J. Am. Chem. Soc. 1983, 105, 4319-4326

Positively Charged Ligands. The Synthesis, Structure, and Bonding of Sulfonium Ion Complexes of Transition Metals and Evidence for a Metal-Induced Acceleration of Their Dealkylation

Richard D. Adams,* Craig Blankenship, Brigitte E. Segmüller, and Mahmoud Shiralian

Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut 06520. *Received January 21, 1983*

Abstract: The complexes $M(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (M = Mo, Ia; M = W, Ib) react with $[O(CH_3)_3]^+BF_4^-$ by methylation of the sulfur atom of the chelating $(C_6H_5)_2P(CH_2)_2SCH_3$ ligand to yield the complexes $M(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (M = Mo, IIa; M = W, IIb) in which the $(C_6H_5)_2P(CH_2)_2S(CH_3)_2^+$ ligand is coordinated to the metal atom through both the phosphorus and the positively charged sulfur atom. Compounds Ia and IIa were investigated by X-ray crystallographic methods. For Ia: space group $P2_12_12_1$, $a = 8.150$ (6) Å, $b = 14.229$ (6) Å, $c = 17.209$ (9) Å, $V = 1996$ (3) Å^3, $Z = 4$, $\rho_{calcd} = 1.56$ g/cm^3. For 1699 reflections ($F^2 \geq 2.0\sigma(F)^2$), $R_F = 0.025$ and $R_{wF} = 0.022$. For IIa: space group $P2_1/c$, $a = 16.928$ (5) Å, $b = 21.786$ (12) Å, $c = 13.900$ (9) Å, $\beta = 106.38$ (4)°, $V = 4918$ (8) Å^3, $Z = 8$, $\rho_{calcd} = 1.54$ g/cm^3. For 4912 reflections ($F^2 \geq 3.0\sigma(F^2)$), $R_F = 0.043$ and $R_{wF} = 0.054$. The metal atoms in both Ia and IIa have octahedral coordination geometries. The Mo–S$^+$ distance in IIa at 2.425 (4) Å is 0.135 Å shorter than the Mo–S distance in Ia of 2.560 (1) Å. All the Mo–C distances in IIa are significantly longer than those in Ia indicating that the sulfonium ligand is more strongly electron withdrawing than the sulfide ligand of Ia. This is supported by IR spectral measurements which show that the CO absorptions of the compounds II occur at 20–30 cm^{-1} higher frequencies than those of the compounds I. When the compounds II are treated with donors such as CO, $P(OCH_3)_3$, and CH_3CN, the sulfonium ion is displaced from the metal atom and the donor becomes coordinated. The $(C_6H_5)_2P(CH_2)_2S(CH_3)_2^+$ ion remains coordinated to the metal atom via the phosphorus atom alone. The compound $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb) was characterized by an X-ray crystallographic analysis. For IIIb: space group $P\bar{1}$, $a = 8.896$ (3) Å, $b = 9.035$ (2) Å, $c = 16.972$ (4) Å, $\alpha = 97.48$ (2)°, $\beta = 100.41$ (3)°, $\gamma = 99.68$ (3)°, $V = 1304$ (1) Å^3, $Z = 2$, $\rho_{calcd} = 1.75$ g/cm^3. Triethylamine produces demethylation of the sulfonium group in the compound IIb and regenerates the compound Ib. The rates of demethylation of the complexes IIb and $W(CO)_4[P(OCH_3)_3][P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb′), in which the sulfonium ion is not coordinated, were measured under pseudo-first-order conditions (excess amine) in CH_2Cl_2 solvent. In addition the rates of demethylation of the coordinated sulfonium ion in $[(C_5H_4CH_3)Mn(CO)_2S(CH_3)_3]^+BF_4^-$ (V) and $[S(CH_3)_3]^+BF_4^-$ (VI) were measured in CH_3CN solvent. In both cases the coordinated sulfonium ions were found to demethylate at rates of from 2 to 3 orders of magnitude faster than those of the uncoordinated sulfonium ions.

The chemistry of sulfonium ions, R_3S^+, is rich and varied.[1] Sulfonium cations have been observed to engage in two fundamentally different, but very important, types of reactions. (1) They can be deprotonated at an α-carbon atom by strong bases (e.g., organolithium reagents) to yield the valuable class of alkylidene transfer agents, the sulfur ylides, eq 1.[2,3] (2) With milder

$$R_2S^+C(H)R_2 + LiR \rightarrow R_2S^+C^-R_2 + RH + Li^+ \quad (1)$$

bases (e.g., OR^-, NR_3) they can be dealkylated in a process believed to proceed by nucleophilic displacement, eq 2.[2-4] This reaction is believed to serve as the basis for the valuable class of biochemical reactions known as transmethylations.[5]

$$R_3S^+ + :N \rightarrow R_2S + RN^+ \quad (2)$$

Sulfonium cations have a pyramidal structure with a lone pair of electrons on the sulfur atom.[1,6-8] Thus, they could, in principle, coordinate to a metal atom via electron-pair donation even though the positive charge should greatly diminish their capacity to serve as nucleophiles and donors. However, in coordination complexes, there can exist an important mode of supplementary bonding, known as π-back-bonding, which can enhance the strength of the coordinate bond. For a $M \leftarrow S^+$ bond this could occur through use of filled d orbitals on the metal atom and empty 3d orbitals on the sulfur atom.

In 1976 we reported the first example of the coordination of a sulfonium ion to a metal atom.[9a] Recently, Taube has prepared another example.[10] Several complexes containing the related positively charged phosphenium ligand (e.g., $P(NR_2)_2^+$) have been made.[11]

Complexes containing sulfonium ligands can be made by "on site" formation via alkylation of the uncoordinated pair of electrons of a coordinated dialkylsulfide molecule, eq 3,[9] or by ligand substitution, eq 4.[10]

$$L_nMSR_2 + R'_3O^+BF_4 \rightarrow [L_nMSR_2R']^+BF_4^- + R'_2O \quad (3)$$

$$L_nML' + SR_3^+ \rightarrow L_nMSR_3^+ + L' \quad (4)$$

In an effort to expand the range of stable complexes containing sulfonium cations, we have now taken advantage of the chelate effect to prepare stable sulfonium ion complexes. The ligand we have made is $(C_6H_5)_2P(CH_2)_2S(CH_3)_2^+$ prepared by methylation of the $(C_6H_5)_2P(CH_2)_2S(CH_3)$ ligand. This positively charged

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0002-7863/83/1505-4319$01.50/0

Table I. Spectroscopic Data

compound	IR (±cm^{-1}) (ν(CO))^a	^{1}H NMR (δ) [^{31}P NMR (δ vs. H_3PO_4)]^b
$Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$ (Ia)	2023 m, 1927 s (sh), 1907 vs, 1869 s^c	7.42-7.61 (m) (C_6H_5; 2.83 (dt), 2.74 (dt) PCH_2; 2.51 (dt) SCH_2; 2.43 (s) SCH_3^{d}
$W(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$ (Ib)	2018 m, 1933 s (sh), 1902 vs, 1863 s^c	7.4-7.6 (m) C_6H_5; 2.88 (m), 2.84 (m) PCH_2; 2.61 (s) SCH_3; 2.52 (dt) SCH_2 ($^4J_{P-H}$ = 7.0 Hz); [−14.6 s]^e
$Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIa)	2048 s, 1965 s (sh), 1943 vs	7.51 (m) C_6H_5; 4.03 (dt) PCH_2, $^2J_{P-H}$ = 21.6 Hz, J_{H-H} = 6.2 Hz; 3.52 (s) SCH_3; 2.74 (dt) SCH_2, ($^4J_{P-H}$ = 6.8 Hz, J_{H-H} = 7.3 Hz)^f
$W(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIb)	2044 m, 1957 sh, 1934 vs	7.4-7.6 (m) C_6H_5; 4.12 (dt) PCH_2 ($^2J_{P-H}$ = 21.9 Hz, J_{H-H} = 6.8 Hz); 3.72 (s), SCH_3; 2.74 (q) SCH_2 (J_{H-H} = 6.8 Hz)^e [45.8 (s)]^f
		7.4-7.8 (m) C_6H_5, 4.50 (dt), 3.53 (m), 3.31 (m), 4.10 (s)^1 SCH_3, 3.16 (s)^2 SCH_3^{e} [48.8 (s),^{1} 25.0 (s)^2]^{e,g}
$Mo(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIa)	2075 m, 1996 w, 1946 vs	7.53 (m) C_6H_5; 3.19 (br) CH_2; 2.93 (s, CH_3); 2.87 (br, CH_2)^c
$W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb)	2019 m, 1945 w (sh), 1898 vs, 1864 s	7.54 (m) C_6H_5; 3.18 (m) PCH_2; 3.03 (m) SCH_2; 2.90 (s) SCH_3
$W(CO)_4[P(OCH_3)_3][P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb′)	2030 m, 1930 m (sh), 1900 s^h	7.4-7.6 (m) C_6H_5; 3.56 (d) OCH_3 ($^3J_{P-H}$ = 11.4 Hz); 3.14 (m) CH_2; 2.90 (m) CH_2; 2.80 (s) SCH_3;^{f} [13.5 (d) $^2J_{P-P}$ = 30.5 Hz; 140.6 (d) J_{P-P} = 30.5 Hz]^e
$W(CO)_4[NCCH_3][P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$	2010 m, 1895 m (sh), 1840 s^h	7.4-7.6 (m) C_6H_5; 3.25 (m) CH_2; 3.01 (m) CH_2, 2.84 (s) SCH_3; 1.74 (d) NCH_3 ($^5J_{P-H}$ = 1.5 Hz)^f

^{a} Unless otherwise indicated IR spectra were recorded in CH_2Cl_2 solvent. ^{b} ^{1}H decoupled. ^{c} Rerecorded by us. For original report see ref 21. ^{d} In $CDCl_3$. ^{e} In $(CD_3)_2C{=}O$. ^{f} In CD_2Cl_2. ^{g} Ratio of resonance 1 to 2 is 3:2. Resonances 2 are attributed to an acetone adduct $W(CO)_4(acetone)[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$. ^{h} Recorded on a Perkin-Elmer 237B spectrophotometer.

Table II. Positional Parameters for $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$ (Ia)

atom	x	y	z	atom	x	y	z
Mo	−0.43808 (5)	0.03628 (3)	0.19255 (2)	C(23)	−0.1158 (7)	0.2949 (3)	0.3728 (3)
S	−0.7157 (1)	0.01298 (8)	0.25934 (6)	C(24)	−0.0136 (6)	0.2764 (3)	0.4336 (3)
P	−0.3453 (1)	0.04188 (9)	0.33349 (6)	C(25)	−0.0121 (7)	0.1895 (4)	0.4664 (3)
O(1)	−0.6351 (4)	0.0335 (3)	0.0362 (2)	C(26)	−0.1120 (7)	0.1193 (3)	0.4386 (3)
O(2)	−0.0914 (4)	0.0386 (3)	0.1141 (2)	H(12)	−0.3863	−0.0937	0.4635
O(3)	−0.4357 (5)	0.2556 (2)	0.1629 (2)	H(13)	−0.2479	−0.2286	0.5016
O(4)	−0.3866 (5)	−0.1836 (2)	0.1746 (2)	H(14)	−0.0243	−0.2816	0.4318
C(1)	−0.5598 (6)	0.0327 (3)	0.0922 (2)	H(15)	0.0654	−0.1999	0.3218
C(2)	−0.2201 (5)	0.0404 (3)	0.1436 (2)	H(16)	−0.0762	−0.0648	0.2815
C(3)	−0.4434 (7)	0.1777 (3)	0.1788 (2)	H(22)	−0.2860	0.2379	0.2998
C(4)	−0.4094 (5)	−0.1053 (3)	0.1862 (2)	H(23)	−0.1191	0.3565	0.3509
C(5)	−0.5333 (5)	0.0573 (3)	0.3922 (2)	H(24)	0.0565	0.3244	0.4533
C(6)	−0.6722 (5)	−0.0040 (3)	0.3620 (3)	H(25)	0.0598	0.1771	0.5091
C(7)	−0.8262 (7)	0.1219 (3)	0.2591 (3)	H(26)	−0.1119	0.0591	0.4636
C(11)	−0.2457 (5)	−0.0652 (3)	0.3686 (2)	H(51)	−0.5101	0.0405	0.4450
C(12)	−0.2944 (6)	−0.1151 (3)	0.4338 (3)	H(52)	−0.5658	0.1217	0.3900
C(13)	−0.2121 (8)	−0.1949 (3)	0.4565 (3)	H(61)	−0.7691	0.0106	0.3909
C(14)	−0.0803 (7)	−0.2260 (3)	0.4155 (3)	H(62)	−0.6438	−0.0683	0.3700
C(15)	−0.0275 (6)	−0.1780 (4)	0.3504 (3)	H(71)	−0.8553	0.1373	0.2066
C(16)	−0.1114 (6)	−0.0979 (3)	0.3270 (2)	H(72)	−0.9229	0.1152	0.2896
C(21)	−0.2140 (5)	0.1343 (3)	0.3748 (2)	H(73)	−0.7587	0.1701	0.2801
C(22)	−0.2154 (6)	0.2244 (3)	0.3430 (3)				

ligand can serve as a chelate by coordination of both the sulfur and phosphorus atoms, or serve as a monodentate ligand through coordination of the phosphorus atom alone. We have prepared both types of complexes and have investigated their molecular structures, bonding, and reactivity. We have also investigated the effect of metal coordination on the transmethylation reaction, eq 2. Interestingly, we have found that the rate of transmethylation is significantly enhanced by the metal atom. A preliminary report of this work has been published.[12]

Results

Methylation of the lone pair of electrons on the coordinated sulfur atom in the chelate complexes $M(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (M = Mo, Ia; M = W, Ib) with $[O(CH_3)_3]^+BF_4^-$ leads to formation of the chelate complexes $M(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (M = Mo, IIa; M = W, IIb) where the coordinated sulfur atom of the chelating $[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+$ ion is formally positively charged, eq 5. IR

$$\underset{\mathrm{M = Mo,W}}{\mathrm{M(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]}} \xrightarrow[\text{room temp/24 h}]{[\mathrm{O(CH_3)_3}]^+\mathrm{BF_4}^-} \mathrm{M(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-} \quad (5)$$

and NMR spectra of the complexes are listed in Table I. The importance of chelation toward the stability of these complexes was indicated by our unsuccessful attempts to prepare sulfonium ion complexes by methylation of $W(CO)_5[S(CH_3)_2]$ and $W(CO)_4[S(CH_3)_2][P(C_6H_5)_3]$. These reactions yielded only $W(CO)_6$ and $W(CO)_5[P(C_6H_5)_3]$, respectively. Similar results were obtained by Eaborn et al. in the reaction of the complex *cis*-$PtCl_2[S(C_2H_5)_2]$ with $SFO_3(CH_3)$.[13] To establish definitively the existence of the metal–sulfur bond as well as details of its

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Table III. Positional Parameters with esds for $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIa)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo(1)	0.25099 (4)	0.16512 (3)	0.05787 (4)	C(13)	0.0821 (5)	0.0666 (4)	0.3600 (5)
Mo(2)	0.63022 (4)	0.13349 (3)	0.45763 (4)	C(14)	0.1527 (5)	0.0800 (4)	0.4344 (5)
S(1)	0.1202 (1)	0.20949 (9)	−0.0354 (1)	C(15)	0.2262 (5)	0.0948 (4)	0.4101 (5)
S(2)	0.7789 (1)	0.12605 (9)	0.5050 (1)	C(16)	0.2257 (4)	0.0968 (3)	0.3077 (5)
P(1)	0.1551 (1)	0.09004 (9)	0.1022 (1)	C(21)	0.1662 (4)	0.0097 (3)	0.0651 (5)
P(2)	0.6473 (1)	0.07399 (9)	0.3085 (1)	C(22)	0.1359 (5)	−0.0067 (4)	−0.0362 (5)
F(1)	0.8122 (3)	0.2094 (3)	0.1862 (4)	C(23)	0.1539 (5)	−0.0659 (4)	−0.0659 (6)
F(2)	0.9398 (3)	0.2147 (3)	0.1725 (4)	C(24)	0.1982 (6)	−0.1067 (4)	0.0051 (7)
F(3)	0.9040 (4)	0.2697 (3)	0.2877 (5)	C(25)	0.2297 (8)	−0.0895 (4)	0.1050 (7)
F(4)	0.9159 (4)	0.1722 (3)	0.3056 (4)	C(26)	0.2133 (6)	−0.0299 (4)	0.1363 (6)
F(5)	0.0325 (3)	0.4232 (3)	0.2415 (3)	C(31)	0.6218 (4)	−0.0075 (3)	0.3110 (4)
F(6)	0.1297 (4)	0.3746 (3)	0.1839 (5)	C(32)	0.5400 (4)	−0.0208 (3)	0.3058 (5)
F(7)	0.0086 (3)	0.4020 (3)	0.0784 (3)	C(33)	0.5146 (5)	−0.0829 (4)	0.3055 (6)
F(8)	0.1017 (3)	0.4714 (3)	0.1512 (5)	C(34)	0.5740 (5)	−0.1300 (4)	0.3131 (5)
O(1)	0.3596 (4)	0.2640 (3)	−0.0105 (4)	C(35)	0.6549 (5)	−0.1159 (4)	0.3194 (6)
O(2)	0.4007 (3)	0.0841 (3)	0.1716 (4)	C(36)	0.6803 (5)	−0.0538 (3)	0.3178 (5)
O(3)	0.2717 (4)	0.2461 (3)	0.2531 (4)	C(41)	0.6030 (4)	0.0946 (3)	0.1774 (5)
O(4)	0.2649 (4)	0.0808 (3)	−0.1248 (4)	C(42)	0.5730 (5)	0.1537 (4)	0.1524 (5)
O(5)	0.6323 (4)	0.1952 (3)	0.6628 (4)	C(43)	0.5363 (6)	0.1706 (4)	0.0485 (6)
O(6)	0.4363 (3)	0.1386 (3)	0.3849 (5)	C(44)	0.5348 (6)	0.1267 (4)	−0.0239 (6)
O(7)	0.6146 (4)	0.0089 (3)	0.5681 (4)	C(45)	0.5653 (7)	0.0680 (5)	0.0010 (6)
O(8)	0.6344 (5)	0.2683 (3)	0.3690 (4)	C(46)	0.5992 (6)	0.0513 (4)	0.1019 (5)
C(1)	0.3204 (5)	0.2278 (4)	0.0135 (5)	C(51)	0.0457 (4)	0.1126 (3)	0.0350 (5)
C(2)	0.3475 (4)	0.1160 (4)	0.1321 (5)	C(52)	0.0393 (4)	0.1505 (4)	−0.0610 (5)
C(3)	0.2618 (4)	0.2169 (3)	0.1838 (5)	C(61)	0.1099 (5)	0.2393 (4)	−0.1613 (5)
C(4)	0.2560 (4)	0.1120 (4)	−0.0630 (5)	C(62)	0.0729 (5)	0.2714 (4)	0.0177 (6)
C(5)	0.6320 (5)	0.1738 (3)	0.5880 (5)	C(71)	0.7593 (4)	0.0774 (3)	0.3165 (5)
C(6)	0.5075 (5)	0.1359 (4)	0.4110 (5)	C(72)	0.8140 (4)	0.0694 (4)	0.4256 (5)
C(7)	0.6222 (4)	0.0533 (4)	0.5267 (5)	C(81)	0.8385 (5)	0.1946 (4)	0.4955 (7)
C(8)	0.6338 (5)	0.2191 (4)	0.3977 (5)	C(82)	0.8312 (5)	0.0981 (4)	0.6310 (5)
C(11)	0.1534 (4)	0.0840 (3)	0.2334 (4)	B(1)	0.8905 (6)	0.2164 (5)	0.2355 (7)
C(12)	0.0795 (4)	0.0678 (4)	0.2575 (5)	B(2)	0.0644 (5)	0.4165 (5)	0.1639 (7)

Table IV. Interatomic Distances with esds for $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (Ia)

atoms	distance, Å	atoms	distance, Å
Mo-S	2.560 (1)	P-C(21)	1.839 (4)
Mo-P	2.542 (1)	P-C(5)	1.848 (4)
Mo-C(1)	1.992 (4)	C(5)-C(6)	1.521 (6)
Mo-C(2)	1.967 (4)	C(1)-O(1)	1.143 (4)
Mo-C(3)	2.026 (4)	C(2)-O(2)	1.165 (5)
Mo-C(4)	2.031 (4)	C(3)-O(3)	1.144 (5)
S-C(7)	1.793 (5)	C(4)-O(4)	1.146 (5)
S-C(6)	1.818 (4)	C-C_{av} (ring 1)	1.380 (5)
P-C(11)	1.829 (4)	C-C_{av} (ring 2)	1.379 (6)

influence on the coordination of the remaining ligands, a single-crystal X-ray diffraction analysis of IIa was performed. For comparative purposes a structural analysis of Ia was also performed. ORTEP diagrams of the structures of both Ia and the cation IIa are shown in Figures 1a and 1b, respectively. Final positional parameters for Ia and IIa are listed in Tables II and III, respectively. Interatomic distances and angles for Ia are listed in Tables IV and V, and interatomic distances and angles for IIa are listed in Tables VI and VII. Compound IIa contains two independent formula units in the asymmetric crystal unit; however, both are essentially identical structurally. The metal atoms in both Ia and IIa contain octahedral six-coordinate geometry. Compound Ia contains an uncharged chelating $[P(C_6H_5)_2(CH_2)_2SCH_3]$ ligand while compound IIa contains the chelating $[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+$ ligand. In comparing bond lengths between Ia and IIa we will use values for IIa that are the *average* of those of the two independent cations[14] (cf. Table VI). First and foremost, the molybdenum–sulfur bond to the positively charged sulfur atom in IIa at 2.425 (4) Å is significantly shorter (0.135 Å) than the corresponding bond to the uncharged sulfur atom in Ia, 2.560 (1) Å. An unusually short metal–sulfur bond was also found in the only other structurally characterized complex containing a coordinated sulfonium ion, $[(C_5H_4CH_3)Mn(CO)_2$-

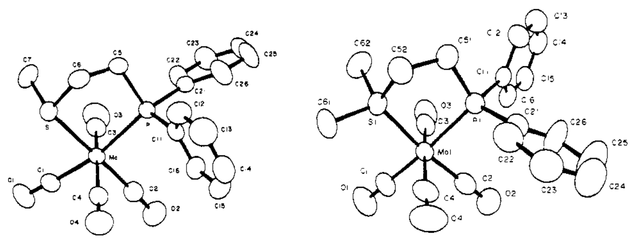

Figure 1. (a, left) An ORTEP diagram of $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (Ia) showing 50% probability thermal-motion ellipsoids. (b, right) An ORTEP diagram of one of the two independent cations of $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+$ (IIa) showing 50% probability thermal-motion ellipsoids.

Table V. Interatomic Angles with esds for $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (Ia)

atoms	angle, deg	atoms	angle, deg
P-Mo-S	80.70 (3)	C(5)-P-C(11)	106.7 (2)
P-Mo-C(1)	167.4 (1)	C(5)-P-C(21)	100.7 (2)
P-Mo-C(2)	98.0 (1)	C(11)-P-C(21)	102.1 (1)
P-Mo-C(3)	95.0 (1)	Mo-C(1)-O(1)	176.7 (4)
P-Mo-C(4)	92.8 (1)	Mo-C(2)-O(2)	177.1 (5)
S-Mo-C(1)	86.9 (1)	Mo-C(3)-O(3)	171.7 (4)
S-Mo-C(2)	174.1 (1)	Mo-C(4)-O(4)	172.5 (4)
S-Mo-C(3)	99.3 (1)	P-C(11)-C(12)	124.5 (4)
S-Mo -C(4)	89.9 (1)	P-C(11)-C(16)	117.3 (3)
C(1)-Mo-C(2)	94.6 (2)	P-C(21)-C(22)	120.1 (3)
C(1)-Mo-C(3)	85.0 (2)	P-C(21)-C(26)	122.8 (3)
C(1)-Mo-C(4)	89.2 (2)	C(11)-C(12)-C(13)	120.9 (5)
C(2)-Mo-C(3)	86.6 (2)	C(12)-C(13)-C(14)	120.4 (5)
C(2)-Mo-C(4)	84.4 (2)	C(13)-C(14)-C(15)	120.4 (5)
C(3)-Mo-C(4)	168.8 (2)	C(14)-C(15)-C(16)	119.2 (5)
Mo-S-C(6)	106.3 (1)	C(15)-C(16)-C(11)	120.9 (4)
Mo-S-C(7)	109.3 (2)	C(16)-C(11)-C(12)	118.1 (4)
Mo-P-C(5)	106.2 (1)	C(21)-C(22)-C(23)	120.9 (4)
Mo-P-C(11)	114.9 (1)	C(22)-C(23)-C(24)	120.1 (4)
Mo-P-C(21)	124.4 (1)	C(23)-C(24)-C(25)	120.0 (5)
C(6)-S-C(7)	102.5 (2)	C(24)-C(25)-C(26)	120.8 (4)
P-C(5)-C(6)	111.2 (3)	C(25)-C(26)-C(21)	121.0 (4)
C(5)-C(6)-S	113.6 (3)	C(26)-C(21)-C(22)	117.1 (4)

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[14] $\sigma_{l_{av}} = [\sum_m (l_m - \bar{l})^2/m(m-1)]^{1/2}$, m = number of values averaged.[15]

[15] Stout, G. H.; Jensen, L. H. "X-ray Structure Determination"; MacMillan Publishing Co.: New York, 1968; Chapter 18.

Table VI. Interatomic Distances with esds for the Two Crystallographically Independent Units of $Mo(CO)_4[P(C_6H_5)(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIa)

molecule 1		molecule 2		
atoms	distance, Å	atoms	distance, Å	av, Å
Mo(1)-S(1)	2.429 (1)	Mo(2)-S(2)	2.421 (1)	2.425 (4)
Mo(1)-P(1)	2.501 (1)	Mo(2)-P(2)	2.530 (1)	2.516 (14)
Mo(1)-C(1)	2.009 (5)	Mo(2)-C(5)	2.006 (4)	2.008 (2)
Mo(1)-C(2)	1.982 (5)	Mo(2)-C(6)	1.994 (5)	1.988 (6)
Mo(1)-C(3)	2.048 (5)	Mo(2)-C(7)	2.016 (5)	2.032 (16)
Mo(1)-C(4)	2.061 (5)	Mo(2)-C(8)	2.050 (5)	2.056 (6)
S(1)-C(61)	1.829 (4)	S(2)-C(81)	1.827 (4)	1.828 (1)
S(1)-C(62)	1.827 (4)	S(2)-C(82)	1.830 (4)	1.828 (1)
S(1)-C(52)	1.838 (4)	S(2)-C(72)	1.860 (4)	1.849 (1)
P(1)-C(11)	1.836 (4)	P(2)-C(31)	1.829 (4)	1.833 (3)
P(1)-C(21)	1.849 (4)	P(2)-C(41)	1.820 (4)	1.834 (14)
P(1)-C(51)	1.888 (4)	P(2)-C(71)	1.869 (4)	1.878 (9)
C(51)-C(52)	1.547 (5)	C(71)-C(72)	1.548 (5)	1.548 (1)
C(1)-O(1)	1.140 (5)	C(5)-O(5)	1.138 (4)	1.139 (1)
C(2)-O(2)	1.147 (5)	C(6)-O(6)	1.158 (5)	1.152 (6)
C(3)-O(3)	1.126 (4)	C(7)-O(7)	1.152 (5)	1.139 (13)
C(4)-O(4)	1.138 (5)	C(8)-O(8)	1.146 (5)	1.142 (4)
$C-C_{av}$ (ring 1)	1.407 (9)	$C-C_{av}$ (ring 3)	1.407 (7)	
$C-C_{av}$ (ring 2)	1.399 (5)	$C-C_{av}$ (ring 4)	1.403 (11)	
$B-F_{av}$	1.342 (11)	$B-F_{av}$	1.358 (5)	

Table VII. Interatomic Angles with esds for $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIa)

molecule 1		molecule 2	
atoms	angle, deg	atoms	angle, deg
S(1)-Mo(1)-P(1)	80.48 (3)	S(2)-Mo(2)-P(2)	80.68 (3)
S(1)-Mo(1)-C(1)	95.2 (1)	S(2)-Mo(2)-C(5)	92.0 (1)
S(1)-Mo(1)-C(2)	170.5 (1)	S(2)-Mo(2)-C(6)	176.2 (1)
S(1)-Mo(1)-C(3)	94.9 (1)	S(2)-Mo(2)-C(7)	91.0 (1)
S(1)-Mo(1)-C(4)	91.7 (1)	S(2)-Mo(2)-C(8)	91.4 (2)
P(1)-Mo(1)-C(1)	175.5 (1)	P(2)-Mo(2)-C(5)	171.3 (1)
P(1)-Mo(1)-C(2)	90.9 (1)	P(2)-Mo(2)-C(6)	95.6 (1)
P(1)-Mo(1)-C(3)	93.3 (1)	P(2)-Mo(2)-C(7)	89.2 (1)
P(1)-Mo(1)-C(4)	90.7 (1)	P(2)-Mo(2)-C(8)	96.3 (1)
C(1)-Mo(1)-C(2)	93.4 (2)	C(5)-Mo(2)-C(6)	91.7 (2)
C(1)-Mo(1)-C(3)	88.2 (2)	C(5)-Mo(2)-C(7)	86.2 (2)
C(1)-Mo(1)-C(4)	88.3 (2)	C(5)-Mo(2)-C(8)	88.6 (2)
C(2)-Mo(1)-C(3)	89.5 (2)	C(6)-Mo(2)-C(7)	88.5 (2)
C(2)-Mo(1)-C(4)	84.5 (2)	C(6)-Mo(2)-C(8)	89.5 (2)
C(3)-Mo(1)-C(4)	172.8 (2)	C(7)-Mo(2)-C(8)	174.3 (2)
Mo(1)-P(1)-C(11)	119.0 (1)	Mo(2)-P(2)-C(31)	113.6 (1)
Mo(1)-P(1)-C(21)	115.2 (1)	Mo(2)-P(2)-C(41)	125.7 (1)
Mo(1)-P(1)-C(51)	108.8 (1)	Mo(2)-P(2)-C(71)	106.2 (1)
Mo(1)-P(1)-C(52)	110.0 (1)	Mo(2)-S(2)-C(72)	111.4 (1)
Mo(1)-P(1)-C(61)	118.6 (2)	Mo(2)-S(2)-C(81)	118.6 (2)
Mo(1)-P(1)-C(62)	121.0 (2)	Mo(2)-S(2)-C(82)	117.8 (2)
C(11)-P(1)-C(21)	103.9 (2)	C(31)-P(2)-C(41)	103.0 (2)
C(11)-P(1)-C(51)	102.9 (2)	C(31)-P(2)-C(71)	106.1 (2)
C(21)-P(1)-C(51)	105.7 (2)	C(41)-P(2)-C(71)	100.1 (2)
C(52)-P(1)-C(61)	101.5 (2)	C(72)-S(2)-C(81)	103.0 (2)
C(52)-P(1)-C(62)	102.0 (2)	C(72)-S(2)-C(82)	101.5 (2)
C(61)-P(1)-C(51)	101.0 (2)	C(81)-S(2)-C(82)	102.3 (2)
S(1)-C(52)-C(51)	109.8 (3)	S(2)-C(72)-C(71)	107.7 (3)
P(1)-C(51)-C(52)	112.7 (3)	P(2)-C(71)-C(72)	111.7 (3)
Mo(1)-C(1)-O(1)	178.8 (4)	Mo(2)-C(5)-O(5)	178.3 (4)
Mo(1)-C(2)-O(2)	175.3 (4)	Mo(2)-C(6)-O(6)	178.5 (4)
Mo(1)-C(3)-O(3)	176.4 (4)	Mo(2)-C(7)-O(7)	176.6 (7)
Mo(1)-C(4)-O(4)	174.3 (4)	Mo(2)-C(8)-O(8)	175.9 (4)
P(1)-C(11)-C(12)	120.7 (3)	P(2)-C(31)-C(32)	115.9 (3)
P(1)-C(11)-C(16)	117.9 (3)	P(2)-C(31)-C(36)	122.4 (3)
C(16)-C(11)-C(12)	121.4 (4)	C(36)-C(31)-C(32)	121.8 (4)
C(11)-C(12)-C(13)	117.4 (4)	C(31)-C(32)-C(33)	119.5 (4)
C(12)-C(13)-C(14)	122.0 (4)	C(32)-C(33)-C(34)	118.8 (4)
C(13)-C(14)-C(15)	120.4 (4)	C(33)-C(34)-C(35)	120.8 (5)
C(14)-C(15)-C(16)	119.2 (4)	C(34)-C(35)-C(36)	120.6 (4)
C(15)-C(16)-C(11)	119.6 (4)	C(35)-C(36)-C(31)	118.5 (4)
P(1)-C(21)-C(22)	118.9 (3)	P(2)-C(41)-C(42)	119.8 (3)
P(1)-C(21)-C(26)	118.3 (3)	P(2)-C(41)-C(46)	120.2 (3)
C(26)-C(21)-C(22)	122.2 (4)	C(46)-C(41)-C(42)	120.0 (4)
C(21)-C(22)-C(23)	118.5 (4)	C(41)-C(42)-C(43)	120.5 (4)
C(22)-C(23)-C(24)	119.8 (5)	C(42)-C(43)-C(44)	117.6 (5)
C(23)-C(24)-C(25)	121.1 (5)	C(43)-C(44)-C(45)	121.8 (5)
C(24)-C(25)-C(26)	119.9 (6)	C(44)-C(45)-C(46)	120.5 (5)
C(25)-C(26)-C(21)	118.3 (5)	C(45)-C(46)-C(41)	119.6 (5)
F(1)-B(1)-F(2)	111.7 (5)	F(5)-B(2)-F(6)	112.8 (5)
F(1)-B(1)-F(3)	111.8 (6)	F(5)-B(2)-F(7)	111.1 (4)
F(1)-B(1)-F(4)	111.1 (5)	F(5)-B(2)-F(8)	107.7 (5)
F(2)-B(1)-F(3)	108.9 (5)	F(6)-B(2)-F(7)	110.6 (5)
F(2)-B(1)-F(4)	108.3 (5)	F(6)-B(2)-F(8)	105.3 (4)
F(3)-B(1)-F(4)	104.7 (5)	F(7)-B(2)-F(8)	109.0 (5)

$\{S(CH_3)_2C_2H_5\}]^+BF_4^-$.[9] The molybdenum–phosphorus distances in Ia and IIa at 2.542 (1) Å and 2.516 (14) Å, respectively, are quite similar. The molybdenum–carbon bond to the carbonyl ligand trans to the sulfur atom is slightly longer in the sulfonium complex, Mo–C(2) = 1.988 (6) Å in IIa vs. 1.967 (4) Å in Ia.[16] This could be indicative of a greater trans influence of the sulfonium ion. Such effects have been observed for other strong π-back-bonding ligands.[17] The metal–carbon bonds to the carbonyl ligands cis to sulfonium ion in IIa are not significantly longer than those in Ia, Mo–C(3) = 2.032 (16) Å and Mo–C(4) = 2.056 (6) Å in IIa and Mo–C(3) = 2.026 (4) Å and Mo–C(4) = 2.031 (5) Å in Ia. The sulfur–carbon bonds in IIa are slightly longer than those in Ia (cf. Tables IV and VI), but this is probably an artifact of the structural analysis of IIa since the contributions of the hydrogen atoms in IIa were not included in the calculations. It is believed, however, this omission will not have a significant effect on bonds between atoms that do not have hydrogen atoms bonded to them (i.e., the metal–ligand bonds). The carbon–sulfur–carbon bond angles in IIa are not significantly different from the one in Ia. The phosphorus–carbon and carbon–carbon bond distances in IIa appear to be slightly longer than those in Ia. This could also be attributed to the omission of the hydrogen atoms in the calculations on IIa (see above). The C–O bond distances in Ia and IIa are not significantly different. The M–C–O bond angles in Ia and IIa do not deviate significantly from linearity. The BF_4^- ions in IIa have no unusual distortions. The shortest interionic contact in IIa was between a fluorine atom and carbon of the chelate, F(8)···C(72) = 2.933 (5) Å. The shortest nonhydrogen contact in Ia was between a carbonyl oxygen atom and a carbon atom of a phenyl ring O(2)···C(12) = 3.298 (6) Å. All the C–O absorptions of carbonyl ligands in the sulfonium complexes II are increased 20–30 cm^{-1} from the positions of the corresponding absorptions of the uncharged complexes I. This indicates that the sulfonium ligand is more electron withdrawing than the sulfide ligand.

Reactions of IIa and IIb with Electron-Pair Donors. Compounds IIa and IIb react with molecules acting as electron-pair donors in two different ways. Lewis bases, such as carbon monoxide, phosphines, nitriles, etc., form 1:1 adducts obtained by displacement of the sulfonium ion portion of the chelate and coordination of the donor to the metal atom to yield the complexes $M(CO)_4L[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIa,b M = Mo, W, L = CO; IIIb′, M = W, L = $P(OCH_3)_3$), eq 6. With poor donors

$$\underset{\text{II}}{M(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+} + L \rightarrow \underset{\text{III}}{M(CO)_4L[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+} \quad (6)$$

reaction 6 may not proceed to completion. For example, in acetone solvent IIb exists as a 3:2 mixture of the IIb and a solvate III, L = acetone (cf. Table I), and when the solvent is removed, IIb is regenerated quantitatively. However, the observation of separate resonances for the two compounds by NMR spectroscopy indicates that they interconvert slowly on the NMR time scale at room temperature. In general, the compound types II and III are readily

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(16) The final results of the structural determination of IIa are slightly different from those quoted previously from results at an earlier stage of refinement. At that time no significant differences were observed between the metal–carbon distances in Ia and IIa.[12]

(17) Plastos, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* **1973**, *12*, 265.

(18) Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *20*, 2711.

Table VIII. Positional Parameters with esds for $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W	0.00882 (6)	0.24312 (6)	0.34716 (3)	C(11)	−0.400 (1)	0.015 (1)	0.3136 (7)
S	−0.2588 (5)	−0.2614 (4)	0.0848 (2)	C(12)	−0.350 (2)	−0.028 (1)	0.3896 (7)
P	−0.2651 (3)	0.1354 (3)	0.2677 (2)	C(13)	−0.462 (2)	−0.122 (1)	0.4218 (8)
O(1)	0.045 (1)	−0.073 (1)	0.4051 (7)	C(14)	−0.616 (2)	−0.170 (2)	0.3785 (9)
O(2)	0.343 (1)	0.388 (2)	0.4495 (7)	C(15)	−0.661 (2)	−0.125 (2)	0.3038 (9)
O(3)	0.145 (1)	0.165 (1)	0.1897 (7)	C(16)	−0.558 (1)	−0.034 (2)	0.2705 (8)
O(4)	−0.010 (2)	0.567 (1)	0.2995 (8)	C(21)	−0.377 (1)	0.281 (1)	0.2399 (7)
O(5)	−0.126 (1)	0.342 (1)	0.5025 (5)	C(22)	−0.411 (2)	0.370 (2)	0.3063 (9)
C(1)	0.029 (2)	0.038 (2)	0.3839 (8)	C(23)	−0.493 (2)	0.491 (2)	0.2871 (11)
C(2)	0.222 (2)	0.334 (2)	0.4114 (9)	C(24)	−0.532 (2)	0.518 (2)	0.2095 (10)
C(3)	0.094 (2)	0.193 (2)	0.2456 (8)	C(25)	−0.496 (2)	0.430 (2)	0.1474 (10)
C(4)	−0.002 (2)	0.441 (2)	0.3159 (8)	C(26)	−0.417 (2)	0.308 (1)	0.1615 (8)
C(5)	−0.074 (2)	0.303 (1)	0.4474 (7)	F(1)	−0.846 (1)	−0.242 (1)	−0.0334 (5)
C(6)	−0.283 (3)	0.017 (1)	0.1661 (7)	F(2)	−0.612 (2)	−0.130 (2)	0.0341 (8)
C(7)	−0.210 (2)	−0.126 (1)	0.1792 (7)	F(3)	−0.799 (2)	−0.165 (2)	0.1015 (9)
C(8)	−0.120 (2)	−0.386 (2)	0.1091 (11)	F(4)	−0.709 (2)	−0.358 (2)	0.0506 (11)
C(9)	−0.172 (2)	−0.155 (2)	0.0157 (9)	B	−0.740 (2)	−0.225 (2)	0.038 (1)

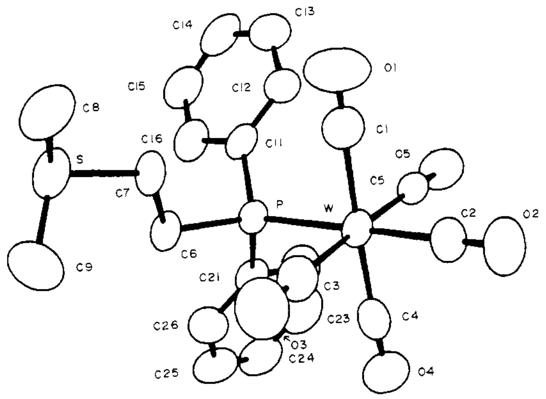

Figure 2. An ORTEP diagram of $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+$ (III) showing 50% probability thermal-motion ellipsoids.

distinguished by ^1H NMR spectroscopy. For example, the methyl resonances of the coordinated sulfonium ions lie in the range δ 3.5–4.2 while the methyl resonances of uncoordinated sulfonium ions lie upfield in the range δ 2.5–3.2 (cf. Table VII).

On the other hand bases, such as $N(C_2H_5)_3$ and $P(CH_3)_2C_6H_5$, produce demethylation of the sulfonium group and yield the methylated base and Ia or Ib, eq 7. These reactions have been studied kinetically and will be described later (see below).

$$M(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+ + L' \rightarrow L'CH_3^+ + M(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)] \quad (7)$$

The character of the compounds III was further established by single-crystal X-ray diffraction analysis. An ORTEP diagram of the cation of $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb) is shown in Figure 2. Table VIII lists final positional parameters. Tables IX and X list interatomic distances and angles, respectively. The metal atom contains an octahedral coordination geometry consisting of five linear terminal carbonyl ligands and the phosphorus atom of the monodentate $(C_6H_5)_2P(CH_2)_2S(CH_3)_2^+$ ion. The metal–carbon distances range from 1.945 (8) Å to 2.054 (7) Å and are similar to those found in $W(CO)_6$, W–C = 2.059 Å.[19] The tungsten–phosphorus distance at 2.525 (1) Å is slightly longer than the tungsten–phosphorus distance of 2.480 (4) Å to the $P(OCH_3)_3$ ligand found in the molecule $HW_2(CO)_8(NO)[P(OCH_3)_3]$.[19] In IIIb there is clearly no metal–sulfur bond, W⋯S = 5.789 (1) Å. The carbon–sulfur distances range from 1.809 (7) to 1.831 (6) Å and are similar to those observed for the coordinated sulfonium ligand in IIa. The sulfonium ion has a pyramidal shape, C–S–C angles 100.0 (3)–103.0 (3)°, which is also essentially identical with that of the coordinated sulfonium ion in IIa. The shortest interionic contact was between carbonyl oxygen atoms in the cations, O(1)⋯O(5) = 3.176 (7) Å.

Table IX. Interatomic Distances with esds for $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb)

atoms	distance (Å)	atoms	distance (Å)
W–P	2.525 (1)	C(21)–C(22)	1.409 (8)
W–C(1)	2.054 (7)	C(21)–C(26)	1.378 (7)
W–C(2)	1.987 (7)	C(22)–C(23)	1.452 (9)
W–C(3)	2.032 (7)	C(23)–C(24)	1.363 (10)
W–C(4)	1.945 (8)	C(24)–C(25)	1.359 (9)
W–C(5)	2.021 (7)	C(25)–C(26)	1.424 (8)
P–C(6)	1.872 (5)	C(1)–O(1)	1.131 (7)
P–C(11)	1.829 (5)	C(2)–O(2)	1.144 (7)
P–C(21)	1.836 (5)	C(3)–O(3)	1.141 (7)
S–C(7)	1.823 (5)	C(4)–O(4)	1.219 (9)
S–C(8)	1.831 (6)	C(5)–O(5)	1.157 (7)
S–C(9)	1.809 (7)	B–F(1)	1.36 (1)
C(6)–C(7)	1.559 (7)	B–F(2)	1.32 (1)
C(11)–C(12)	1.417 (7)	B–F(3)	1.38 (1)
C(11)–C(16)	1.425 (7)	B–F(4)	1.31 (1)
C(12)–C(13)	1.429 (8)	W⋯S	5.789 (1)
C(13)–C(14)	1.401 (9)	$B–F_{av}$	1.34 (2)
C(14)–C(15)	1.392 (9)	$C–C_{(phenyl)av}$	1.402 (8)
C(15)–C(16)	1.375 (8)		

Table X. Interatomic Angles with esds for $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb)

atoms	angle, deg	atoms	angle, deg
P–W–C(1)	91.5 (2)	P–C(11)–C(16)	118.3 (4)
P–W–C(2)	177.9 (2)	C(12)–C(11)–C(16)	120.6 (5)
P–W–C(3)	90.1 (2)	C(11)–C(12)–C(13)	118.1 (5)
P–W–C(4)	91.0 (2)	C(12)–C(13)–C(14)	120.4 (6)
P–W–C(5)	90.5 (2)	C(13)–C(14)–C(15)	119.9 (6)
C(1)–W–C(2)	90.0 (3)	C(14)–C(15)–C(16)	121.8 (6)
C(1)–W–C(3)	93.6 (3)	C(11)–C(16)–C(15)	119.2 (6)
C(1)–W–C(4)	177.5 (3)	P–C(21)–C(22)	114.5 (5)
C(1)–W–C(5)	89.1 (2)	P–C(21)–C(26)	123.4 (4)
C(2)–W–C(3)	91.3 (3)	C(22)–C(21)–C(26)	122.1 (5)
C(2)–W–C(4)	87.6 (3)	C(21)–C(22)–C(23)	116.1 (6)
C(2)–W–C(5)	88.1 (3)	C(22)–C(23)–C(24)	121.7 (1)
C(3)–W–C(4)	86.9 (3)	C(23)–C(24)–C(25)	120.3 (6)
C(3)–W–C(5)	177.3 (3)	C(24)–C(25)–C(26)	121.2 (6)
C(4)–W–C(5)	90.4 (3)	C(21)–C(26)–C(25)	118.7 (6)
W–P–C(6)	116.3 (2)	W–C(1)–O(1)	177.6 (6)
W–P–C(11)	119.1 (2)	W–C(2)–O(2)	178.9 (6)
W–P–C(21)	113.9 (2)	W–C(3)–O(3)	178.4 (6)
C(6)–P–C(11)	102.1 (2)	W–C(4)–O(4)	177.2 (6)
C(6)–P–C(21)	101.3 (2)	W–C(5)–O(5)	176.5 (6)
C(11)–P–C(21)	101.6 (2)		
C(7)–S–C(8)	100.0 (3)	F(1)–B–F(2)	109.3 (7)
C(7)–S–C(9)	103.0 (3)	F(1)–B–F(3)	110.1 (7)
C(8)–S–C(9)	102.0 (4)	F(1)–B–F(4)	110.1 (8)
P–C(6)–C(7)	108.4 (3)	F(2)–B–F(3)	108.2 (8)
S–C(7)–C(6)	109.7 (4)	F(2)–B–F(4)	110.7 (8)
P–C(11)–C(12)	121.2 (4)	F(3)–B–F(4)	108.4 (8)

The sulfonium complexes IIb and IIIb′ react with triethylamine by demethylation of the sulfonium ion to yield $N(CH_3)(C_2H_5)_3^+$

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(19) Love, R. A.; Chin, H. B.; Koetzle, T. F.; Kirtley, S. W.; Whittlesey, B. R.; Bau, R. *J. Am. Chem. Soc.* **1976**, *98*, 4491.

Table XI

	(A) Crystallographic Data for X-ray Diffraction Studies		
compound	Ia	IIa	IIIb
formula	$MoSPO_4C_{19}H_{17}$	$MoSPF_4O_4C_{20}BH_{20}$	$WSPF_4O_5C_{21}BH_{20}$
temp, °C	24	25	25
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a, Å	8.150 (6)	16.928 (5)	8.896 (3)
b, Å	14.229 (6)	21.786 (12)	9.035 (2)
c, Å	17.209 (9)	13.900 (9)	16.972 (4)
α, deg			97.48 (2)
β, deg		106.38 (4)	100.41 (3)
γ, deg			99.68 (3)
V, Å^3	1996 (3)	4918 (8)	1304 (1)
M_r	468.32	570.16	686.08
Z	4	8	2
ρ_{calcd}, g/cm^3	1.56	1.54	1.75
	(B) Measurement of Intensity Data		
radiation	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)	Mo K$\bar{\alpha}$ (0.71073 Å)
monochromator	graphite	graphite	graphite
detector aperture, mm			
horizontal ($A + B \tan \theta$):			
A	3.0	3.0	3.0
B	1.0	1.0	1.0
vertical	4.0	4.0	4.0
crystal faces	$010, 0\bar{1}0, 01\bar{1}, 0\bar{1}1$ $011, 0\bar{1}\bar{1}, 110, 1\bar{1}0$	$100, \bar{1}00, 0\bar{1}1$ $01\bar{1}, 010, 0\bar{1}0$	$001, 00\bar{1}, 0\bar{1}1$ $010, \bar{1}00, 2\bar{1}\bar{1}$
crystal size, mm	0.12 × 0.16 × 0.50	0.22 × 0.46 × 0.52	0.58 × 0.50 × 0.37
crystal orientation direction; deg from ϕ axis	a; 5.7	a; 6.6	normal to $\bar{2}10$; 11.25
reflections measured	$+h, +k, +l$	$+h, +k, \pm l$	$+h, \pm k, \pm l$
max 2θ, deg	52	47	50
scan type	moving crystal, stationary counter	moving crystal, stationary counter	moving crystal, stationary counter
ω-scan width: ($A + 0.347 \tan \theta$), deg	0.95	0.95	1.10
background	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan	$^1/_4$ additional scan at each end of scan
ω-scan rate (variable)			
max, deg/min	10.0	10.0	10.0
min, deg/min	1.5	1.5	1.7
no. of reflections measured	2215	7666	4523
data used ($F^2 \geqslant 3.0\sigma(F^2)$)	1699[a]	4912	3751
	(C) Treatment of Data		
absorption correction			
coefficient, cm^{-1}	8.5	7.3	47.2
grid			14 × 10 × 6
transmission coefficient			
max			0.27
min			0.20
decay correction			
max		1.13	
min		0.97	
P factor	0.01	0.01	0.01
final residuals: R_F	0.025	0.043	0.063
R_{wF}	0.022	0.054	0.075
esd of unit wt observation	1.32	3.68	5.90
largest shift/error value of final cycle	0.00	0.08	0.45
largest peak in final diff Fourier, e$^-$/Å^3	0.13	0.50	3.00

[a] $F^2 \geqslant 2.0\sigma(F^2)$ for this structure.

and the corresponding sulfide complexes Ib, eq 7, and $W(CO)_4L[P(C_6H_5)_2(CH_2)_2SCH_3]$ (IVb, L = CO; IVb′, L = $P(OCH_3)_3$, respectively). In an effort to glean some information about the influence, if any, of metal coordination on this reaction, the kinetics with various sulfonium ions, complexes and uncomplexed, have been investigated under pseudo-first-order reaction conditions with an excess of triethylamine. The results are summarized in Table XI. Due to solubility and reactivity (e.g., sulfonium ion displacement) problems, the measurements were made in either of the two solvents CH_2Cl_2 or CH_3CN. Unfortunately, due to significant effects of solvent which have been observed previously on reactions such as these, it is probably not a good idea to compare the results of the reactions obtained in different solvents.[20] The reactions were conducted at 28 °C and were monitored by ^1H NMR spectroscopy. All the demethylations were followed as a function of time for periods of 2–4 half-lives. All the plots (ln concentration of the ion (complex) vs. $1/T$), except for that of IIb because the rate of reaction was too rapid to follow, were linear thus, verifying the first-order dependence on sulfonium ion concentrations. The chelated sulfonium ion complex IIb demethylates so rapidly in CH_2Cl_2 solvent that the reaction is complete within 30 s. With the assumption that 1 half-life equals 30 s (a conservative upper limit), a rate constant of 2.3×10^{-2} was calculated. The demethylation of IIIb′ in which the sulfonium ion is not coordinated thus occurs more slowly by over three orders of magnitude.

In a second comparison, we studied the demethylation of the known compounds $[(C_5H_4CH_3)Mn(CO)_2\{S(CH_3)_3\}]^+BF_4^-$ (V),[9] in which the sulfonium ion is coordinated, and $[S(CH_3)_3]^+BF_4^-$ (VI) in CH_3CN. Although these demethylations were considerably slower on an absolute basis (perhaps due to solvent effects),[20] it was observed that the sulfonium ligand in V deme-

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[20] Hughes, E. D.; Whittingham, D. J. *J. Chem. Soc.* **1960**, 806.

thylated considerably faster than the uncoordinated sulfonium ion in VI. The difference was slightly less than two orders of magnitude.

Discussion

It has been found that the chelate complexes I can be alkylated to yield the new class of sulfonium ion complexes II. The importance of the chelate effect in the stabilization of these complexes was indicated by unsuccessful attempts to prepare sulfonium ion complexes by alkylation of the related complexes $W(CO)_4L[S(CH_3)_2]$ ($L = CO, P(C_6H_5)_3$).

The existence and nature of the metal–sulfur bonds in these compounds was established by X-ray crystallographic analyses of the compounds Ia and IIa. The $Mo \leftarrow S^+$ bond in IIa was found to be significantly shorter than the Mo–S bond in Ia where the sulfur atom is not charged. This suggests that the molybdenum–sulfur bond in IIa is stronger than that in Ia even though the sulfonium group in IIa can be readily displaced by a variety of donors, eq 6. Intuitively, it seems that a sulfonium ion could not possibly serve as effectively as an uncharged sulfur atom as a σ donor; thus, it is believed that the strength of the $M \leftarrow S^+$ bond is achieved, in large part, by supplemental d–d π-back-bonding. This should be much greater for the positively charged sulfur atom than the uncharged sulfur atom due to a lowering in energy of the empty 3d orbitals in the ion. Indirect evidence for the existence of a greater degree of metal–sulfur d–d π-back-bonding is obtained from the IR spectra of the carbonyl ligands. A greater metal–sulfur π-back-bonding in the sulfonium ion complexes should cause a relative decrease in the π-back-bonding to the carbonyl ligands, and the C–O bonds should in turn become stronger. This is supported by the observation of significant increases in the frequencies of the IR absorptions of the carbonyl ligands (cf. Table I) of the sulfonium ion complexes compared to those of the starting materials.

A particularly notable finding is the observation that the demethylation reaction is dramatically accelerated when the sulfonium ion is coordinated to the metal atom. The reasons for this are not clear but electronic and ring-strain factors could be important. For example, there may be a net increase in the positive charge on the coordinated sulfur atom due to the withdrawal of electron density that occurs when the electrons of the lone pair are shared between the molybdenum and sulfur atoms. The observed downfield shift of the SCH_3 proton resonances of the coordinated sulfonium ions compared to the uncoordinated sulfonium would be consistent with such an effect.

In addition, when the sulfur atom is coordinated to the metal atom, the $[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+$ ligand, as a chelate, forms a five-membered ring. In the event that this produces any strain on the bonding of the sulfur atom, it could influence the demethylation reaction. However, the comparison of the demethylation of compound V where no chelation exists and compound VI suggests that factors other than chelation are also important. Further studies on this subject are planned.

The scope and generality of this acceleration of the demethylation by metal coordination remain to be established, but it could be operative even in biochemical reactions such as the transmethylations of *S*-adenosylmethionine which are known to be catalyzed in many cases by metalloenzymes.[4c]

Experimental Section

General. All reactions and manipulations were performed under a nitrogen atmosphere. Reagent grade methylene chloride was purged with nitrogen and distilled from P_2O_5 under nitrogen before use. Reagent grade hexanes and acetone were purged with nitrogen and stored over molecular sieves under nitrogen. Anhydrous ethyl ether was used as purchased. Acetonitrile was stirred over calcium hydride, filtered, and fractionally distilled from P_2O_5; it was stored over molecular sieves under nitrogen. Acetonitrile-d_3 and acetone-d_6 were obtained from Aldrich and stored over molecular sieves. Methylene-d_2 chloride was obtained from Aldrich or Stohler. The compounds $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$,[21] $W(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$,[21] and $[C_5H_4(CH_2)Mn(CO)_2S(CH_3)_3]^+BF_4^-$[9] were prepared as previously reported. $[S(CH_3)_3]^+BF_4^-$ was made from $S(CH_3)_2$ and $[O(CH_3)_3]^+BF_4^-$ by known procedures.[22] ^1H NMR spectra were obtained from Jeol FX-90Q (90-MHz) or Bruker HX-270 (270-MHz) spectrometers. ^{31}P NMR spectra were obtained from a Varian CFT-20 spectrometer. IR spectra were recorded on a Nicolet 7199 FT-IR. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental microanalyses, performed by Midwest Microlab Ltd., Indianapolis, IN, were obtained for all the isolated compounds which were not analyzed by X-ray crystallographic methods.

Preparation of $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIa). $Mo(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$ (0.100 g, 0.213 mmol) and $[O(CH_3)_3]^+BF_4^-$ (0.100 g, 0.675 mmol) were vigorously stirred at room temperature under nitrogen in 40 mL of CH_2Cl_2 solvent for 3 days. The solution was filtered and IIa was crystallized by addition of hexane and cooling to –5 °C to give white crystals, yield 65%, mp 110–115 °C dec.

Preparation of $W(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIb). $W(CO)_4[P(C_6H_5)_2(CH_2)_2SCH_3]$ (0.40 g, 0.72 mmol) and $[O(CH_3)_3]^+BF_4^-$ (2.52 g, 17 mmol) were stirred in 110 mL of CH_2Cl_2 solvent for 4 days at room temperature. The resulting blue-green reaction mixture was filtered through Celite under nitrogen. A clear yellow filtrate was obtained. Evaporation of the solvent in vacuo gave an off-white semisolid residue which was washed with ether. The crude product was dissolved in methylene chloride and crystallized by adding 20 mL of hexanes and allowing the mixture to stand at room temperature overnight. The mother liquor was decanted and filtered. The product was washed with two 10-mL portions of hexanes to give 0.28 g. The filtrate was concentrated to $^3/_4$ of its original volume and stored at 0 °C for 24 h. Another 0.12 g of product was obtained resulting in 85% total yield. The product is beige in color, but develops a green tinge, mp 130–132 °C dec.

Preparation of $Mo(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIa). At room temperature CO was bubbled through a CH_2Cl_2 (40 mL) solution of IIa (46 mg, 0.08 mmol) for 3 h. The mixture was filtered, followed by addition of hexanes to give white microcrystalline powder, yield 88%, mp 186 °C dec.

Preparation of $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb). Method A. At room temperature CO was bubbled through a CH_2Cl_2 (40 mL) solution of IIb (100 mg, 0.15 mmol) for 7 days and the mixture was filtered. Addition of hexanes gave a white microcrystalline powder. The product was recrystallized by slow evaporation of an acetonitrile solution at room temperature, yield 83%, mp 193–196 °C dec.

Method B. $[(CH_3CN)W(CO)_5]$ (500 mg, 1.37 mmol) and $(C_6H_5)_2P(CH_2)_2S(CH_3)$ (356 mg, 1.37 mmol) were heated at 50 °C in a hexanes/CH_2Cl_2 (3:1) solution for 10 h. The solvent was removed in vacuo, and the residue was crystallized from hexanes to give white crystalline $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)]$, yield 80%. $W(CO)_5[P(C_6H_5)_2(CH_2)_2S(CH_3)]$ (200 mg, 0.34 mmol) and excess $[O(CH_3)_3]^+BF_4^-$ (200 mg, 1.35 mmol) were vigorously stirred in CH_2Cl_2 (40 mL) for 3 h at room temperature. The mixture was filtered, and addition of hexanes to the filtrate gave crude product as a white microcrystalline powder. This was washed with ether and dried in vacuo, yield 71%.

Preparation of $W(CO)_4[P(OCH_3)_3][P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb'). Compound IIb (0.151 g, 0.23 mmol) and $P(OCH_3)_3$ (0.035 g, 0.28 mmol) were stirred in 10 mL of acetone solvent for 30 h at room temperature. The solvent was removed in vacuo to give a dark oil. The residue was dissolved in 5 mL of methylene chloride, then 10 mL of hexane was added. After the mixture was left standing overnight at room temperature, a dark viscous oil as well as some white needles of product were obtained. The crystals were separated yielding 0.028 g of IIIb'. The supernatant was filtered. The viscous oil was dissolved in CH_2Cl_2, filtered, and combined with the supernatant. The solvents were removed in vacuo and the residue was dissolved in 7 mL of CH_2Cl_2. Five milliliters of hexane was added and the solution was allowed to stand 5 days at 0 °C. This yielded a second crop (0.041 g) of product. A third crop (0.057 g) was also obtained. The total yield was 70%.

Reaction of IIb with CH_3CN. A sample of IIb was dissolved in CH_3CN. After 5 min at room temperature, the solvent was removed. The residue in methylene chloride solvent produced the spectra given in Table I. These are consistent with formation of the compound $W(CO)_4(NCCH_3)[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$. The yield appears to be quantitative, but a solid form of the product could not be obtained.

Reactions of $W(CO)_4L[S(CH_3)_2]$ with $[O(CH_3)_3]^+BF_4^-$ ($L = P(C_6H_5)_3$, CO). $W(CO)_4[P(C_6H_5)_3]S(CH_3)_2$ was prepared by the reaction of $W(CO)_5[P(C_6H_5)_3]$[23] with $(CH_3)_3NO$ in the presence of $S(CH_3)_2$ in CH_2Cl_2 solvent over 2 days at room temperature. $W(CO)_4[P(C_6H_5)_3]$-

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Table XII. Data on Rates of Demethylation of Sulfonium Ions by Triethylamine

compound	concn range (initial) studied, mol/L	k,[a] s^{-1}	$t_{1/2}$, min
$W(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIb)	0.020-0.025[b]	$>2.3 \times 10^{-2}$	<0.5
$W(CO)_4[P(OCH_3)_3][P(C_6H_5)_2(CH_2)_2S(CH_3)_2]^+BF_4^-$ (IIIb)	0.020-0.040[b]	2.1×10^{-5}	550
$(C_5H_4CH_3)Mn(CO)_2[S(CH_3)_3]^+BF_4^-$ (V)	0.020-0.030[c]	8.8×10^{-5}	140
$[S(CH_3)_3]^+BF_4^-$ (VI)	0.030-0.045[c]	2.8×10^{-6}	4100

[a] Pseudo-first-order rate constants. Triethylamine excess 10-fold or greater. [b] In CH_2Cl_2. [c] In CH_3CN.

$S(CH_3)_2$ is a yellow solid whose IR spectrum is consistent with a cis structure (ν(CO) in CH_2Cl_2: 2020 s, 1900 vs, 1870 s).

Treatment of $W(CO)_4[P(C_6H_5)_3]S(CH_3)_2$ (70 mg) with excess $[O(CH_3)_3]^+BF_4^-$ in CH_2Cl_2 solvent over 24 h yielded $W(CO)_5[P(C_6H_5)_3]$ as the only metal carbonyl containing product.

By a similar procedure, $W(CO)_5S(CH_3)_2$ yielded only $W(CO)_6$ on treatment with $[O(CH_3)_3]^+BF_4^-$.

Reaction of IIb with Dimethylphenylphosphine. Compound IIb (0.0315 g, 0.048 mmol) and dimethylphenylphosphine (0.0076 g, 0.055 mmol) were stirred in 10 mL of methylene chloride at room temperature for 20 h. Addition of 5 mL of hexanes to the reaction mixture resulted in the formation of a fine, white crystalline material. NMR analyses showed this to be trimethylphenylphosphonium tetrafluoroborate by comparison with an authentic sample prepared from the reaction of dimethylphenylphosphine with trimethyloxoniumtetrafluoroborate (^1H NMR (acetone-d_6) δ 7.6–8.2 (m, 5 H), 2.36 (d, J = 14.7 Hz, 9 H); ^{31}P NMR (acetone-d_6) δ 25.4). Evaporation of the filtrate and analysis by ^1H and ^{31}P NMR and IR spectroscopy showed $W(CO)_4[P(C_6H_5)_2(CH_2)_2S(CH_3)]$ as the only other product.

Reaction of Sulfonium Complexes with Triethylamine. The reactions of compounds IIb and IIIb′ with $N(C_2H_5)_3$ were studied in CD_2Cl_2 solvent. The reactions of V and VI with $N(C_2H_5)_3$ were studied in CD_3CN solvent. The reactions were followed by ^1H NMR spectroscopy. In all cases the only observed reaction was demethylation, and the only products were the appropriate sulfide and $[N(CH_3)(C_2H_5)_3]^+BF_4^-$. All reactions proceeded to completion.

Kinetic Studies of the Reaction of the Sulfonium Complexes with Triethylamine. All the reactions were performed in nitrogen-purged 5-mm NMR tubes under pseudo-first-order conditions by using $N(C_2H_5)_3$ concentrations in 10-fold or greater excess. Initial concentrations of the sulfonium ion complexes ranged from 0.02 to 0.05 M. The rates of the reactions were determined by observing the disappearance of the sulfonium complexes, usually by monitoring the methyl resonances of the sulfonium ion. However, due to peak overlap difficulties the rate of disappearance of IIIb′ was determined by following the disappearance of one of the methyl resonances of the $P(OCH_3)_3$ ligand. The reactions were followed from 2 to 4 half-lives and were carried out at 28.0 ± 0.5 °C. The relative amounts of the compound present were determined by the peak areas of the resonance. This was done in all cases by the cut and weigh method. However, in a few cases the areas was also determined by electronic integration using the spectrometer. The results between the two methods were not significantly different. Plots of ln concentration vs. 1/time were all linear, thus confirming the first-order dependence on the concentration of the sulfonium ion. The calculated rate constants given in Table XI are an average of two or more independent determinations.

Crystallographic Analyses. Crystals of each of the compounds suitable for diffraction analysis were obtained from solutions in CH_2Cl_2/hexane solvent by cooling to −15 °C. All crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer with graphite monochromatized Mo K$\bar{\alpha}$ radiation. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters are listed in Table XII. Data processing was performed on Digital Equipment Corp. PDP 11/45 or VAX 11/750 computers using the Enraf-Nonius SDP program libraries. Neutral atom scattering factors were calculated by the standard procedures.[24a] Anomalous dispersion corrections were applied to all atoms.[24b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F^2{}_o)/2F_o$, and $\sigma(F^2{}_o) = [\sigma(I_{raw})^2 + (PF^2{}_o)^2]^{1/2}/Lp$.

All nonhydrogen atoms were refined anisotropically.

For compounds Ia and IIa the space groups were determined from the systematic absences observed during data collection. For IIIb the space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All the structures were solved by the heavy-atom method.

For Ia the positions of the hydrogen atoms were calculated. Their contributions to scattering were included in the structure factor calculations but their positions were not refined. For IIa and IIIb the hydrogen atoms were ignored. The crystal of IIa showed a slight (13%) decay during data collection. A linear rescale correction was therefore applied to the data. The absorption coefficient for IIIb is 47.2 cm^{-1}; thus, an absorption correction of a Gaussian integration type was applied to the data of this compound.

Estimated standard deviations for the bond distance and angle calculations were obtained by using the inverse matrix obtained on the final cycle of refinement for each structure. Tables of structure factor amplitudes and thermal parameters are available for all three structures; see supplementary material.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administrated by the American Chemical Society, for support of this research. NMR studies were supported by Grant No. CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. R. Adams wishes to thank the A. P. Sloan Foundation for a Fellowship.

Supplementary Material Available: Structure factor amplitudes and thermal parameters (Tables XIII–XVIII) are available for structures I–III (61 pages). Ordering information is given on any current masthead page.

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[24] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–101; (b) Table 2.3.1, pp 149 and 150.