$. A solution of W(CO)$_5$(CH$_3$COCH$_3$) was prepared by adding dropwise a solution of $AgBF_4$ (0.033 g, 0.17 mmol) in 2 ml of acetone to Et$_4$N[W(CO)$_5$(I)] (0.10 g, 0.167 mmol) in 10 ml of acetone. This solution was drawn into a syringe and added dropwise to a stirred suspension of W(CO)(CS)(diphos)$_2$ (0.15 g, 0.142 mmol) in 80 ml of CH_2Cl_2. The suspension gradually became a clear orange solution. After 30 min of stirring, the solution was filtered and concentrated to 50 ml. Hexane (30 ml) was added, and the evaporation was continued until precipitation was nearly complete. Cooling to −20 °C gave 0.19 g (97% crude yield) of orange solid. The complex was crystallized by dissolving in 10 ml of warm $\mathrm{CS_2}$, filtering, diluting with 10 ml of pentane, and cooling to −20 °C. Anal. Calcd for $\mathrm{W(CO)(CS)(diphos)_2W(CO)_5}$: C, 51.45; H, 2.87; S, 2.32. Found: C, 51.76; H, 3.54; S, 1.75.

Preparation of $\mathbf{[(diphos)_2(CO)W(CSCH_3)]FSO_3}$. A suspension of $\mathrm{W(CO)(CS)(diphos)_2}$ (0.10 g, 0.095 mmol) in 10 ml of $\mathrm{CH_2Cl_2}$ was stirred as $\mathrm{CH_3SO_3F}$ (0.011 g, 0.096 mmol) was added to the mixture. The complex dissolved very rapidly, and the clear solution was filtered and diluted with 15 ml of hexane. Cooling to −20 °C gave pink-orange crystals of the product (0.10 g, 86%): NMR ($\mathrm{DCCl_3}$) τ 2.7 (m, $\mathrm{C_6H_5}$), 7.9 (s, $\mathrm{-CH_3}$), 8.4 (s, $\mathrm{CH_2CH_2}$); $\Lambda = 21.6\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$. Anal. Calcd for $\mathrm{[W(CO)(diphos)_2(CSCH_3)]FSO_3}$: C, 56.60; H, 4.37; S, 5.49. Found: C, 56.35; H, 4.42; S, 5.71.

Preparation of $\mathbf{[(diphos)_2(CO)W(CSC_2H_5)]BF_4}$. A suspension of $\mathrm{W(CO)(CS)(diphos)_2}$ (0.425 g, 0.404 mmol) in 25 ml of $\mathrm{CH_2Cl_2}$ was stirred as $\mathrm{[Et_3O]BF_4}$ (0.078 g, 0.41 mmol) in 2 ml of $\mathrm{CH_2Cl_2}$ was added. The solution was stirred for 10 min and then filtered and concentrated to 10 ml. Addition of hexane (~40 ml) and cooling to 0 °C gave dark pink crystals (0.43 g, 91%): NMR ($\mathrm{DCCl_3}$) τ 2.7 (m, $\mathrm{C_6H_5}$), 7.9 (q, $\mathrm{CH_2}$), 8.6 (s, $\mathrm{CH_2CH_2}$), 9.25 (t, $\mathrm{CH_3}$); $\Lambda = 25.6\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$. Anal. Calcd for $\mathrm{[W(CO)(diphos)_2(CSC_2H_5)]BF_4}$: C, 57.53; H, 4.54; S, 2.74. Found: C, 57.72; H, 4.90; S, 2.27.

Preparation of $\mathbf{[W(CO)_2(diphos)_2(C_2H_5)]BF_4}$. A mixture of $\mathrm{W(CO)_2(diphos)_2}$ (0.50 g, 0.48 mmol) and $\mathrm{[Et_3O]BF_4}$ (0.09 g, 0.475 mmol) in 50 ml of $\mathrm{CH_2Cl_2}$ was stirred until most of the complex had dissolved (~4 h). The solution was filtered and ethyl ether was added until it became cloudy. Cooling to −20 °C gave a yellow crystalline product (0.55 g, ~90%) which contained $\mathrm{CH_2Cl_2}$. After two recrystallizations from $\mathrm{CH_2Cl_2}$–ethyl ether, the product was dried under high vacuum at 100 °C for 6 h. Magnetic susceptibility measurements on a Gouy balance showed that this complex is diamagnetic: NMR ($\mathrm{DCCl_3}$) τ 2.74 (m, $\mathrm{C_6H_5}$), 6.51 (q, $J = 7$ Hz, $\mathrm{CH_2}$), 8.30 (s, $\mathrm{CH_2CH_2}$), 8.79 (t, $J = 7$ Hz, $\mathrm{CH_3}$); $\Lambda = 24.0\ \Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$. Anal. Calcd for $\mathrm{[W(CO)_2(diphos)_2(C_2H_5)]BF_4}$: C, 58.84; H, 4.64; P, 10.86. Found: C, 57.63; H, 4.37; P, 10.49.

Preparation of $\mathbf{W(CO)_4(I)(CSCH_3)}$. A suspension of $\mathrm{Bu_4N[W(CO)_4(CS)(I)]}$ (0.58 g, 0.82 mmol) in a mixture of 50 ml of pentane and 5 ml of $\mathrm{CH_2Cl_2}$ at 0 °C was stirred while $\mathrm{CH_3SO_3F}$ (0.10 g, 0.88 mmol) in 2 ml of $\mathrm{CH_2Cl_2}$ was added dropwise. After being stirred 30 min, the solution was decanted from the dark oil which had formed. The oil was extracted once with pentane, and the combined reaction solution and pentane extract were evaporated. The residue was extracted with pentane (~20 ml) and the solution was concentrated under a stream of $\mathrm{N_2}$ to about 3 ml. Cooling to −80 °C gave yellow crystals (0.07 g, 18%). The complex is quite pure at this stage but may be recrystallized from pentane: NMR ($\mathrm{DCCl_3}$) τ 7.40 (s, $\mathrm{CH_3}$); ^{13}C NMR ($\mathrm{DCCl_3}$) δ(CO) −188.8, δ(CS) −252.7; mass spectrum, parent ion, *m/e* 482 (for ^{184}W-containing ion). Anal. Calcd for $\mathrm{W(CO)_4(I)(CSCH_3)}$: C, 14.93; H, 0.62; I, 26.35. Found: C, 14.19; H, 0.7; I, 25.99.

Preparation of $\mathbf{W(CO)_4(I)(CSC(O)CF_3)}$. A suspension of $\mathrm{Bu_4N[W(CO)_4(CS)(I)]}$ (0.50 g, 0.705 mmol) in a mixture of 3 ml of $\mathrm{CH_2Cl_2}$ and 50 ml of pentane was vigorously stirred for 30 min after the addition of trifluoroacetic anhydride (0.25 g, 1.19 mmol). The yellow solution was then decanted from the dark oil and concentrated to about 5 ml. This solution was filtered under $\mathrm{N_2}$ and cooled to −80 °C to give yellow crystals which rapidly darkened: mass spectrum, parent ion, calcd for $\mathrm{^{182}W(I)(CO)_4(CSC(O)CF_3)}$ *m/e* 561.7905, found 561.7924 ± 0.0028.

Preparation of $\mathbf{W(CO)_4(I)(CSC(O)CH_3)}$. Acetic anhydride (1.0 g, 9.8 mmol) in 10 ml of $\mathrm{CH_2Cl_2}$ was treated with excess gaseous $\mathrm{BF_3}$, and the solution was added to $\mathrm{Bu_4N[W(CO)_4(CS)(I)]}$ (4.0 g, 5.65 mmol) in 125 ml of $\mathrm{CH_2Cl_2}$. The mixture was stirred for 30 min and diluted with 100 ml of pentane, which precipitated a dark oil. The supernatant solution was decanted under $\mathrm{N_2}$, evaporated to dryness, and extracted with pentane. Cooling of the solution at −80 °C gave bright yellow crystals. After two recrystallizations from pentane using Schlenk techniques, the yield was 0.28 g (10%): NMR ($\mathrm{DCCl_3}$) τ 7.60 (s); ^{13}C NMR ($\mathrm{DCCl_3}$) δ(CO) −188.1, δ(C=O) −186.7, δ(CS) −233.9; mass spectrum, parent ion, *m/e* 510 (for ^{184}W-containing ion). Anal. Calcd for $\mathrm{W(CO)_4(I)(CSC(O)CH_3)}$: C, 16.47; H, 0.59; I, 24.90. Found: C, 16.15; H, 0.54; I, 25.70.

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Registry No. $\mathrm{W(CO)_2(CS)(PPh_3)_2Br_2}$, 59831-40-2; $\mathrm{[(2\text{-}CH_3C_6H_4)_3PH)][W(CO)_3(CS)Br_3]}$, 59831-42-4; $\mathrm{W(CO)_2(CS)(diphos)I_2}$, 59831-43-5; $\mathrm{[W(CO)(CS)(diphos)_2I]I_3}$, 59831-45-7; $\mathrm{[HW(CO)(CS)(diphos)_2]CF_3SO_3}$, 56030-98-9; $\mathrm{[HW(CO)_2(diphos)_2]CF_3SO_3}$, 56031-02-8; $\mathrm{(diphos)_2(CO)W(CS\cdot HgCl_2)}$, 54204-86-3; $\mathrm{(diphos)_2(CO)W(CS\cdot HgI_2)}$, 54204-87-4; $\mathrm{[\{(diphos)_2(CO)WCS\}_2Ag]BF_4}$, 54386-82-2; $\mathrm{(diphos)_2(CO)WCSW(CO)_5}$, 54204-89-6; $\mathrm{[(diphos)_2(CO)W(CSCH_3)]FSO_3}$, 59831-47-9; $\mathrm{[(diphos)_2(CO)W(CSC_2H_5)]BF_4}$, 59831-49-1; $\mathrm{[W(CO)_2(diphos)_2(C_2H_5)]BF_4}$, 55914-36-8; $\mathrm{W(CO)_4(I)(CSCH_3)}$, 59831-50-4; $\mathrm{W(CO)_4(I)(CSC(O)CF_3)}$, 59859-51-7; $\mathrm{W(CO)_4(I)(CSC(O)CH_3)}$, 59831-51-5; $\mathrm{W(CO)_2(diphos)_2}$, 28978-17-8; $\mathrm{W(CO)_5(CS)}$, 50358-92-4; $\mathrm{W(CO)_3(CS)(diphos)}$, 59872-37-6; $\mathrm{W(CO)(CS)(diphos)_2}$, 59872-38-7; $\mathrm{Bu_4N[}$*trans*-$\mathrm{W(CO)_4(CS)(I)]}$, 56031-00-6; *trans*-$\mathrm{W(CO)_4(CS)(PPh_3)}$, 50358-94-6.

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