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Preliminary communication

POSITIVELY CHARGED LIGANDS. THE COORDINATION BEHAVIOR OF SULFONIUM CATIONS

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SUMMARY

It is shown that alkylation of the metal sulfide complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2SRR'$; $R=R'=CH_3$; $R=CH_3$, $R'=C_6H_5$; $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2S(CH_3)_2$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2S(CH_3)_2$; occurs at the sulfur atom and results in the formation of coordinated sulfonium cations. Spectroscopic studies show that this new ligand is strongly electron withdrawing. The coordinated sulfonium cation can be readily displaced from the metal atom by neutral ligands, however, anions cause dealkylation and formation of the original metal sulfide complexes.

Although the ability of a small molecule to serve as a ligand depends principly on its ability to provide electrons for donation to a metal atom, several poorly donating molecules have also been shown to be very effective and useful ligands. These latter molecules invariably possess a supplementary bonding interaction known as π-backbonding, which makes a significant contribution toward the stabilization of that metal-ligand bond.[1] We now wish to report our recent finding that sulfonium cations, R_3S^+, which are presumably also very poor donors, may form strong metal-ligand bonds.

TABLE I

Compound	M.P.	Infrared (ν-CO)	PMR[c] (ppm)	Molar conductivity[d,e]
$(C_5H_5)Mn(CO)_2(S(CH_3)_3)BF_4$, V	155.0-155.5°C (dec)	1983, 1923[a]	5.1 s (5) C_5H_5 3.3 s (9) CH_3	147
$(C_5H_5)Mn(CO)_2((CH_3)_2S(C_6H_5))BF_4$, VI	94.5-95.5°C (dec)	1980, 1920[a]	8.26-7.70 m (5) C_6H_5 5.02 s (5) C_5H_5 3.95 s (6) CH_3	152
$(CH_3C_5H_4)Mn(CO)_2(S(CH_3)_3)BF_4$, VII	94.5-97.0°C	1977, 1915[a]	5.08 m (2), 4.80 m (2) C_5H_4 3.57 s (9) $S(CH_3)_3$ 1.98 s (3) $(C\text{-}CH_3)$	150
$(C_6H_6)Cr(CO)_2(S(CH_3)_3)OSO_2F$, VIII	94.5-95.5°C (dec)	1930, 1860[b]	4.85 s (6) C_6H_6 2.85 s (9) CH_3	140

a = CH_2Cl_2; b = acetone; c = d_6-acetone; d = acetonitrile, 25°C, approx 10^{-3} $\underline{M}$; e = $cm^2 \cdot ohm^{-1} \cdot mole^{-1}$

Treatment of the organometallic sulfide complexes I-IV with strong alkylating agents has yielded alkylation of the uncoordinated lone pair of electrons on the sulfide atom and formation of complexes, V-VIII, which contain coordinated sulfonium ligand groupings, eq. 1,

1) $$\mathrm{MSRR'} + \mathrm{CH_3X} \xrightarrow[\mathrm{CH_2Cl_2}]{\substack{25^\circ \\ \text{2-24 hrs.}}} [\mathrm{MS(CH_3)RR'}]^+$$

$M = (\eta^5\text{-}C_5H_5)Mn(CO)_2$, $R=R'=CH_3$; I $X = [(CH_3)_2O\cdot BF_4]$

$M = (\eta^5\text{-}C_5H_5)Mn(CO)_2$, $R=CH_3, R'=C_6H_5$; II $X =$ "

$M = (\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2$, $R=R'=CH_3$; III $X =$ "

$M = (\eta^6\text{-}C_6H_6)Cr(CO)_2$, $R=R'=CH_3$; IV $X = SO_3F$

Pertinent spectral and physical properties are listed in Table I.* The observation of a single methyl resonance of intensity nine in compounds, V, VII, and VIII, confirms that the alkylation has taken place at the sulfur atom. Molar conductivities, Λ_M, range from 140-152 $ohm^{-1}\cdot cm^2\cdot mole^{-1}$, and are characteristic of 1:1 electrolytes in acetonitrile solvent.[2] Evidence for the strength of the association of the sulfonium ligand to the metal atom was provided by a ^1H nmr spectrum of a 1:1 mixture of VII and $[(CH_3)_3S]^+[BF_4]^-$. At 27°C, the spectrum showed no evidence of exchange occuring between the coordinated and uncoordinated $(CH_3)_3S^+$ ligand. In d_6-acetone the chemical shift difference between the resonances of the methyl groups on the coordinated and uncoordinated ligands was 40.5 Hz (1 ppm = 90 Hz). From this, we can estimate that the rate of exchange can be no greater than 90 sec^{-1}, and therefore $\Delta G^*_{300^\circ}$ for this process must be greater than 15 kcal./mole.[3]

The net electronic effect of the sulfonium ligand on the metal complex is revealed by examination of the stretching frequencies of the carbonyl ligands. In all cases, there is a sharp increase (30-40 cm^{-1}) in frequency compared to those of the starting sulfide complexes.[4] This indicates that although it does

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*Satisfactory elemental analyses have been obtained.

serve as a donor, it is also a strongly electron withdrawing ligand. Strohmeier has classified the electron withdrawing character of a series of phosphine ligands in $C_5H_5Mn(CO)_2PR_3$ complexes.[5] In comparison, we see that the sulfonium ligand is very similar to PCl_3 and $PCl_2(C_6H_5)$, but is not as electron withdrawing as PF_3. As is believed to occur with phosphines[1], we believe that the ability of the sulfonium cation to serve as a ligand derives largely through an ability to engage in a form of d → d π backbonding.

Although the sulfonium ligand is firmly attached to the metal atom, with moderate heating, it is easily replaced by neutral ligands to give the corresponding monosubstituted, neutral complexes, eq. 2.

$$2)\quad [CH_3C_5H_4Mn(CO)_2S(CH_3)_3]^+ + L \xrightarrow[\text{THF}]{\text{reflux}} CH_3C_5H_4Mn(CO)_2L + S(CH_3)_3^+$$

$$L = P(C_6H_5)_3,\ P(OCH_3)_3,\ CNCH_3,\ \text{and}\ (CH_3)_2SO$$

However, with anionic ligands attack occurs at the sulfonium ligand and gives dealkylation with formation of the metal sulfide complex, eq. 3.

$$3)\quad [(CH_3C_5H_4)Mn(CO)_2S(CH_3)_3]^+ + L \xrightarrow[CH_3OH]{\text{reflux}} (CH_3C_5H_4)Mn(CO)_2S(CH_3)_2$$

$$L = OCH_3^-,\ CN^-$$

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