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S-Alkylation and S-Acylation of the Thiocarbonyl Ligand in Metal Complexes

Sir:

We recently reported the formation of stable sulfur-bound adducts of an electron-rich metal thiocarbonyl complex with metal-containing Lewis acids.[1] We now wish to communicate the results of some reactions of electron-rich metal thiocarbonyl complexes with organic electrophiles.

Methyl fluorosulfonate (eq 1) and triethyloxonium tetrafluoroborate react rapidly with a CH_2Cl_2 suspension of

$$W(CO)(CS)(DPE)_2 + CH_3SO_3F \longrightarrow [(DPE)_2(CO)W(CSCH_3)]SO_3F \quad (1)$$

cis-$W(CO)(CS)(DPE)_2$[1] (**1**) (DPE = ethylenebis(diphenylphosphine)) to give the S-alkylated derivatives. Crystallization by addition of hexane and cooling gives excellent yields (>90%) of the orange methylated product[2] and the red ethylated analog.[3] The former exhibits a singlet in its proton NMR spectrum at τ 7.90 assignable to the methyl group and is a two-ion conductor in nitrobenzene (Table I). Its infrared spectrum shows a band near 1260 cm^{-1} which is attributed to the fluorosulfonate anion; there are no other new absorptions in the region of 1160-1400 cm^{-1}. The thiocarbonyl band has apparently shifted to lower frequency and appears overlapped with a DPE ligand absorption, as occurred with the metal complex adducts.[1] The ethylated derivative exhibits no new infrared absorptions from 1160 to 1400 cm^{-1}, suggesting that the thiocarbonyl ν(CS) frequency is lowered in this complex also; unfortunately the 1100-cm^{-1} region is further obscured by absorption of the tetrafluoroborate anion. The NMR spectrum exhibits a quartet at τ 7.90 and a triplet at τ 9.25 (J = 7 Hz), characteristic of an ethyl group. Both complexes are air-stable and can be crystallized from solution repeatedly without decomposition. These derivatives are the first known complexes of the *S*-alkylthiocarbonylium ligand, $CS\text{-}R^+$.

For comparison, the carbonyl analog of **1**, *cis*-$W(CO)_2(DPE)_2$[4] (**2**) was stirred in CH_2Cl_2 with 1 equiv of $(Et_3O)BF_4$ under N_2 for 3 hr. A yellow complex crystallized upon addition of diethyl ether; residual solvent was removed by heating the solid at 100° under vacuum. The air-stable, ionic product contains two terminal carbonyl groups in a nearly trans configuration, as suggested by the intensities of the two ν(CO) absorptions in its ir spectrum (Table I). The same arrangement of two CO groups was seen in the related complexes $[W(CO)_2(DPE)_2HgX]HgX_3$[5] and *trans*-$W(CO)_2(DPE)_2{}^{2+}$.[6] The presence of an ethyl group in the complex is confirmed by the NMR spectrum which has a quartet at τ 6.51 and a triplet at τ 8.79 (J = 7 Hz). This product is therefore formulated as a seven-coordinate W(II) alkyl complex, $[(C_2H_5)W(CO)_2(DPE)_2]BF_4$.

A similar product, $[HW(CO)_2(DPE)_2]CF_3SO_3$, is obtained when **2** is treated with CF_3SO_3H in CH_2Cl_2 under N_2. The yellow, ionic product crystallizes on addition of ether; heating at 100° under vacuum removes the CH_2Cl_2 of solvation to give the pure product. The NMR spectrum of this complex gives definite proof that the metal is the site of protonation. The proton appears as a triplet of triplets (J_{PMH} = 74 Hz, $J_{P'MH}$ = 13 Hz) centered at 4.91 ppm upfield from TMS. This splitting pattern was previously seen for $[HMo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]HCl_2$[7] and is evidence that the carbonyl groups are trans to each other with the proton coordinating through an octahedral face.

The thiocarbonyl complex **1** also is protonated by CF_3SO_3H, but, in contrast to its reactions with Et_3O^+ and $MeSO_3F$, the addition occurs at the metal. The infrared spectrum of this product shows that *both* the carbonyl ν(CO) and thiocarbonyl ν(CS) frequencies have increased; the thiocarbonyl absorption appears as a strong, distinctive band at 1207 cm^{-1}. Further evidence that the metal is protonated is provided by the NMR spectrum. The proton again appears as a triplet of triplets (J_{PMH} = 72 Hz, $J_{P'MH}$ = 13 Hz) centered at 2.79 ppm upfield from TMS. This pattern indicates that the complex has rearranged to the geometry in which the CO and CS groups are trans to each other and the proton occupies an octahedral face, as suggested for $HW(CO)_2(DPE)_2{}^+$. The difference in chemical shifts of the metal protons in the two metal hydride complexes is an indication of a substantial decrease in electron density at the metal caused by replacing CO with CS.

Just as metal-containing Lewis acids were found to be unreactive toward them, $W(CO)_5(CS)$,[8] $W(CO)_4(CS)(PPh_3)$,[8] and $W(CO)_3(CS)(DPE)$[1] (having ν(CS) frequencies of 1258, 1247, and 1215 cm^{-1}, respectively) also do not react with the triethyloxonium ion. The metal thiocarbonyl anion, *trans*-$IW(CO)_4(CS)^-$ (**3**), however, does react with alkylating agents. This thiocarbonyl derivative was prepared in good yield (>80%) by heating a tetrahydrofuran solution of $W(CO)_5(CS)$ and equimolar tetra-*n*-butylammonium iodide at 50° for 2 hr; it crystal-

Table I. Infrared and Conductivity Measurements

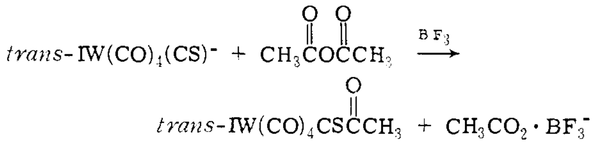
Compound	ν(CO),[a] cm^{-1}	ν(CS),[a] cm^{-1}	Λ,[b] ohm^{-1} cm^2 mol^{-1}
$W(CO)(CS)(DPE)_2$	1838 s	1161 s	
$[W(CO)(DPE)_2(CSCH_3)]FSO_3$	1898 s	*c*	21.6
$[W(CO)(DPE)_2(CSC_2H_5)]BF_4$	1898 s	*c*	25.6
$[HW(CO)(CS)(DPE)_2]CF_3SO_3$	1958 s	1207 s	19.8
$W(CO)_2(DPE)_2$	1846 s, 1781 s		
$[(C_2H_5)W(CO)_2(DPE)_2]BF_4$	1970 vw, 1864 vs		24.0
$[HW(CO)_2(DPE)_2]CF_3SO_3$	1968 w, 1862 vs		19.8
$(n\text{-}C_4H_9)_4N[IW(CO)_4(CS)]$	2062 w, 1947 vs	1195 s	25.6
$IW(CO)_4(CSCH_3)$	2115 w, 2033 vs[d]	1118 m[d]	
$IW(CO)_4[CSC(O)CH_3]$	2124 w, 2049 vs, 2040 vs[d,e]	1081 m[d]	
$IW(CO)_4[CSC(O)CF_3]$	2137 w, 2057 vs, 2052 vs[d,f]	*g*	

[a] Recorded in CH_2Cl_2 solvent unless specified otherwise. [b] Approximately 10^{-3} *M* in nitrobenzene. [c] This peak overlaps a DPE ligand absorption near 1095 cm^{-1}. [d] Pentane solution. [e] Also ν(C=O) at 1753 cm^{-1}. [f] Also ν (C=O) at 1737 cm^{-1}. [g] Obscured by C–F absorption.

lized upon addition of diethyl ether and cooling. The complex reacts with methyl fluorosulfonate (eq 2) or triethyloxonium tetrafluoroborate to give neutral, pentane-soluble products. These reactions differ from the reported reaction[9] of $IW(CO)_5^-$ with Et_3O^+ in which EtI is produced. The product of the methyl fluorosulfonate reaction in CH_2Cl_2 was isolated in low yield by removing the solvent at reduced pressure, extracting the residue with pentane, and crystallizing at −80°. The complex[10] is quite air-sensitive in solution but more stable in the solid state. The $\nu(CO)$ peaks occur at relatively high frequencies in the ir spectrum, and the thiocarbonyl $\nu(CS)$ absorption appears (Table I) as a sharp peak of medium intensity nearly 80 cm^{-1} lower than in the thiocarbonyl anion, **3.** The complex exhibits a singlet in its NMR spectrum at τ 7.40, and an abundant parent ion is observed in its mass spectrum.

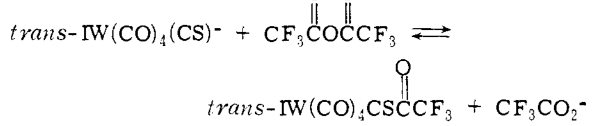
$$\textit{trans}\text{-}IW(CO)_4(CS)^- + CH_3SO_3F \longrightarrow \textit{trans}\text{-}IW(CO)_4(CSCH_3) + SO_3F^- \quad (2)$$

Although **3** does not react with acetic anhydride in CH_2Cl_2, the reaction does proceed in the presence of BF_3 (eq 3). The neutral S-acetylthiocarbonylium complex[11] has $\nu(CO)$ bands (Table I) at higher frequencies than the methylated derivative, and the thiocarbonyl $\nu(CS)$ absorption is lowered by more than 110 cm^{-1} relative to that of **3.** The splitting seen in the strong $\nu(CO)$ E band and the appearance of a B_1 band suggest that the asymmetric acylthiocarbonylium ligand causes some distortion of the local C_{4v} symmetry of the complex.[12] Only a singlet at τ 7.60 is observed in its proton NMR spectrum at room temperature, and the acyl carbonyl $\nu(CO)$ absorption is seen as a sharp peak at 1753 cm^{-1}.



$$\textit{trans}\text{-}IW(CO)_4(CS)^- + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{BF_3} \textit{trans}\text{-}IW(CO)_4CS\overset{O}{\overset{\|}{C}}CH_3 + CH_3CO_2\cdot BF_3^- \quad (3)$$

Trifluoroacetic anhydride also reacts with **3** to yield a similar product (eq 4). When carried out in CH_2Cl_2 the ir spectrum shows complete consumption of the starting complex, but removal of the solvent under reduced pressure also removes the trifluoroacetic anhydride, reversing the reaction and leaving mainly **3.** When the reaction is carried out in pentane, in which the trifluoroacetate salt product is insoluble, the solution may be concentrated and cooled to −80° to yield yellow crystals. This product is quite unstable, and the crystals darken even on standing in the mother liquor under N_2 at −80°. An elemental analysis was not attempted, but the high-resolution mass spectrum supports the assigned formula.[13] The acyl carbonyl exhibits a single band at 1737 cm^{-1}. Although the $\nu(CS)$ absorption could not be located because of the strong C-F absorption, its very high-frequency metal carbonyl $\nu(CO)$ bands[14] show that the S-trifluoroacetylthiocarbonylium ligand is a strong electron acceptor.



$$\textit{trans}\text{-}IW(CO)_4(CS)^- + CF_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CF_3 \rightleftharpoons \textit{trans}\text{-}IW(CO)_4CS\overset{O}{\overset{\|}{C}}CF_3 + CF_3CO_2^- \quad (4)$$

Analogous O-alkylcarbonylium and O-acylcarbonylium complexes derived from metal carbonyl complexes are unknown.[16] That the reactions of cis-$W(CO)(CS)(DPE)_2$ with alkylating agents yield only the S-alkylated $W(CO)(DPE)_2(CSR)^+$ products shows that the sulfur of the CS group is more nucleophilic than the oxygen of the carbonyl. While the carbonyl groups in cis-$W(CO)_2(DPE)_2$ should be somewhat more nucleophilic than the CO in $W(CO)(CS)(DPE)_2$ (because of the greater π acidity of CS relative to CO), alkylating agents still do not react with a carbonyl oxygen but at the metal instead.

In metal carbonyl chemistry CO stretching frequencies or force constants are useful indicators of the electron density on the carbonyl oxygen atom.[17] The electron density on the sulfur of a metal thiocarbonyl complex is apparently influenced in much the same manner. Our results indicate that metal thiocarbonyl complexes with $\nu(CS)$ absorptions below approximately 1200 cm^{-1} will be reactive toward electrophiles such as those described in this and our preceding communication.[1] Complexes with $\nu(CS)$ frequencies above this value have been found not to react.

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(3) Anal. Calcd for $[(DPE)_2(CO)W(CSC_2H_5)]BF_4$: C, 57,53; H, 4.54; S, 2.74. Found: C, 57.72; H, 4.90; S, 2.27.
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Interaction of Paramagnetic Niobium(IV) Hydrides with Olefins. Electron Spin Resonance Studies of Metastable Intermediates

Sir:

We wish to describe a useful method to probe for *transient* species present during the reaction of paramagnetic metal complexes with olefins, involving the application of careful temperature modulation to electron spin resonance (ESR) techniques. Although a variety of catalytic reactions of olefins involve transition metal hydrides and alkyls as intermediates, due to their transitory existence little is known about the actual metal species participating in these reactions.[1] We have felt that metastable paramagnetic metal