

Positively Charged Ligands. The Coordination Behavior of Sulfonium Cations

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Abstract: Treatment of the sulfide complexes $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{SRR}'$ (I, R = CH₃, R' = CH₃; II, R = CH₃, R' = C₆H₅), $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2$ (III), and $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{S}(\text{CH}_3)_2$ (IV) with strong alkylating agents such as $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$, $(\text{C}_2\text{H}_5)_3\text{O}^+\text{PF}_6^-$, or $\text{CH}_3\text{SO}_3\text{F}$ has resulted in alkylation of the lone pair of electrons on the coordinated dialkyl sulfide ligand and formation of the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{SR}_2\text{R}']^+\text{BF}_4^-$ (V, R = CH₃, R' = CH₃; VI, R = CH₃, R' = C₆H₅), $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{SR}_2\text{R}']^+\text{X}$ (VII, R = CH₃, R' = CH₃, X = BF₄⁻; VIII, R = CH₃, R' = C₂H₅, X = PF₆⁻), and $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2\text{S}(\text{CH}_3)_3]^+\text{[SO}_3\text{F]}^-$ (IX), containing the first examples of coordinated sulfonium ions. All products are 1:1 electrolytes in acetonitrile solvent. Infrared spectra show that the sulfonium ligand is strongly electron withdrawing. Details of the nature of the metal-sulfur bond have been revealed by an x-ray crystallographic analysis of VIII. Compound VIII crystallizes in the space group $P\bar{1}$, [C_i], no. 2. Unit cell parameters are $a = 8.945$ (2), $b = 9.324$ (2), $c = 10.544$ (2) Å, $\alpha = 92.01$ (2)°, $\beta = 94.28$ (2)°, $\gamma = 98.36$ (2)°, $V = 866.7$ Å³; $Z = 2$; $\rho_{\text{calcd}} = 1.637$ g/cm³, $\rho_{\text{obsd}} = 1.654$ g/cm³. The structure was solved by heavy atom methods; 2179 reflections having $F_o^2 > 3.0\sigma(F_o^2)$ were refined to the conventional residuals $R = 0.064$ and $R_w = 0.083$. The structure consists of discrete ions of $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2(\text{C}_2\text{H}_5)]^+$ and PF₆⁻. An unusually short Mn-S bond of 2.167 (1) Å has been interpreted in terms of partial d-d π back-bonding. Reactions of the sulfonium complexes with neutral ligands lead to displacement of the sulfonium cation and formation of the corresponding mono-substituted metal complexes. Anions dealkylate the sulfonium ligand and produce the original metal-sulfide complexes.

Introduction

The chemistry of sulfonium cations has already been shown to be wide and varied. They serve as precursors to the valuable class of alkylidene transfer reagents, the sulfur ylides.¹ Biochemically, they have been demonstrated as key intermediates in a variety of valuable transmethylation reactions.² We now wish to report a new feature of their chemistry which may have considerable scope and generality and may have profound implications in some of the previously reported areas.

The sulfonium cation contains a lone pair of electrons on the sulfur atom. In spite of a formal positive charge, it is conceivable that this pair of electrons could coordinate to metal ions. Several poorly donating molecules such as carbon monoxide³ and nitric oxide⁴ (sometimes visualized as NO⁺ when coordinated) are well known to be valuable ligands. These ligands invariably possess a supplementary bonding interaction known as π back-bonding which makes a substantial contribution toward the stabilization of the coordinate bond. A d-d π back-bonding interaction may also be available to a coordinated sulfur cation.

We wish to report that we have now prepared the first examples of coordinated sulfonium ions.⁵ Anticipating a low nucleophilicity for the sulfonium cations, we have chosen to synthesize this ligand through the alkylation of metal coordinated dialkyl sulfides. This method works quite well for the systems reported here, although a previous report for other systems showed that coordinated sulfonium ligands were not obtained.⁶

Experimental Section

General. All reactions were performed under an inert atmosphere of prepurified nitrogen. The solvents THF and hexanes were dried by refluxing over sodium-benzophenone and distilled just prior to use. CH₂Cl₂ solvent was stored for several weeks over molecular sieves and deoxygenated by bubbling nitrogen through it thoroughly before use. The reagents $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$, $(\text{CH}_3\text{CH}_2)_3\text{O}^+\text{PF}_6^-$, $\text{CH}_3\text{SO}_3\text{F}$, and the various dialkyl sulfides were obtained commercially and used without further purification. The metal-sulfide complexes were prepared by established procedure.⁷ Infrared spectra were recorded on a Perkin-Elmer 237 infrared spectrophotometer and were calibrated with polystyrene 1601.4 cm⁻¹. ¹H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer and were calibrated with Me₄Si. Elemental micro-

analyses were performed by Midwest Microlab Ltd., Indianapolis, Ind. Conductivity measurements were obtained under a nitrogen atmosphere at room temperature using a Beckman Instruments Model A-01 conductivity cell and Model RC16B2 conductivity bridge. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Syntheses of Sulfonium Complexes. All complexes are prepared similarly. A sample preparation is listed below.

To a solution of 0.34 g (1.43 mmol) of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2$ dissolved in 100 mL of CH₂Cl₂ at -78 °C was added 0.21 g (1.43 mmol) of $[(\text{CH}_3)_3\text{O}]^+\text{BF}_4^-$. With stirring the reaction mixture was allowed to warm to room temperature and to stir for 24 h. Light yellow flakes of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_3]^+\text{BF}_4^-$ precipitated from the reaction solution. The reaction solvent was removed and the product recrystallized from acetone/hexanes at -20 °C, yield 0.420 g (86%). All the manganese compounds are easily chromatographed over Al₂O₃·6% H₂O and eluted with methylene chloride/acetone. Pertinent spectral and physical properties of all compounds are listed in Table I.

Reactions of VII with Uncharged Ligands. VII (0.5 g) was allowed to react with stoichiometric amounts of each of the compounds P(C₆H₅)₃, P(OCH₃)₃, CNCH₃, and (CH₃)₂SO in 100 mL of refluxing THF for 2 h. Each of the known compounds $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{L}$, L = P(C₆H₅)₃, P(OCH₃)₃, CNCH₃, and (CH₃)₂SO, was chromatographically isolated in yields ranging from 15 to 80%. Uncoordinated (CH₃)₃S⁺ was observed spectroscopically in some of these reactions.

Reactions of VII with Anions. Approximately 1-mmol quantities of VII were allowed to react with equivalents of either KCN or NaOC₂H₅ in refluxing methanol for about 4 h. In each case $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2$ was the only metal carbonyl compound that was subsequently identified.

Structural Analysis of VIII. Collection and Reduction of Data. Large crystals of VIII were grown from CH₂Cl₂ solutions cooled to -20 °C. A crystal suitable for diffraction analysis was cleaved from one of these large crystals, and was sealed in a thin-walled capillary. Its dimensions were 0.16 × 0.18 × 0.35 mm. An orientation matrix and tentative unit cell were derived by the centering and processing of 25 randomly collected reflections on an Enraf-Nonius CAD-4 automatic diffractometer. A unit cell having triclinic symmetry was selected. The refined unit cell was subsequently obtained from the centering and least-squares refinement of 24 high-angle ($2\theta > 40^\circ$) reflections. Crystal data and data collection parameters are listed in Table II. The crystal faces were identified as {001}, {021}, and {221}. A unique set of data was collected in the scan range $2\theta = 0\text{--}50^\circ$. Four standard reflections monitored approximately every 100 reflections showed an approximately 5% decrease in intensity during collection. A linear

Table I

Compd	Mp, °C	IR (ν CO), cm ⁻¹	¹ H NMR, ^c ppm	Molar conduc- tivity ^{d,e}	Yield, %	Anal. (theory, %) (found, %)		
						C	H	S
(η^5 -C ₅ H ₅)Mn(CO) ₂ (S(CH ₃) ₃)BF ₄ (V)	115.0–115.5 dec	1983, 1923 ^a	5.1 s (5) C ₅ H ₅ 3.3 s (9) CH ₃	147	86	35.32 (35.48)	4.15 (4.40)	
(η^5 -C ₅ H ₅)Mn(CO) ₂ ((CH ₃) ₂ S(C ₆ - H ₅))BF ₄ (VI)	94.5–95.5 dec	1980, 1920 ^a	8.25–7.70 m (5) C ₆ H ₅ 5.02 s (5) C ₅ H ₅ 3.95 s (6) CH ₃	152	85	44.81 (44.13)	4.01 (4.29)	7.97 (7.54)
(η^5 -CH ₃ C ₅ H ₄)Mn(CO) ₂ (S(CH ₃) ₃)BF ₄ (VII)	94.5–97.0	1977, 1915 ^a	5.08 m (2), 4.80 m (2) C ₅ H ₄ 3.57 s (9) S(CH ₃) ₃ 1.98 s (3) (C-CH ₃)	150	85	37.32 (35.17)	4.56 (4.45)	9.06 (8.93)
(η^5 -CH ₃ C ₅ H ₄)Mn(CO) ₂ (S- (CH ₃) ₂ (C ₂ H ₅))PF ₆ (VIII)	111.5–112.0	1975, 1915 ^a	5.03 m (2), 4.77(2) m C ₅ H ₄ 3.70 q (2), <i>J</i> = 7.0, CH ₂ 3.84 s (6) SCH ₃ 2.02 s (3) C ₅ H ₄ CH ₃ 1.57 t (3) <i>J</i> = 7.0, CH ₃	134	59	<i>f</i>		
(η^6 -C ₆ H ₆)Cr(CO) ₂ (S(CH ₃) ₃)SO ₃ F (IX)	94.5–95.5 dec	1930, 1860 ^b	4.85 s (6) C ₆ H ₆ 2.85 s (9) CH ₃	140	78	36.46 (35.93)	4.17 (4.30)	17.70 (17.27)

^a CH₂Cl₂. ^b Acetone. ^c Acetone-*d*₆. ^d Acetonitrile, 25 °C, ~10⁻³ M. ^e Cm² ohm⁻¹ mol⁻¹. *f* Verified crystallographically.

correction was later applied to the data for this decay. A total of 3192 reflections were collected. These yielded 2179 unique reflections conforming to the relation $F_o^2 > 3.0\sigma(F_o^2)$ after correction for Lorentz and polarization effects.⁸ Only these data were used in the subsequent solution and refinement of the structure. $\sigma(I)$ was determined from counting statistics employing a *p*-factor value of 0.02.⁹ The linear absorption coefficient for VIII is 10.72 cm⁻¹ and an absorption correction was applied to the data using the Gaussian integration method and a grid of 6 × 6 × 6. Minimum and maximum transmission coefficients were 0.745 and 0.918, respectively.

Solution and Refinement of the Structure. The space group $P\bar{1}$ was selected and later shown to be correct by the successful solution and refinement of the structure. The structure was solved by the heavy-atom method. A three-dimensional Patterson synthesis revealed the coordinates of the manganese, sulfur, and phosphorus atoms. Full matrix least-squares refinement (based on *F*) of these three atoms with isotropic temperature factors produced values for the residuals,

$$R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$$

$$R_w = \frac{(\sum w_i(|F_o| - |F_c|)^2 / \sum w_i F_o^2)^{1/2}}$$

of 0.346 and 0.441, respectively. The weights, *w*, were taken as 1/ $\sigma(F_o)^2$, and the function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$. Neutral atom scattering factors were calculated from the tables of Cromer and Waber.¹⁰ Anomalous dispersion corrections¹¹ were made for all nonhydrogen atoms. A difference Fourier synthesis at this time revealed the positions of all remaining nonhydrogen atoms. Three cycles of refinement on all atoms with isotropic temperature factors reduced the values of the residuals to 0.137 and 0.193. Three additional cycles of full matrix refinement with all atoms given anisotropic thermal parameters reduced the residuals to 0.081 and 0.121. A difference Fourier synthesis next revealed the positions of many of the hydrogen atoms in chemically reasonable positions within the top 35 peaks listed. The positions of the remaining hydrogen atoms were calculated assuming idealized tetrahedral geometry and bond distances of 0.95 Å.¹² In subsequent refinements contributions from the hydrogen atoms were added to the structure factor calculations, but these atoms were not refined. Least-squares refinement converged after six additional full matrix cycles and produced the final residuals $R = 0.064$ and $R_w = 0.083$. The largest shift/error parameter on the final cycle was 0.13 for a fluorine atom. The largest shift/error among nonfluorine atoms was 0.02. The error in an observation of unit weight was 4.67. The largest peaks in a final difference Fourier synthesis were approximately 1.0 e/Å³, slightly larger than hydrogen atoms, and were in the vicinity of the PF₆⁻ ion. These may have been due to some minor disorder of the ion which could also have been responsible for the slight deviations of this ion from idealized octahedral geometry that we observed (vide infra). The remainder of the final difference Fourier synthesis was featureless. A list of final atomic coordinates and thermal parameters is presented in Tables III and IV, respectively.

Table II. Experimental X-Ray Diffraction Data for [(η^5 -CH₃C₅H₄)Mn(CO)₂(S(CH₃)₂C₂H₅)]PF₆

A. Crystal Data	
Space group	$P\bar{1}$, <i>C</i> ₁ , no. 2
Temp	25 °C
Cell parameters	<i>a</i> = 8.945 (2) Å <i>b</i> = 9.324 (2) Å <i>c</i> = 10.544 (2) Å α = 92.01 (2)° β = 94.28 (2)° γ = 98.36 (2)° <i>V</i> = 866.7 Å ³
<i>Z</i>	2
ρ_{calcd}	1.637 g cm ⁻³
ρ_{exptl}	1.654 g cm ⁻³ (floatation)
μ	10.723 cm ⁻¹
B. Intensity Measurement Data	
Radiation	Mo K α 0.710 69
Monochromator	Graphite
Takeoff angle	2.5°
Detector aperture	Horizontal, 3 mm (increasing with 2 θ angle); vertical, 4 mm
Reflections measured	+ <i>h</i> , ± <i>k</i> , ± <i>l</i>
12 θ data range	0.0–50.0°
Scan type	$\omega/2\theta$ (moving crystal–moving counter)
θ scan speed	Variable (1.1–6.7 deg/min)
θ scan width	<i>A</i> + <i>B</i> tan θ <i>A</i> = 0.70 <i>B</i> = 0.35
No. data	3192
No. obsd data	
$F^2 < 3\sigma(F^2)$	2179
<i>p</i> factor	0.02

Bond distances and angles are presented in Tables V and VI. Table VII includes interionic contacts and least-squares planes. Tables of final observed and calculated structure factor amplitudes and root mean square amplitudes of vibration are available.¹³

Results

Treatment of the organometallic sulfide complexes I–IV with strong alkylating agents such as (CH₃)₃O⁺BF₄⁻, (CH₃CH₂)₃O⁺PF₆⁻, or CH₃SO₃F has resulted in alkylation of the lone pair of electrons on the sulfur atom and the formation of the complexes V–IX:



Table III. Atomic Coordinates for $[(\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5)]\text{PF}_6^a$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mn	0.1213 (1)	0.3531 (1)	0.1959 (1)	H11	0.266	0.656	0.389
S	0.2944 (2)	0.2141 (2)	0.2219 (2)	H12	0.135	0.743	0.392
P	0.2941 (2)	0.1163 (2)	0.7020 (2)	H13	0.209	0.718	0.266
F1	0.2575 (9)	0.2351 (7)	0.7981 (6)	H2	-0.083	0.550	0.191
F2	0.4468 (8)	0.1369 (11)	0.7771 (7)	H3	-0.185	0.291	0.235
F3	0.2508 (13)	0.0009 (8)	0.7945 (6)	H4	-0.012	0.197	0.391
F4	0.1415 (8)	0.0957 (13)	0.6304 (8)	H5	0.199	0.401	0.458
F5	0.3378 (12)	0.2339 (8)	0.6129 (6)	H31	0.465	0.094	0.109
F6	0.3298 (11)	-0.0027 (8)	0.6093 (6)	H32	0.268	0.063	0.029
O1	0.2925 (7)	0.5536 (6)	0.0299 (5)	H33	0.419	0.238	0.027
O2	-0.0446 (7)	0.1781 (7)	-0.0208 (5)	H41	0.299	0.000	0.277
C1	0.2263 (8)	0.4736 (8)	0.0955 (7)	H42	0.199	0.063	0.389
C2	0.0245 (8)	0.2434 (9)	0.0624 (7)	H43	0.166	0.000	0.221
CP1	0.0988 (8)	0.5311 (8)	0.3293 (7)	H51	0.432	0.281	0.443
CP2	-0.0362 (9)	0.4895 (9)	0.2468 (8)	H52	0.533	0.188	0.305
CP3	-0.0940 (9)	0.3479 (11)	0.2669 (11)	H61	0.465	0.500	0.305
CP4	-0.0014 (10)	0.2959 (9)	0.3578 (8)	H62	0.555	0.430	0.209
CP5	0.1180 (9)	0.4079 (8)	0.3962 (7)	H63	0.621	0.462	0.349
CP11	0.1896 (13)	0.6752 (11)	0.3453 (10)				
C3	0.3713 (10)	0.1565 (10)	0.0804 (8)				
C4	0.2399 (10)	0.0434 (9)	0.2914 (9)				
C5	0.4651 (8)	0.2806 (9)	0.3274 (7)				
C6	0.5360 (9)	0.4289 (11)	0.2985 (10)				

^a Hydrogen atoms were not refined.

Table IV. Thermal Parameters for $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5)]\text{PF}_6$

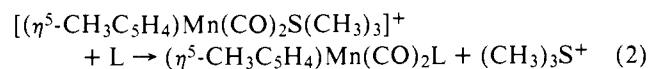
Atom	$\beta(1,1)^{a-c}$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Mn	0.113 (1)	0.107 (1)	0.079 (1)	0.054 (2)	0.016 (2)	0.028 (2)
S	0.131 (2)	0.108 (2)	0.066 (2)	0.070 (3)	0.006 (3)	0.013 (3)
P	0.163 (3)	0.125 (2)	0.079 (2)	0.075 (4)	0.022 (4)	0.048 (4)
F1	0.640 (16)	0.330 (10)	0.160 (7)	0.530 (18)	0.066 (18)	0.016 (15)
F2	0.267 (11)	0.717 (22)	0.278 (11)	0.318 (25)	-0.153 (18)	-0.118 (27)
F3	1.120 (30)	0.250 (10)	0.173 (8)	-0.430 (30)	0.090 (30)	0.120 (20)
F4	0.298 (12)	0.740 (26)	0.341 (12)	0.152 (30)	-0.291 (20)	-0.057 (31)
F5	0.940 (27)	0.300 (12)	0.162 (7)	-0.272 (22)	0.191 (23)	0.176 (15)
F6	0.961 (20)	0.444 (11)	0.155 (7)	0.889 (20)	0.046 (21)	-0.112 (16)
O1	0.230 (10)	0.198 (9)	0.137 (6)	0.040 (16)	0.087 (13)	0.138 (12)
O2	0.230 (10)	0.245 (11)	0.118 (6)	0.034 (17)	-0.095 (13)	-0.071 (14)
C1	0.153 (10)	0.136 (10)	0.090 (7)	0.065 (16)	0.004 (15)	0.060 (14)
C2	0.147 (11)	0.155 (11)	0.104 (8)	0.044 (18)	0.000 (16)	0.030 (16)
CP1	0.176 (10)	0.106 (9)	0.113 (8)	0.044 (17)	0.122 (15)	0.001 (15)
CP2	0.195 (12)	0.189 (11)	0.145 (10)	0.207 (17)	0.007 (19)	0.047 (18)
CP3	0.116 (11)	0.224 (15)	0.278 (15)	0.002 (23)	0.118 (22)	-0.123 (27)
CP4	0.253 (14)	0.138 (11)	0.169 (9)	0.050 (21)	0.242 (19)	0.080 (18)
CP5	0.200 (10)	0.159 (10)	0.075 (7)	0.133 (17)	0.083 (15)	0.042 (14)
CP11	0.410 (22)	0.154 (14)	0.197 (12)	0.038 (30)	0.260 (26)	-0.040 (23)
C3	0.250 (13)	0.246 (13)	0.101 (8)	0.278 (20)	0.044 (18)	0.021 (19)
C4	0.228 (14)	0.133 (11)	0.170 (11)	0.121 (20)	0.013 (22)	0.067 (19)
C5	0.138 (10)	0.163 (11)	0.125 (9)	0.080 (17)	-0.046 (16)	0.028 (17)
C6	0.116 (11)	0.227 (15)	0.225 (14)	0.017 (23)	-0.047 (22)	-0.008 (26)

^a The form of the expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b Anisotropic temperature factors multiplied by 10.0. ^c Hydrogen atoms were assigned isotropic thermal factors of 5.0. This was not varied in the refinement.

Pertinent physical and spectral properties are listed in Table I. The carbonyl stretching vibrations in the sulfonium complexes show significant increases in frequency (30–40 cm^{-1}) compared to those of the starting sulfide complexes.⁷ Molar conductivities, Δ_M , range from 134 to 152 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ in acetonitrile solvent and are characteristic of 1:1 electrolytes.¹⁴ The ^1H NMR spectra of compounds V, VII, and IX show a single methyl resonance of intensity nine, and confirm that methylation has occurred at the sulfur atom. Evidence for the kinetic stability of the metal-sulfonium association was provided by an ^1H NMR investigation of a mixture of VII and $[(\text{CH}_3)_3\text{S}]^+\text{BF}_4^-$. At 27 $^\circ\text{C}$ the spectrum showed no evidence of exchange occurring between coordinated and uncoordinated $(\text{CH}_3)_3\text{S}^+$ ligand. The shift difference observed between the

coordinated and uncoordinated ligands was 40.5 Hz. From this we can estimate that the rate of exchange can be no greater than 90 s^{-1} , and therefore ΔG^\ddagger_{300} for this process must be greater than 15 kcal/mol.¹⁵

The sulfonium ligand can, however, be displaced from the metal atom. This is demonstrated by the reactions with uncharged ligands and leads to the formation of monosubstituted manganese complexes and uncoordinated sulfonium cations (eq 2, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OCH}_3)_3$, CNCH_3 , and $(\text{CH}_3)_2\text{SO}$).



On the other hand, the reactions with anions result in deal-

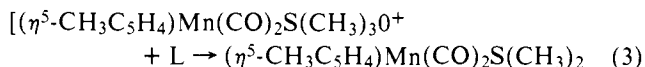
Table V. Bond Distances for $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5)]\text{PF}_6$

Atoms	Distance, Å	Atoms	Distance, Å
Mn-S	2.167 (1)	C5-C6	1.487 (6)
Mn-Cl	1.786 (4)	CP1-CP11	1.463 (6)
Mn-C2	1.799 (4)	CP1-CP2	1.431 (5)
Mn-CP1	2.179 (4)	CP1-CP5	1.394 (5)
Mn-CP2	2.116 (4)	CP2-CP3	1.376 (6)
Mn-CP3	2.113 (4)	CP3-CP4	1.368 (7)
Mn-CP4	2.139 (4)	CP4-CP5	1.405 (6)
Mn-CP5	2.159 (3)	P-F1	1.561 (3)
S-C3	1.787 (4)	P-F2	1.510 (3)
S-C4	1.794 (4)	P-F3	1.506 (3)
S-C5	1.837 (4)	P-F4	1.494 (3)
Cl-O1	1.164 (4)	P-F5	1.497 (3)
C2-O2	1.138 (4)	P-F6	1.537 (3)

Table VI. Pertinent Bond Angles for $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5)]\text{PF}_6$

Atoms	Angle, deg	Atoms	Angle, deg
S-Mn-Cl	94.8 (1)	F1-P-F2	84.3 (2)
S-Mn-C2	93.1 (1)	F1-P-F3	90.3 (2)
Cl-Mn-C2	92.6 (1)	F1-P-F4	94.9 (3)
Mn-Cl-O1	178.8 (3)	F1-P-F5	88.3 (2)
Mn-C2-O2	175.7 (4)	F1-P-F6	178.9 (2)
Mn-S-C3	116.0 (1)	F2-P-F3	84.7 (3)
Mn-S-C4	116.8 (1)	F2-P-F4	178.7 (3)
Mn-S-C5	118.5 (1)	F2-P-F5	94.6 (3)
C3-S-C4	101.0 (2)	F2-P-F6	95.5 (3)
C3-S-C5	102.6 (2)	F3-P-F4	94.3 (3)
C4-S-C5	99.0 (2)	F3-P-F5	178.5 (2)
S-C5-C6	112.8 (3)	F3-P-F6	88.7 (3)
CP11-CP1-CP2	126.9 (4)	F4-P-F5	86.4 (3)
CP11-CP1-CP5	127.9 (4)	F4-P-F6	85.3 (3)
CP2-CP1-CP5	105.1 (4)	F5-P-F6	92.7 (2)
CP1-CP2-CP3	109.0 (4)		
CP2-CP3-CP4	108.8 (4)		
CP3-CP4-CP5	107.8 (4)		
CP4-CP5-CP1	109.3 (4)		

kylation of the sulfonium ligand and formation of the original metal sulfide complexes (eq 3, L = OC_2H_5^- and CN^-).



Crystal and Molecular Structure of $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5)]^+\text{PF}_6^-$ (VIII). To establish the finer details of this new coordinative arrangement we have performed an x-ray crystallographic analysis of compound VIII. The structure was found to consist of discrete well-separated ions of $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5]^+$ and PF_6^- . The structure of the manganese cation is shown in Figure 1. Figure 2 shows a stereoscopic view of the entire unit cell, including the hexafluorophosphate counterions.

The structure unequivocally establishes the existence of a formal bond between the manganese and sulfur atoms. The Mn-S distance at 2.167 Å is considerably shorter than the 2.43 Å expected on the basis of assigned covalent radii for the Mn¹⁶ and S¹⁷ atoms. It is also significantly shorter than the 2.310 (4) Å Mn-S distance found for the coordinated dialkyl sulfide ligand in $(\text{C}_6\text{H}_4\text{CH}_2\text{SCH}_3)\text{Mn}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$,¹⁸ but is somewhat longer than the 2.037 (5) Å found for the coordinated SO₂ ligand in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{SO}_2$.¹⁹ Short metal-sulfur distances found in sulfur dioxide complexes have been attributed to multiple bonding.^{19,20} Except for its coordination to the metal atom the sulfonium ligand appears to be

Table VII. Selected Interionic Distances (Å) and Least-Squares Planes for $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2(\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5)]\text{PF}_6$

Atoms	Distance, Å	Atoms	Distance, Å
A. Nonhydrogen Atom-Nonhydrogen Atom: <i>d</i> Less Than 3.5 Å			
C3---F1 ^I	3.216(5)	O2---F1 ^I	3.414(5)
C6-F5 ^{II}	3.261(6)	C5---F6 ^{IV}	3.442(5)
C3---F2 ^I	3.321(6)	O2---F3 ^{III}	3.453(5)
C3---F3 ^I	3.332(5)	CP11---C4 ^V	3.470(6)
CP3---F3 ^{III}	3.370(6)	CP2---F1 ^{VI}	3.488(5)
B. Nonhydrogen Atom-Hydrogen Atom: <i>d</i> Less Than 3.0 Å			
F6---H52 ^{IV}	2.419	F2---H33 ^{VII}	2.811
F3---H32 ^{VII}	2.510	F5---H63 ^{III}	2.815
F2---H31 ^{IV}	2.686	F2---H41 ^{IV}	2.850
O2---H43 ^{VIII}	2.696	F5---H61 ^{II}	2.919
F3---H3 ^{III}	2.701	O1---H2 ^{IX}	2.934
F1---H2 ^{VI}	2.712	F1---H32 ^{VII}	2.970
F1---H33 ^{VII}	2.716	CP4---H12 ^{VI}	2.988
O2---H32 ^{VIII}	2.771		
F4---H4 ^{III}	2.799		
C. Hydrogen Atom-Hydrogen Atom: <i>d</i> Less Than 3.0 Å			
H41---H13 ^{XI}	2.63	H3---H62 ^{XIII}	2.82
H5---H63 ^{II}	2.67	H3---H63 ^{XIII}	2.83
H4---H12 ^{VI}	2.69	H42---H12 ^{XI}	2.95
H52---H3 ^{XII}	2.73	H41---H12 ^{XI}	2.96
H43---H13 ^{XI}			
Symmetry Transforms			
I. <i>x, y, z</i> - 1		VIII. - <i>x, -y, -z</i>	
II. 1 - <i>x, 1 - y, 1 - z</i>		IX. - <i>x, 1 - y, -z</i>	
III. - <i>x, -y, 1 - z</i>		X. 1 - <i>x, 1 - y, -z</i>	
IV. 1 - <i>x, -y, 1 - z</i>		XI. <i>x, y - 1, z</i>	
V. <i>x, 1 + y, z</i>		XII. 1 + <i>x, y, z</i>	
VI. - <i>x, 1 - y, 1 - z</i>		XIII. <i>x - 1, y, z</i>	
VII. <i>x, y, 1 + z</i>			
D. Weighted Least-Squares Plane through the Cyclopentadienyl Ring			
Atoms	Distance from plane		
Cp1	-0.005 (7)		
Cp2	0.004 (8)		
Cp3	-0.002 (10)		
Cp4	-0.001 (9)		
Cp5	0.004 (7)		
Mn ^a	1.782 (1)		
Cp11 ^a	-0.099 (11)		

^a Not included in calculation of the plane. Equation for plane is of form $Ax + By + Cz - D = 0$. $A = 0.6463$, $B = -0.2768$, $C = -0.7111$, $D = -3.8272$

normal in all respects. S-C distances range from 1.787 (4) to 1.837 (4) Å while the C-S-C angles range from 99.0 (2) to 102.6 (2)°. These values are very similar to those reported for the uncoordinated sulfonium cations $(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{S}^+$, 1.81-1.83 (2) Å and 102-105 (1)°;²¹ $(\text{C}_5\text{H}_{10}\text{S})\text{CH}_3^+$, 1.79-1.80 Å and 100.1-106.4°;²² and $(\text{C}_6\text{H}_{11})_2\text{S}(\text{CH}_3)^+$, 1.799 (4)-1.882 (3) Å and 101.1-107.5°.²³ It appears that the effects of coordination have not appreciably altered the pyramidal geometry of this cation. The conformational arrangement about the Mn-S bond is of a staggered ethane type such that the three R substituents on the sulfur atom are oriented as far as possible from the three remaining ligands on the manganese atom.

The geometry at the manganese atom is very similar to that of other cyclopentadienylmanganese carbonyl complexes that have been studied. Relevant comparisons are made in Table VIII. The cyclopentadienyl ring is planar with no atom deviating from the least-squares plane by more than 0.005 Å (cf. Table VII). The manganese atom is 1.782 (1) Å from this plane while the methyl group attached to the ring is 0.099 (11)

Table VIII. Comparisons of Various Cyclopentadienylmanganese Carbonyl Complexes

Complex	Bond, Å M-C (CO)	Bond, Å M-C (ring)	Bond, Å C-C (ring)	Angle, deg C-M-C (CO)	Angle, deg M-CO
$[\eta^5\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2\text{C}_2\text{-H}_5]^+\text{PF}_6^-$ ^a	1.786-1.799	2.113-2.179	1.376-1.431	92.6 (1)	175.7-178.8
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ ^b	1.788-1.812	2.127-2.176	1.35-1.43	91.94	176-180
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$ ^c	1.740-1.766	2.123-2.161	1.39-1.43	92.4	177-179
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{SO}_2)$ ^d	1.710-1.788	2.077-2.113	1.27-1.39	90	177-178

^a This work. ^b A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963). ^c C. Barbeau, K. S. Dichman, and L. Richard, *Can. J. Chem.*, **51**, 3027 (1973). ^d Reference 19.

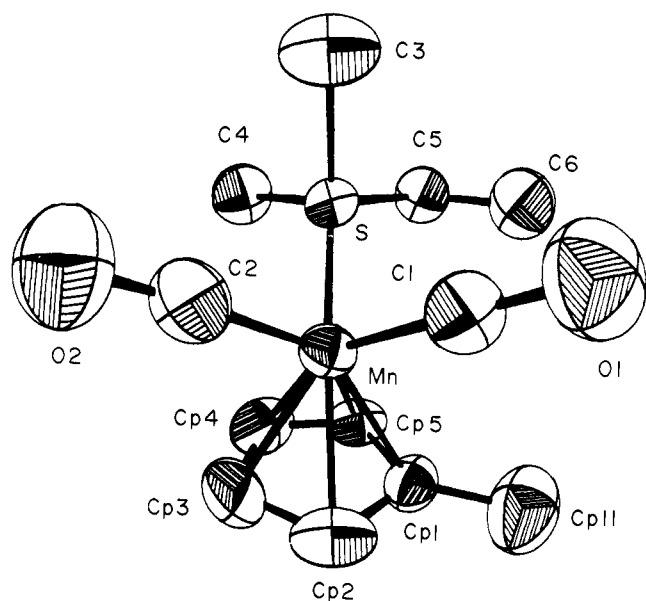


Figure 1. An ORTEP diagram of the $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5]^+$ cation: 50% probability thermal ellipsoids are shown.

Å from it on the side opposite the metal. The folding back of methyl groups away from the site of coordination appears to be a characteristic feature of methylated cyclopentadienyl rings.²⁴

The PF_6^- ion appears to be normal, although there are slight deviations from a formal octahedral geometry. This may have been caused by minor disorder effects around this ion which we were unable to sort out. The crystal shows discrete well-separated ions with the shortest interionic separations being between fluorine atoms and the alkyl groups of the sulfonium ligand (cf. Table VII).

Discussion

We have now prepared the first examples of metal-coordinated sulfonium cations. The sharp increases observed for the carbonyl stretching vibrations verify that it is a strongly electron-withdrawing ligand. Strohmeier et al.²⁵ have categorized the electron-withdrawing power of an extensive series of phosphine ligands through an analysis of the stretching frequencies of the carbonyl ligands when the phosphines were bound to the $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2$ moiety. In comparison, we see that the sulfonium ligand is more electron withdrawing than phosphite ligands, similar to $\text{PCl}_2(\text{C}_6\text{H}_5)$ and PCl_3 , but not as withdrawing as PF_3 .

Our ^1H NMR measurements show that the sulfonium ligand is firmly attached to the metal atom. This has been corroborated crystallographically. The manganese-sulfur bond distance is unusually short. The combination of measurements seems to imply that a significant amount of d-d π back-bonding is probably occurring and contributes toward the stabilization of this unusual coordinative bond.

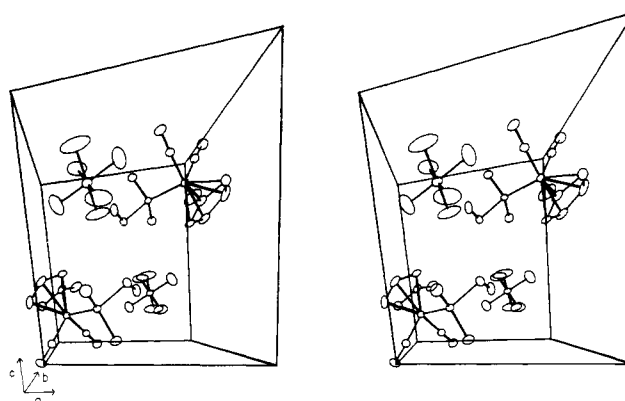


Figure 2. A stereoscopic view of the crystallographic unit cell for the complex $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2\text{S}(\text{CH}_3)_2\text{C}_2\text{H}_5]^+\text{PF}_6^-$: 20% probability thermal ellipsoids are shown.

The reaction chemistry of these sulfonium complexes is interestingly variable. Neutral ligands appear to attack the metal center and produce substitution while anionic ligands appear to react at the sulfonium ligand and cause dealkylation and formation of manganese dialkyl sulfide complexes.²⁶

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Supplementary Material Available: Structure factor amplitudes and root mean square amplitudes of vibration (17 pages). Ordering information is given on any current masthead page.

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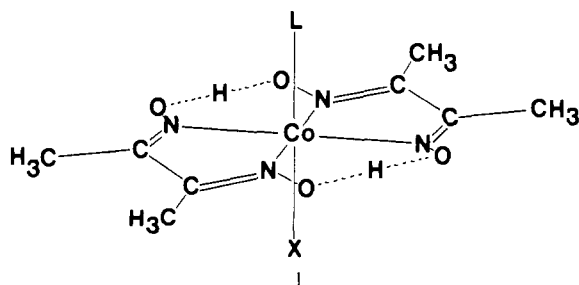
A Mechanistic Investigation of Cobaloxime Complexes Containing Good Trans Labilizing Ligands, Including Spectroscopic and Rate Comparisons

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Abstract: Observed and extrapolated first-order rate constants are reported for trans ligand substitution reactions in a series of six-coordinate cobalt(III) complexes known as cobaloximes. These complexes are of the type *trans*-LCo(DH)₂X, where (DH) = the monoanion of bisdimethylglyoxime (HON=C(CH₃)C(CH₃)=NO⁻), and L and X are neutral and anionic ligands, respectively. The trans labilizing ability of X was sufficient to allow monitoring the substitution reactions by conventional spectrophotometric techniques at 25 °C. The nonaqueous solvent, CH₂Cl₂, was employed for these measurements. Under pseudo-first-order excess of entering ligand, L' = 4-*tert*-butylpyridine, 1-methylimidazole, trimethyl phosphite, trimethylphosphine, dimethylphenylphosphine, tri-*n*-butylphosphine, and tri-*n*-octylphosphine, the observed rate constants for the substitution of L = 4-cyanopyridine trans to CH₃ was found to be independent of both the concentration and chemical identity of L'. The observed rate constants for the substitution of LCo(DH)₂CH₃ by tri-*n*-butylphosphine depended on L in the following order: 4-*tert*-butylpyridine ($1.32 \pm 0.04 \times 10^{-4} \text{ s}^{-1}$) < 4-cyanopyridine ($5.7 \pm 1.6 \times 10^{-2} \text{ s}^{-1}$) < triphenylphosphine ($8.0 \pm 0.1 \times 10^{-2} \text{ s}^{-1}$). The relative trans effect of a total of 11 different X ligands was found to increase in the following order: *p*-SO₂C₆H₄CH₃ < CHBr₂ ≤ SC(C₆H₅)₃ < CH₂Br < *p*-C₆H₄Br < *p*-C₆H₄OCH₃ < C₆H₅ < *p*-CH₂C₆H₄CN < CH₃ < CH₂C₆H₅ < C₂H₅. The relative increase in the observed rate constants for substitution of 4-cyanopyridine by tri-*n*-butylphosphine was ca. 10⁴ as the trans labilizing X ligand was varied from the S-bonded *p*-SO₂C₆H₄CH₃ ligand to the C-bonded ethide ligand. Addition of leaving ligand, L, to reaction mixtures resulted in a mass-law rate retardation. Competition ratios were determined for 9 of the 11 X ligands and found to be ca. one for most ligands but tri-*n*-butylphosphine and tri-*n*-octylphosphine proved to be poorer competitors. Competition ratios were essentially independent of the nature of the leaving ligand L. These results provide evidence for a dissociative mechanism with the generation of a highly reactive five-coordinate intermediate which does not discriminate between sterically unhindered nucleophiles. Correlations of the observed rate constants with ¹H and ¹³C NMR shift and coupling data reported previously are consistent with ground-state bond weakening for cobaloximes with good trans activating ligands. One of the parameters which correlated well with these rate constants was the α-¹³C NMR chemical shift of 4-*tert*-butylpyridine (Bupy) in (Bupy)Co(DH)₂X.

Vitamin B₁₂ coenzyme as well as methylcobalamin are octahedral Co(III) compounds containing direct Co-C bonds which occupy an axial coordinating position relative to a corrinoid ring system.^{1,2} It is now very clear that the bond between the Co(III) center and the ligating atom in the trans position



is weakened (relative to when a normal ligand such as Cl or NH₃ replaces the alkyl ligand) leading to increased bond lengths to cobalt and higher rates of substitution of the trans ligand.¹ These phenomena are not limited to the cobalt corrinoids but have also been observed in many other cobalt(III) alkyl complexes.

The cobaloximes I (LCo(DH)₂X where DH = monoanion of dimethylglyoxime) are often studied as models for cobalamins and the alkyl complexes (X = R) have been the subject of extensive kinetic and mechanistic studies.³⁻⁷ This activity has been motivated by the possibility that axial base release may be involved in biological mechanisms. One of the principal advantages in investigating cobaloximes is the solubility of these compounds in noncoordinating solvents. Under such conditions, it is possible to observe the substitution process uncomplicated by the intermediacy of solvato complexes.⁸ Thus, although numerous studies had implied that substitution of the trans ligand in organocobaloximes and organocobalamins should be a dissociative (first order in [complex]) process, experimental studies had typically yielded second-order kinetics. Subsequently, using nonaqueous noncoordinating solvent media, Brown was able to demonstrate experimentally using equilibrium NMR relaxation techniques that the trans ligand substitution reactions were first order in complex concentration and independent of entering ligand concentration.³ Subsequently, we confirmed this observation using similar complexes and solvents but employing spectrophotometric techniques.⁷