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Registry No. $(n\text{-}Bu_4N)_2[Mo_2O_5(3,5\text{-}DBCat)_2]$, 74521-90-7.

Supplementary Material Available: Listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, and University of California, Berkeley, California 94720

Modes of Phosphite Reactions with Transition-Metal Complexes. Crystal Structures of $(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$ and $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$

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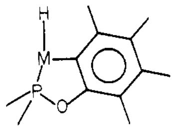
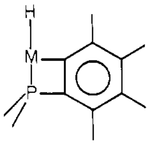
Trialkyl phosphites typically interact with transition-metal ions or complexes to form phosphite–metal donor–acceptor bonds. Aberrant forms of interactions include P–O and R–O (ROP) cleavage reactions. Crystal structures of two complexes that are the end result of P–O and R–O (ROP) bond cleavage reactions between metal complexes and trimethyl phosphite are described. The complexes are $(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$ (**1**) and $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$ (**2**), respectively. Crystals of **1** were monoclinic with space group $P2_1/n$ (a = 7.853 (1) Å, b = 29.761 (5) Å, c = 15.203 (2) Å, β = 105.02 (1)°, Z = 8, V = 3432 Å^3). The asymmetric unit of the crystal contained two crystallographically independent molecules, which differed essentially only in the sense of the orientation of the methyl groups of the trimethyl phosphite ligand. Square pyramidal is a simple and accurate description of the observed chromium coordination sphere with the unique apical ligand represented by the C_5 centroid–Cr vector; here the C_5H_5–Cr interaction formally is considered as a single coordination site. There is a significantly longer Cr–P distance for the phosphonate ligand than for the neutral phosphite ligand. Crystals of **2** were triclinic with space group $P\bar{1}\text{-}C_i^1$ (a = 10.336 (2) Å, b = 12.700 (2) Å, c = 15.518 (3) Å, α = 92.72 (1)°, β = 105.52 (1)°, γ = 87.86 (1)°, Z = 2, V = 1960 Å^3) and contained $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}$ and $PF_6{}^-$ ions. An octahedral array of phosphorus ligands prevailed in the molybdenum cationic complex. Close packing of CH_3O groups on the periphery of the complex gave close CH_3–O···P interligand contacts, and this feature may be responsible for the facile exchange of CH_3O groups between inequivalent phosphorus atoms.

Introduction

Formation of metal–phosphorus donor–acceptor bonds with organophosphines and phosphites can lead to subsequent reaction sequences in which C–H bonds are cleaved to finally generate structures of types **3–5**. Such C–H bond scission



3



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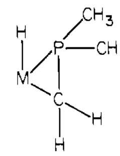

5

is most facile for aryl phosphites,[2-4] **3**, followed by arylphosphines,[2-4] **4**, and then alkylphosphines,[2-4] **5**—especially for those intermediates that are coordinately unsaturated. For a period of time, we had thought that trialkyl phosphites were relatively immune to subsequent reactivity problems except at high temperatures but it is clear from literature reports and from our own research that reactivity problems do arise and the reaction sequences are qualitatively distinct. For example, we have found that $(CH_3O)_3P$ reacts with $Ir_4(CO)_{12}$ at elevated temperatures through a catalytic Arbuzov rearrangement to yield $CH_3P(O)(OCH_3)_2$.[5] Also, it has been shown[6] that thermolysis of metal trimethyl phosphite complexes can generate polyfunctional phosphite ligands: $Os_3(CO)_{11}P(OCH_3)_3$ yields a complex, $HOs_5C(CO)_{12}[OP(OCH_3)OP(OCH_3)_2]$, with the trifunctional ligand $O\text{–}P(OCH_3)\text{–}O\text{–}P(OCH_3)_2$.

Methyl group migration is a relatively common reaction of coordinated trimethyl phosphite. For example, a simple and clean illustration is the transformation of $Ru[P(OCH_3)_3]_5$ to $CH_3Ru[P(O)(OCH_3)_2][P(OCH_3)_3]_4$ at temperatures above 150 °C.[7] An analogous, but much more facile, methyl group transfer takes place in the reaction of $\{\eta^5\text{-}C_5H_5Cr(CO)_2P(OCH_3)_3\}_2$ with trimethyl phosphite to give $(\eta^5\text{-}C_5H_5)Cr(CH_3)(CO)_2P(OCH_3)_3$ and the phosphonate complex $(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2P(OCH_3)_3$ (**1**).[8] Similar molybdenum chemistry has been reported earlier.[9] Another example of phosphite methyl group transfer is the conversion of $\{(C_5H_5)(CH_3)Rh[P(OCH_3)_3]_2{}^+\}I^-$ to $(C_5H_5)(CH_3)Rh[P(O)(OCH_3)_2]P(OCH_3)_3$ and CH_3I.[10] Phosphite addition[11] on the π-arene ligand, not the metal atom, in $(C_6H_6)_2M^{2+}$ (M = Fe, Ru) yields the phosphonium complex $\{\eta^6\text{-}C_6H_6M[\eta^5\text{-}C_6H_6P(OCH_3)_3]^{2+}\}$, which can be converted to the phosphonate, $\{(\eta^6\text{-}C_6H_6)M[(\eta^5\text{-}C_6H_6)P(O)(OCH_3)_2]^+\}$, by $CH_3{}^+$ loss. Another surprising aspect of coordinated trimethyl phosphite chemistry is the rapid cleavage of the P–O bond on protonation of $M[P(OCH_3)_3]_6$, M = Mo[12] or W,[13] by trifluoroacetic acid to give $\{(CH_3O)_2PM[P(OCH_3)_3]_5{}^+\}$ rather than the selective formation of $\{HM[P(OCH_3)_3]_6{}^+\}$. Single crystals of the molybdenum salt $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$ (**2**) were

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(2) For discussions of this type of behavior in coordinated phosphines, see ref 3 and 4.

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isolated. We report here the full crystallographic details for the complexes **1** and **2**, which are formed from a C–O and P–O bond cleavage reaction, respectively.

Experimental Section

Single crystals of $(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2P(OCH_3)_3$ (**1**) and $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$ (**2**) were grown from tetrahydrofuran–hexane[8] and from methanol,[12] respectively. Crystals of **1** and **2** with respective dimensions of 0.50 × 0.50 × 0.21 and 0.60 × 0.48 × 0.34 mm were employed for the data collection and were sealed under nitrogen in thin-walled glass capillaries. The crystal of complex **1** was monoclinic $P2_1/n$ (a special setting of $P2_1/c\text{-}C_{2h}^5$ (No. 14),[14a] with $a = 7.853$ (1) Å, $b = 29.761$ (5) Å, $c = 15.203$ (2) Å, $\beta = 105.02$ (1)°, $Z = 8$, $V = 3432$ Å^3, $d_{calcd} = 1.578$ g/cm^{-3}, and $\mu_a(\text{Mo K}\bar{\alpha})^{15} = 0.87$ mm^{-1}. Although a Delauney reduction for the lattice constants of **1** indicated the possibility of an orthorhombic description, the Laue symmetry was monoclinic, $2/m$. For **2**, the crystal was triclinic $P\bar{1}\text{-}C_i^1$ (No. 2),[14b] with $a = 10.336$ (2) Å, $b = 12.700$ (2) Å, $c = 15.518$ (3) Å, $\alpha = 92.72$ (1)°, $\beta = 105.52$ (1)°, $\gamma = 87.86$ (1)°, $Z = 2$, $V = 1960$ Å^3, $d_{calcd} = 1.623$ g/cm^{-3}, and $\mu_a(\text{Mo K}\bar{\alpha})^{15} = 0.69$ mm^{-1}. Intensity measurements were made on a Nicolet P$\bar{1}$ autodiffractometer using 1° wide ω scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. A total of 8011 independent reflections of **1** having $2\theta_{\text{Mo K}\bar{\alpha}} < 55°$ (the equivalent of 1.0 limiting Cu K$\bar{\alpha}$ sphere) were measured in concentric shells of increasing 2θ. For **2**, a total of 4378 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ (the equivalent of 0.50 limiting Cu K$\bar{\alpha}$ sphere) were measured. For data collection and reduction procedure, see ref 16.

After derivation of the atomic coordinates of the metal atoms of **1** and **2**, from three-dimensional Patterson syntheses, the remaining nonhdydrogen atoms of their totally general-position asymmetric units were located from a series of least-squares refinement cycles followed by difference Fourier syntheses. Unit-weighted isotropic full-matrix least-squares refinement of the structural parameters for the 46 nonhydrogen atoms of **1** gave R_1(unweighted and based on F)[17] = 0.104 and R_2(weighted)[17] = 0.104 for those 3021 reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > 3[\sigma(I)]$. These and all subsequent structure factor calculations for both compounds employed the atomic form factors compiled by Cromer and Mann[18] and an anomalous dispersion correction to the scattering factors of the chromium, molybdenum, and phosphorus atoms.[19] Utilization of anisotropic thermal parameters for all nonhydrogen atoms of **1** in further cycles of least-squares refinement gave $R_1 = 0.054$ and $R_2 = 0.062$ for 3021 reflections. A difference Fourier synthesis calculated at this point showed the 40 hydrogen atoms of the asymmetric unit in chemically anticipated positions. The final cycles of the empirically weighted[20] least-squares refinement, which employed a least-squares refineable extinction correction[21] of the form $1/(1 + 2gI)^{1/2}$ (where the extinction coefficient, g, refined to a value of 1.87×10^{-6}), anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for all hydrogen atoms, converged to final values of 0.049 and 0.057 for R_1 and R_2, respectively, for 4743 independent reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 55°$ and $I > 3[\sigma(I)]$.

Unit-weighted isotropic full-matrix least-squares refinement of the structural parameters for the 48 nonhydrogen atoms of **2** gave $R_1 = 0.132$ and $R_2 = 0.139$ for those 2964 reflections having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > 3[\sigma(I)]$. Utilization of anisotropic thermal parameters for nonhydrogen atoms of **2** in further cycles of unit-weighted refinement gave $R_1 = 0.070$ and $R_2 = 0.074$ for 2964 reflections. Empirical weights[20] were then calculated; least-squares refinement utilizing these weights and anisotropic thermal parameters for all nonhydrogen atoms gave $R_1 = 0.070$ and $R_2 = 0.082$ for 2964 reflections of **2** having $2\theta_{\text{Mo K}\bar{\alpha}} < 43°$ and $I > 3[\sigma(I)]$. Since a careful examination of the final F_o and F_c values for **2** indicated the absence of extinction effects, extinction corrections were not made.

During the final cycles of refinement for both compounds,[22] no parameter (including those for the hydrogen atoms of **1**) shifted by more than $0.70\sigma_p$ with the average shift being less than $0.20\sigma_p$ for **1** and less than $0.07\sigma_p$ for **2**, where σ_p is the estimated standard deviation of the parameter. The computer programs used are described in ref 16.

Results and Discussion

$(\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$ (1). The dimer, $\{(\eta^5\text{-}C_5H_5)Cr(CO)_2[P(OCH_3)_3]\}_2$, has a very long Cr–Cr bond, 3.343 Å, suggestive of a relatively weak metal–metal bond.[8] In fact, the dimer in solution at 20 °C is largely dissociated into monomeric $(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OCH_3)_3$ units. These react rapidly at 20 °C with trimethyl phosphite with net cleavage of the carbon–oxygen bond to give a methyl and a phosphonate complex:[8]

$$2(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OCH_3)_3 + P(OCH_3)_3 \rightarrow \\ (\eta^5\text{-}C_5H_5)Cr(CH_3)(CO)_2P(OCH_3)_3 + \\ (\eta^5\text{-}C_5H_5)Cr[P(O)(OCH_3)_2](CO)_2[P(OCH_3)_3]$$

The phosphonate complex **1** was obtained in single-crystal form for the crystallographic study, described below, to rigorously establish the character and the structural parameters of the unique phosphorus ligand.

Final atomic coordinates and thermal parameters for this complex are presented in Tables I and II.[22] As the bond lengths and angles of Tables V–VII[22] indicate, the two crystallographically independent molecules[23] (Figure 1) in the totally general-position asymmetric unit of crystalline **1** are nearly identical in stereochemical detail with the only major difference between them the orientation of the methyl groups in the trimethyl phosphite ligand. An accurate shape description of the molecule, **1**, is square pyramidal with the cyclopentadienyl ligand occupying the unique apical position although this description is simply a convenience since this complex electronically is not a five-coordinate complex but a higher coordinate species.

Unlike the other pseudo-square-pyramidal species, $[(\eta^5\text{-}C_5H_5)Cr(CH_3)(CO)_2P(OCH_3)_3]$ (**6**), which formed in the

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(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I: (a) p 99; (b) p 75.

(15) Atomic absorption coefficients for all elements were taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968, Vol. III, p 166.

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(17) The R values are defined as

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| \qquad R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$$

where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

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(20) Empirical weights ($w = 1/\sigma^2$) were calculated for both compounds from the equation

$$\sigma = \sum a_n|F_o|^n = 1.29 - 6.30 \times 10^{-4}|F_o| + 7.10 \times 10^{-5}|F_o|^2$$

for **1** and

$$\sigma = 2.10 - 2.67 \times 10^{-2}|F_o| + 7.74 \times 10^{-4}|F_o|^2 - 3.13 \times 10^{-6}|F_o|^3$$

for **2**, the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum a_n|F_o|^n$$

where the F_c values were calculated from the fully refined models with use of unit weighting and an $I > 3[\sigma(I)]$ rejection criterion.

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(22) See the paragraph at the end of paper regarding supplementary material.

(23) The numbering scheme used to designate atoms of **1** and **2** are as follows: Atoms for a particular phosphite ligand in both compounds are distinguished from each other by the first numerical subscript to the appropriate atomic symbol. Phosphite oxygen and carbon atoms carry a second numerical subscript to distinguish between different methoxy arms of the same ligand. Methyl hydrogen atoms contain a third numerical subscript to distinguish between hydrogens on the same carbon. Atoms for the phosphonate ligands of **1** and phosphino ligands of **2** are designated by a subscript 1 and 6, respectively; oxygen, carbon, and hydrogen (for **1** only) atoms for these ligands are denoted in a manner similar to that already described for methoxy arms of the phosphite ligands. Carbonyl oxygen and carbon atoms of **1** along with the seven atoms of the phosphorus hexafluoride anion of **2** carry a single numerical subscript. Carbon and hydrogen atoms of the cyclopentadienyl rings of **1** carry a letter subscript, p, followed by a numerical subscript.

Table I. Atomic Coordinates in Crystalline $(\eta^5\text{-}C_5H_5)Cr[PO(OCH_3)_2](CO)_2[P(OCH_3)_3]$[a]

Molecule I

atom type[b]	fractional coordinates			B,[c] Å^2	atom type[b]	fractional coordinates			B,[c] Å^2
	10^4x	10^4y	10^4z			10^3x	10^3y	10^3z	
Cr	668.1 (8)	1424.3 (2)	4443.4 (4)	2.88	H_{121}	−518 (8)	219 (2)	287 (4)	5 (2)
P_1	−2018 (1)	1396 (1)	3302 (1)	3.4	H_{122}	−518 (9)	170 (2)	316 (4)	5 (2)
P_2	1944 (1)	1975 (1)	5427 (1)	3.3	H_{123}	−465 (15)	215 (4)	372 (5)	14 (3)
O_1	−2164 (5)	1590 (1)	5393 (2)	4.9	H_{131}	−330 (11)	162 (3)	139 (6)	8 (2)
O_2	1181 (4)	2136 (1)	3141 (2)	4.5	H_{132}	−238 (11)	130 (3)	109 (6)	7 (2)
O_{11}	−3350 (4)	1056 (1)	3374 (2)	4.6	H_{133}	−371 (13)	109 (3)	160 (6)	9 (3)
O_{12}	−2923 (4)	1885 (1)	3178 (2)	4.0	H_{211}	208 (9)	244 (2)	705 (5)	6 (2)
O_{13}	−1490 (4)	1345 (1)	2350 (2)	4.4	H_{212}	218 (7)	198 (2)	773 (4)	4 (1)
O_{21}	1985 (6)	1853 (1)	6443 (2)	4.9	H_{213}	390 (10)	219 (2)	737 (5)	6 (2)
O_{22}	3926 (5)	2071 (1)	5427 (3)	5.6	H_{221}	422 (7)	268 (2)	582 (4)	3 (1)
O_{23}	1232 (5)	2471 (1)	5298 (3)	5.0	H_{222}	586 (13)	238 (3)	615 (6)	10 (3)
C_1	−1069 (6)	1535 (1)	5024 (3)	3.5	H_{223}	507 (13)	259 (4)	522 (7)	11 (3)
C_2	935 (5)	1869 (1)	3648 (3)	3.2	H_{231}	−51 (8)	293 (2)	496 (4)	4 (1)
C_{12}	−4704 (8)	1958 (2)	3195 (6)	5.5	H_{232}	−111 (10)	245 (2)	451 (5)	6 (2)
C_{13}	−2841 (9)	1319 (3)	1518 (4)	5.6	H_{233}	−92 (6)	254 (1)	542 (3)	1 (1)
C_{21}	2516 (9)	2134 (2)	7221 (4)	5.1	H_{p1}	18 (8)	63 (2)	504 (4)	4 (1)
C_{22}	4976 (9)	2455 (2)	5772 (5)	5.5	H_{p2}	16 (10)	66 (3)	357 (5)	7 (2)
C_{23}	−476 (8)	2618 (2)	4958 (6)	5.3	H_{p3}	259 (10)	101 (2)	339 (5)	7 (2)
C_{p1}	822 (10)	726 (2)	4872 (7)	5.5	H_{p4}	431 (11)	125 (3)	501 (6)	9 (2)
C_{p2}	815 (11)	738 (2)	3958 (6)	5.8	H_{p5}	255 (7)	98 (2)	591 (4)	3 (1)
C_{p3}	2297 (11)	956 (2)	3901 (5)	5.4					
C_{p4}	3209 (8)	1082 (2)	4735 (5)	5.1					
C_{p5}	2326 (10)	942 (2)	5354 (4)	5.1					

Molecule II

atom type[b]	fractional coordinates			B,[c] Å^2	atom type[b]	fractional coordinates			B,[c] Å^2
	10^4x	10^4y	10^4z			10^3x	10^3y	10^3z	
Cr	3317.0 (9)	3951.5 (2)	3326.8 (4)	3.01	H_{121}	915 (11)	460 (3)	510 (5)	7 (2)
P_1	5989 (1)	3829 (1)	4445 (1)	3.3	H_{122}	926 (10)	413 (3)	484 (5)	7 (2)
P_2	2066 (2)	4573 (1)	2558 (1)	3.9	H_{123}	875 (11)	447 (3)	408 (6)	8 (3)
O_1	6145 (5)	4209 (1)	2426 (3)	5.6	H_{131}	752 (7)	383 (2)	631 (3)	3 (1)
O_2	2880 (4)	4524 (1)	4869 (2)	4.2	H_{132}	635 (9)	348 (2)	658 (5)	5 (2)
O_{11}	7283 (5)	3506 (1)	4248 (2)	4.7	H_{133}	737 (9)	330 (2)	605 (4)	5 (2)
O_{12}	6932 (4)	4304 (1)	4766 (2)	4.1	H_{211}	254 (10)	485 (2)	81 (5)	7 (2)
O_{13}	5450 (4)	3685 (1)	5362 (2)	4.0	H_{212}	264 (7)	439 (2)	99 (4)	3 (1)
O_{21}	1238 (6)	4541 (2)	1503 (3)	6.0	H_{213}	142 (8)	456 (2)	28 (4)	4 (1)
O_{22}	380 (5)	4737 (1)	2866 (3)	5.7	H_{221}	−18 (10)	534 (2)	229 (5)	7 (2)
O_{23}	3207 (5)	5014 (1)	2578 (8)	4.3	H_{222}	−141 (12)	506 (3)	182 (6)	10 (3)
C_1	5072 (6)	4118 (2)	2780 (3)	4.0	H_{223}	−131 (9)	518 (2)	276 (5)	6 (2)
C_2	3111 (5)	4316 (1)	4274 (3)	3.1	H_{231}	490 (8)	545 (2)	318 (4)	5 (2)
C_{12}	8681 (7)	4404 (3)	4749 (6)	5.5	H_{232}	517 (8)	496 (2)	368 (4)	4 (1)
C_{13}	6819 (8)	3577 (2)	6159 (4)	4.7	H_{233}	369 (11)	531 (3)	371 (5)	7 (2)
C_{21}	1963 (12)	4609 (3)	821 (5)	7.9	H_{p1}	378 (8)	318 (2)	229 (4)	5 (2)
C_{22}	−667 (10)	5112 (2)	2458 (6)	7.1	H_{p2}	391 (7)	309 (2)	377 (4)	3 (1)
C_{23}	4402 (9)	5188 (2)	3381 (4)	4.8	H_{p3}	132 (8)	348 (2)	401 (4)	3 (1)
C_{p1}	3018 (8)	3298 (2)	2640 (4)	5.0	H_{p4}	−27 (10)	383 (2)	280 (5)	6 (2)
C_{p2}	3111 (12)	3226 (2)	3524 (5)	5.4	H_{p5}	119 (7)	365 (2)	164 (4)	3 (1)
C_{p3}	1689 (16)	3447 (3)	3735 (5)	5.8					
C_{p4}	709 (8)	3649 (2)	2931 (5)	5.2					
C_{p5}	1567 (7)	3549 (2)	2271 (4)	4.4					

[a] Figures in parentheses are the estimated standard deviation for the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] For nonhydrogen atoms, this is the equivalent isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$ where the β_{ij} are the dimensionless anisotropic temperature factors employed during refinement; for hydrogen atoms, this is the isotropic thermal parameter actually refined.

reaction of trimethyl phosphite with $(\eta^5\text{-}C_5H_5)Cr(CO)_2P(OCH_3)_3$,[8] molecules of **1** exist only in the stereoisomeric form with the carbonyl ligands occupying trans coordination sites of the "square" base. The nearly equal amounts of the cis and trans stereoisomeric forms observed[8] for **6** and the exclusively trans form for **1** would be expected from steric considerations for these two molecules. While the two bulky phosphorus-containing ligands in **1** should remain as far apart as possible and give exclusively the trans form, **6**, the methyl complex, contains only one bulky basal ligand and therefore should have nearly equal amounts of both isomeric forms present after reaction. The ligand···ligand contacts presented in Table V for the coordination sphere of **1** are totally consistent with these arguments. Although the coordination geometry of **1** is accurately described as pseudo square pyramidal, the Cr atom is *formally* seven-coordinate and would be expected to be sterically crowded, especially with two relatively bulky phosphorus ligands. Consistently, there are several P···C and C···C contacts[24] in both molecules of **1**, which have intramolecular separations that are significantly less than the corresponding van der Waals values[25] of 3.60 and 3.40 Å, respectively.

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(24) The first number in parentheses following an averaged value for a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively; the fourth number is the number of individual values included in the average.

(25) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 260.

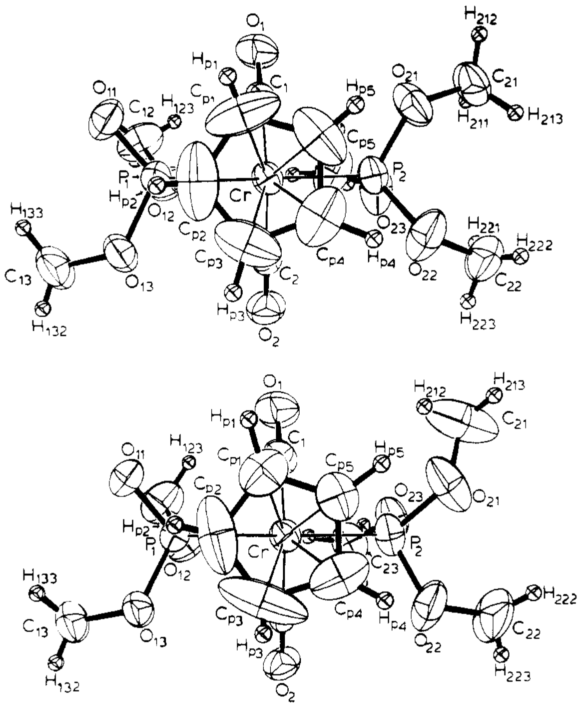

Figure 1. Perspective ORTEP drawings of the two crystallographically independent molecules in the asymmetric unit of $(\eta^5\text{-}C_5H_5)Cr[PO(OCH_3)_2](CO)_2[P(OCH_3)_3]$ (**1**) (top, molecule I; bottom, molecule II). All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; hydrogen atoms are represented by arbitrarily sized spheres, which are in no way representative of their true thermal motion. The labeling scheme is described in footnote 23. The following atoms are hidden from view and/or are not labeled in the drawing: C_{23}, H_{121}, H_{122}, H_{131}, H_{231}, H_{232}, and H_{233} of molecule I; C_{12}, H_{121}, H_{122}, H_{131}, H_{211}, H_{221}, H_{231}, H_{232}, H_{233} of molecule II.

The coordination group in **1** approximates rather closely its maximum possible symmetry of C_{2v} with the three major planar groupings[26] in each molecule (the cyclopentadienyl C_5 ring mean plane, P_1CrP_2, and $O_1C_1CrC_2O_2$) intersecting in dihedral angles of 85.2–89.4°. Both independent cyclopentadienyl C_5 rings are coplanar to within 0.007 Å. There is an elongation of the square pyramid with C_5H_5(centroid)–Cr–L average angles[24] of 122.6 (-, 1, 2, 4)° for CO, 112.7 (-, 1, 1, 2)° for phosphonate, and 114.9 (-, 4, 4, 2)° for trimethyl phosphite. The large L_{apical}–M–L_{basal} angles are a necessary consequence of the spatial demands of the cyclopentadienyl ligand.

Both molecules have cyclopentadienyl Cr–C and carbonyl Cr–C distances that are normal and experimentally equivalent with average values of 2.181 (6,8,17,10) and 1.843 (5,4,9,4) Å,[24] respectively. The phosphonate Cr–P bond is expectedly longer (by 0.092 Å) than the phosphite Cr–P bond; all other bond distances and angles in the chromium complex are unexceptional. There is no *inter*molecular contact significantly less than the van der Waals value.[25]

Table III. Atomic Coordinates in Crystalline $\{[(CH_3O)_2P]Mo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$[a]

atom type[b]	fractional coordinates 10^3x	10^3y	10^3z	B,[c] Å^2
		Cation		
Mo	345.8 (1)	247.6 (1)	222.4 (1)	3.79
P_1	124.0 (4)	286.0 (3)	127.5 (3)	6.3
P_2	396.9 (4)	432.4 (3)	252.5 (3)	6.0
P_3	571.5 (4)	210.5 (3)	318.2 (3)	6.1
P_4	313.9 (4)	58.8 (3)	213.3 (2)	5.4
P_5	243.2 (4)	263.3 (3)	350.5 (3)	6.4
P_6	419.5 (4)	245.6 (3)	99.8 (3)	6.1
O_{11}	−1 (1)	295 (1)	172 (1)	7.9
O_{12}	71 (1)	205 (1)	49 (1)	7.4
O_{13}	89 (1)	393 (1)	69 (1)	9.3
O_{21}	426 (1)	471 (1)	353 (1)	7.7
O_{22}	517 (3)	474 (2)	227 (2)	12.5
O_{23}	292 (3)	513 (1)	208 (1)	13.2
O_{31}	629 (1)	289 (1)	398 (1)	8.1
O_{32}	592 (1)	99 (1)	359 (1)	7.5
O_{33}	700 (1)	213 (1)	275 (1)	7.5
O_{41}	426 (1)	−5 (1)	176 (1)	6.1
O_{42}	325 (1)	9 (1)	308 (1)	6.9
O_{43}	183 (1)	−1 (1)	151 (1)	6.5
O_{51}	141 (1)	172 (1)	347 (1)	6.7
O_{52}	165 (1)	371 (1)	357 (1)	8.2
O_{53}	338 (1)	267 (1)	454 (1)	9.7
O_{61}	395 (1)	178 (1)	9 (1)	8.0
O_{62}	510 (1)	329 (1)	75 (1)	7.9
C_{11}	−76 (2)	386 (2)	187 (1)	9.4
C_{12}	−59 (2)	212 (2)	−14 (1)	10.1
C_{13}	164 (2)	415 (2)	2 (1)	9.4
C_{21}	469 (3)	571 (2)	395 (1)	10.3
C_{22}	617 (2)	512 (2)	227 (2)	11.1
C_{23}	224 (2)	591 (2)	204 (2)	12.4
C_{31}	759 (2)	323 (2)	441 (2)	10.5
C_{32}	717 (2)	53 (2)	412 (1)	9.3
C_{33}	715 (2)	135 (1)	201 (1)	8.8
C_{41}	449 (2)	−115 (1)	174 (2)	9.5
C_{42}	284 (2)	−91 (1)	325 (1)	10.3
C_{43}	49 (1)	20 (1)	162 (1)	7.1
C_{51}	61 (2)	153 (2)	405 (1)	10.1
C_{52}	129 (2)	423 (2)	430 (1)	9.9
C_{53}	411 (2)	181 (2)	497 (1)	10.1
C_{61}	307 (2)	91 (1)	−20 (1)	7.9
C_{62}	542 (2)	338 (2)	−10 (1)	10.3
		Anion		
P_7	102.5 (5)	243.5 (4)	699.3 (4)	7.8
F_1	−14 (2)	239 (1)	735 (2)	17.8
F_2	34 (2)	181 (2)	622 (1)	19.8
F_3	138 (2)	137 (1)	736 (2)	19.0
F_4	221 (2)	245 (2)	665 (1)	17.7
F_5	176 (3)	297 (2)	776 (1)	19.6
F_6	78 (2)	343 (2)	663 (2)	20.7

[a] Figures in parentheses are the estimated standard deviation for the last significant digit. [b] Atoms are labeled in agreement with Figure 2. [c] This is the equivalent isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$ where the β_{ij} are the dimensionless anisotropic temperature factors employed during refinement.

$\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}$ $(PF_6{}^-)$ (2). Protonic attack[12] of $Mo[P(OCH_3)_3]_6$ proceeded with nearly quantitative cleavage of a phosphite ligand phosphorus–oxygen bond to give the diamagnetic cation $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}$:

$$Mo[P(OCH_3)_3]_6 + H^+ \rightarrow CH_3OH + \{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}$$

This cationic and six-coordinate d^4 complex was relatively nonreactive and was isolated as a salt with a wide variety of counterions. All these salts gave essentially identical ^1H and ^{31}P NMR spectra for the cationic complex. The hexafluorophosphate salt, **2**, was selected specifically for the crystallographic study, described below, because of the crystal quality.

Final atomic coordinates and thermal parameters for **2** are presented in Tables III and IV,[22] and bond lengths and angles

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(26) The least-squares mean planes for the following groups of atoms in **1** are defined by the equation $aX + bY + cZ = d$, where X, Y, and Z are orthogonal coordinates measured along $\vec{a}$, $\vec{b}$ and $\vec{c}^*$, respectively, of the crystal system. Molecule I: (a) C_{p1}, C_{p2}, C_{p3}, C_{p4}, and C_{p5} (coplanar to within 0.002 Å): $a = -0.486$, $b = 0.867$, $c = -0.108$, $d = 1.723$. (b) Cr, P_1, and P_2: $a = -0.659$, $b = -0.344$, $c = 0.669$, $d = 3.719$. (c) Cr, O_1, O_2, C_1, and C_2 (coplanar to within 0.007 Å): $a = 0.487$, $b = 0.461$, $c = 0.742$, $d = 6.199$. Molecule II: (d) C_{p1}, C_{p2}, C_{p3}, C_{p4}, and C_{p5} (coplanar to within 0.007 Å): $a = 0.506$, $b = 0.830$, $c = 0.234$, $d = 9.722$. (e) Cr, P_1, and P_2: $a = -0.669$, $b = 0.192$, $c = 0.718$, $d = 4.900$. (f) Cr, O_1, O_2, C_1, and C_2 (coplanar to within 0.002 Å): $a = -0.503$, $b = 0.576$, $c = -0.644$, $d = 2.979$.

Table V. Bond Distances, Short Ligand–Ligand Contacts, and Bond Angles Subtended at the Cr Atom in the Coordination Group of $(\eta^5\text{-}C_5H_5)Cr[PO(OCH_3)_2](CO)_2[P(OCH_3)_3]$[a]

	dist, Å				angle, deg		
type[b]	molecule I	molecule II	av[c]	type[b]	molecule I	molecule II	av[c]
$Cr-C_{p1}$	2.171 (6)	2.191 (5)	2.181 (6,8,17,10)[c]	C_gCrC_1[d]	122.7	122.5	122.6 (-,1,2,4)[c]
$Cr-C_{p2}$	2.186 (6)	2.192 (5)		C_gCrC_2[d]	122.7	122.4	
$Cr-C_{p3}$	2.191 (6)	2.164 (6)		C_gCrP_1[d]	112.7	112.6	112.7 (-,1,1,2)
$Cr-C_{p4}$	2.181 (6)	2.174 (5)		C_gCrP_2[d]	115.3	114.5	114.9 (-,4,4,2)
$Cr-C_{p5}$	2.176 (6)	2.182 (5)		P_1CrP_2	131.9 (1)	133.0 (1)	132.4 (1,5,6,2)
$Cr-P_1$	2.360 (1)	2.362 (1)	2.361 (1,1,1,2)	C_1CrC_2	114.3 (2)	114.8 (2)	114.6 (2,3,3,2)
$Cr-P_2$	2.268 (1)	2.271 (1)	2.269 (1,2,2,2)	P_1CrC_1	74.1 (1)	74.9 (1)	75.7 (1,12,16,4)
$Cr-C_1$	1.836 (5)	1.852 (5)	1.843 (5,4,9,4)	P_1CrC_2	77.0 (1)	76.7 (1)	
$Cr-C_2$	1.841 (4)	1.843 (5)		P_2CrC_1	79.0 (1)	79.9 (1)	79.2 (1,3,7,4)
$Cr-C_g$[d]	1.846 (-)	1.840 (-)	1.843 (-,3,3,2)	P_2CrC_2	78.9 (1)	78.9 (1)	
$P_1\cdots C_1$	2.562 (5)	2.593 (5)	2.626 (5,24,64,8)				
$P_1\cdots C_2$	2.645 (5)	2.641 (5)					
$P_2\cdots C_1$	2.633 (5)	2.667 (5)					
$P_2\cdots C_2$	2.633 (5)	2.636 (5)					
$C_1\cdots C_2$	3.089 (7)	3.113 (7)	3.101 (7,12,12,2)				
$C_1\cdots C_{p1}$	2.868 (7)	2.902 (7)	2.883 (7,23,31,4)				
$C_2\cdots C_{p3}$	2.908 (7)	2.852 (7)					
$C_1\cdots C_{p5}$	3.127 (7)	3.152 (7)	3.133 (7,14,23,4)				
$C_2\cdots C_{p4}$	3.143 (7)	3.110 (7)					

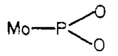
[a] The number in parentheses following each entry is the estimated standard deviation of the last significant digit. [b] Atoms are labeled to agree with Figure 1 and Tables I and II. [c] See ref 24. [d] C_g refers to the center of gravity of the five-carbon cyclopentadienyl ring.

Table VI. Bond Lengths and Angles Involving Nonhydrogen Ligand Atoms in $(\eta^5\text{-}C_5H_5)Cr[PO(OCH_3)_2](CO)_2[P(OCH_3)_3]$[a]

	value				value		
type[b]	molecule I	molecule II	av[c]	type[b]	molecule I	molecule II	av[c]
			Bond Lengths (Å)				
P_1-O_{11}	1.482 (3)	1.483 (3)	1.482 (3,1,1,2)	$C_{p1}-C_{p2}$	1.389 (11)	1.343 (10)	1.371 (10,18,34,10)
P_1-O_{12}	1.610 (3)	1.613 (4)	1.613 (3,2,4,4)	$C_{p1}-C_{p5}$	1.377 (10)	1.356 (8)	
P_1-O_{13}	1.612 (3)	1.617 (3)		$C_{p2}-C_{p3}$	1.356 (11)	1.403 (13)	
P_2-O_{21}	1.578 (4)	1.570 (4)	1.580 (4,6,11,6)	$C_{p3}-C_{p4}$	1.337 (9)	1.400 (12)	
P_2-O_{22}	1.583 (4)	1.591 (3)		$C_{p4}-C_{p5}$	1.369 (9)	1.378 (8)	
P_2-O_{23}	1.573 (4)	1.585 (4)		$O_{12}-C_{12}$	1.422 (6)	1.412 (6)	
C_1-O_1	1.154 (5)	1.143 (6)	1.151 (5,4,8,4)	$O_{13}-C_{13}$	1.427 (6)	1.433 (6)	
C_2-O_2	1.157 (5)	1.150 (5)		$O_{21}-C_{21}$	1.420 (6)	1.321 (8)	1.410 (7,24,89,10)
			Bond Angles (Deg)				
CrP_1O_{11}	118.9 (2)	118.8 (1)	118.8 (2,1,1,2)	$O_{22}-C_{22}$	1.427 (7)	1.430 (7)	
CrP_1O_{12}	109.7 (1)	109.6 (1)	107.8 (1,18,21,4)	$O_{23}-C_{23}$	1.378 (7)	1.430 (6)	
CrP_1O_{13}	105.9 (1)	106.2 (1)		$O_{11}P_1O_{12}$	109.2 (2)	110.1 (2)	110.1 (2,4,9,4)
CrP_2O_{21}	112.0 (1)	119.0 (2)	116.2 (1,37,47,6)	$O_{11}P_1O_{13}$	110.6 (2)	110.4 (2)	
CrP_2O_{22}	113.4 (1)	112.3 (1)		$O_{12}P_1O_{13}$	100.9 (2)	100.0 (2)	101.6 (2,26,41,8)
CrP_2O_{23}	120.9 (1)	119.8 (1)		$O_{21}P_2O_{22}$	105.7 (2)	99.4 (3)	
CrC_1O_1	177.8 (11)	178.0 (11)	176.8 (9,12,18,4)	$O_{21}P_2O_{23}$	104.7 (2)	98.8 (2)	
CrC_2O_2	176.2 (4)	175.0 (6)		$O_{22}P_2O_{23}$	98.5 (2)	104.5 (2)	
$P_1O_{12}C_{12}$	122.7 (4)	123.5 (4)	124.6 (4,32,58,10)	$C_{p5}C_{p1}C_{p2}$	107.5 (6)	108.9 (6)	108.0 (6,10,17,10)
$P_1O_{13}C_{13}$	119.8 (3)	118.8 (3)		$C_{p1}C_{p2}C_{p3}$	107.1 (6)	108.3 (6)	
$P_2O_{21}C_{21}$	127.4 (4)	130.0 (5)		$C_{p2}C_{p3}C_{p4}$	109.3 (6)	106.9 (5)	
$P_2O_{22}C_{22}$	128.3 (4)	122.7 (4)		$C_{p3}C_{p4}C_{p5}$	109.0 (6)	106.3 (6)	
$P_2O_{23}C_{23}$	128.7 (4)	123.9 (3)		$C_{p4}C_{p5}C_{p1}$	107.0 (6)	109.5 (6)	

[a] The number in parentheses following each entry is the estimated standard deviation of the last significant digit. [b] Atoms are labeled to agree with Figure 1 and Tables I and II. [c] See ref 24.

are presented with estimated standard deviations in Tables VIII–X. The crystal was comprised of discrete octahedral PF_6^- and $\{(CH_3O)_2PMo[P(OCH_3)_3]_5^+\}$ ions. The phosphorus atoms in the cation define the vertices of an octahedron (Figure 2) with nearly regular angles—the range is 86.4 (1) to 93.8 (1)° with an average value of 90.0 (1,28,38,12)°. All three MoP_4 units are coplanar[27] to within 0.13 Å and intersect in dihedral angles of 89.4–89.8°; thus the molybdenum atom is well centered in the octahedron. For the equivalent set of four trimethyl phosphite ligands, the molybdenum–phosphorus distances are all very similar, ranging from 2.417 (4) to 2.450 (4) Å with an average value of 2.428 (4,11,22,4) Å.[24] However, the molybdenum–phosphorus distance for the phosphite ligand trans to the unique $P(OCH_3)_2$ ligand is somewhat longer at 2.488 (4) Å. Uniquely short is the molybdenum–phosphorus distance 2.229 (4) Å for the $P(OCH_3)_2$ ligand. Multiple bond order was expected for this bond, and fully supportive of this was the very short molybdenum–phosphorus distance and the coplanarity,[28] to within 0.036 Å, of the basic



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[27] The least-squares mean planes for the following groups of atoms in **2** are defined by the equation given in ref 26 where *X*, *Y*, and *Z* are measured along $(\vec{b} \times \vec{c}^*)$, $\vec{b}$, and $\vec{c}^*$, respectively, of the crystal system. (a) Mo, P_1, P_2, P_3, and P_4 (coplanar to within 0.06 Å): $a = -0.599$, $b = -0.011$, $c = 0.801$, $d = 1.071$. (b) Mo, P_1, P_3, P_5, and P_6 (coplanar to within 0.03Å): $a = 0.149$, $b = 0.982$, $c = 0.120$, $d = 3.879$. (c) Mo, P_2, P_4, P_5, and P_6 (coplanar to within 0.13 Å): $a = 0.781$, $b = -0.186$, $c = 0.595$, $d = 3.482$.

[28] Least-squares mean plane defined[27] by $0.706X - 0.559Y + 0.434Z = 1.590$.

Table VIII. Bond Distances, Polyhedral Edge Lengths, and Bond Angles Subtended at the Mo Atom in the Coordination Group of $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}$[a]

type[b]	value	type[b]	value
		Bond Distances (Å)	
$\mathrm{Mo-P_1}$	2.417 (4)	$\mathrm{Mo-P_4}$	2.424 (4)
$\mathrm{Mo-P_2}$	2.421 (4)	average	2.428 (4,11,22,4)
$\mathrm{Mo-P_3}$	2.450 (4)		
$\mathrm{Mo-P_5}$	2.488 (4)	$\mathrm{Mo-P_6}$	2.229 (4)
		Polyhedral Edge Lengths (Å)	
$P_1\cdots P_2$	3.507 (5)	$P_3\cdots P_5$	3.596 (5)
$P_2\cdots P_3$	3.340 (6)	$P_4\cdots P_5$	3.462 (5)
$P_3\cdots P_4$	3.349 (5)	$P_1\cdots P_6$	3.216 (6)
$P_1\cdots P_4$	3.534 (5)	$P_2\cdots P_6$	3.319 (5)
$P_1\cdots P_5$	3.371 (6)	$P_3\cdots P_6$	3.375 (6)
$P_2\cdots P_5$	3.363 (5)	$P_4\cdots P_6$	3.396 (5)
		Bond Angles (Deg)	
P_1MoP_3	179.4 (2)	P_5MoP_6	173.6 (2)
P_2MoP_4	172.0 (2)	average	175.0 (2,29,44,3)[c]
P_1MoP_2	92.9 (1)	P_4MoP_5	89.6 (1)
P_2MoP_3	86.5 (1)	P_1MoP_6	87.5 (1)
P_3MoP_4	86.8 (1)	P_2MoP_6	91.0 (1)
P_1MoP_4	93.8 (1)	P_3MoP_6	92.2 (1)
P_1MoP_5	86.8 (1)	P_4MoP_6	93.6 (1)
P_2MoP_5	86.4 (1)	average	90.0 (1,28,38,12)[c]
P_3MoP_5	93.5 (1)		

[a] The number in parentheses following each entry is the estimated standard deviation in the last significant digit.
[b] Atoms are labeled in agreement with Figure 2 and Tables III and IV.[22] [c] See ref 24.

Table IX. Bond Lengths Involving Nonhydrogen Atoms in $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$[a]

type[b]	bond length, Å	type[b]	bond length, Å
		Cation	
$\mathrm{P_1-O_{11}}$	1.610 (10)	$\mathrm{O_{11}C_{11}}$	1.418 (18)
$\mathrm{P_1-O_{12}}$	1.552 (10)	$\mathrm{O_{12}-C_{12}}$	1.440 (18)
$\mathrm{P_1-O_{13}}$	1.639 (11)	$\mathrm{O_{13}-C_{13}}$	1.496 (19)
$\mathrm{P_2-O_{21}}$	1.565 (10)	$\mathrm{O_{21}-C_{21}}$	1.433 (17)
$\mathrm{P_2-O_{22}}$	1.524 (17)	$\mathrm{O_{22}-C_{22}}$	1.159 (23)
$\mathrm{P_2-O_{23}}$	1.506 (17)	$\mathrm{O_{23}-C_{23}}$	1.198 (24)
$\mathrm{P_3-O_{31}}$	1.556 (10)	$\mathrm{O_{31}-C_{31}}$	1.408 (19)
$\mathrm{P_3-O_{32}}$	1.564 (10)	$\mathrm{O_{32}-C_{32}}$	1.445 (18)
$\mathrm{P_3-O_{33}}$	1.643 (10)	$\mathrm{O_{33}-C_{33}}$	1.511 (17)
$\mathrm{P_4-O_{41}}$	1.606 (9)	$\mathrm{O_{41}-C_{41}}$	1.411 (18)
$\mathrm{P_4-O_{42}}$	1.605 (10)	$\mathrm{O_{42}-C_{42}}$	1.417 (18)
$\mathrm{P_4-O_{43}}$	1.627 (9)	$\mathrm{O_{43}-C_{43}}$	1.448 (16)
$\mathrm{P_5-O_{51}}$	1.588 (9)	$\mathrm{O_{51}-C_{51}}$	1.405 (18)
$\mathrm{P_5-O_{52}}$	1.574 (11)	$\mathrm{O_{52}-C_{52}}$	1.409 (18)
$\mathrm{P_5-O_{53}}$	1.637 (12)	$\mathrm{O_{53}-C_{53}}$	1.397 (20)
average	1.586 (11,35,80,15)[c]	average	1.400 (19,59,241,15)[c]
$\mathrm{P_6-O_{61}}$	1.580 (10)	$\mathrm{O_{61}-C_{61}}$	1.433 (17)
$\mathrm{P_6-O_{62}}$	1.566 (10)	$\mathrm{O_{62}-C_{62}}$	1.449 (19)
average	1.573 (10,7,7,2)[c]	average	1.441 (18,8,8,2)[c]
		Anion	
$\mathrm{P_7-F_1}$	1.453 (24)	$\mathrm{P_7-F_5}$	1.392 (21)
$\mathrm{P_7-F_2}$	1.441 (20)	$\mathrm{P_7-F_6}$	1.392 (27)
$\mathrm{P_7-F_3}$	1.485 (17)	average	1.438 (22,30,47,6)[c]
$\mathrm{P_7-F_4}$	1.463 (21)		

[a] The number in parentheses following each entry is the estimated standard deviation in the last significant digit.
[b] Atoms are labeled to agree with Figure 2 and Tables III and IV.[22] [c] See ref 24.

Table X. Bond Angles Involving Nonhydrogen Atoms in $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}(PF_6{}^-)$[a]

type[b]	bond angle, deg	type[b]	bond angle, deg
		Cation	
MoP_1O_{11}	118.7 (5)	MoP_3O_{33}	119.0 (4)
MoP_1O_{12}	115.5 (4)	MoP_4O_{41}	112.1 (3)
MoP_1O_{13}	122.2 (5)	MoP_4O_{42}	113.7 (4)
MoP_2O_{21}	115.3 (4)	MoP_4O_{43}	125.2 (4)
MoP_2O_{22}	118.6 (8)	MoP_5O_{51}	112.0 (4)
MoP_2O_{23}	118.0 (8)	MoP_5O_{52}	114.0 (5)
MoP_3O_{31}	117.7 (4)	MoP_5O_{53}	120.5 (5)
MoP_3O_{32}	115.0 (4)	average	117.2 (5,30,80,15)[c]
MoP_6O_{61}	135.6 (4)	MoP_6O_{62}	127.3 (4)
		average	131.9 (4,46,46,2)[c]
$P_6O_{61}C_{61}$	127.7 (9)	$P_6O_{62}C_{62}$	128.4 (11)
		average	128.1 (10,4,4,2)[c]
$O_{61}P_6O_{62}$	95.8 (6)		
$P_1O_{11}C_{11}$	129.0 (12)	$P_3O_{33}C_{33}$	121.6 (9)
$P_1O_{12}C_{12}$	124.5 (11)	$P_4O_{41}C_{41}$	127.0 (9)
$P_1O_{13}C_{13}$	120.6 (11)	$P_4O_{42}C_{42}$	128.1 (11)
$P_2O_{21}C_{21}$	129.9 (12)	$P_4O_{43}C_{43}$	122.4 (9)
$P_2O_{22}C_{22}$	164.7 (2)	$P_5O_{51}C_{51}$	130.3 (11)
$P_2O_{23}C_{23}$	155.7 (19)	$P_5O_{52}C_{52}$	130.9 (14)
$P_3O_{31}C_{31}$	133.1 (12)	$P_5O_{53}C_{53}$	124.6 (13)
$P_3O_{32}C_{32}$	126.9 (10)	average	131.3 (13,79,342,15)[c]
$O_{11}P_1O_{12}$	101.0 (6)	$O_{32}P_3O_{33}$	100.9 (6)
$O_{11}P_1O_{13}$	97.6 (6)	$O_{41}P_4O_{42}$	104.3 (5)
$O_{12}P_1O_{13}$	97.6 (6)	$O_{41}P_4O_{43}$	98.2 (5)
$O_{21}P_2O_{22}$	101.6 (8)	$O_{42}P_4O_{43}$	100.5 (5)
$O_{21}P_2O_{23}$	101.6 (8)	$O_{51}P_5O_{52}$	107.2 (6)
$O_{22}P_2O_{23}$	98.7 (14)	$O_{51}P_5O_{53}$	104.7 (6)
$O_{31}P_3O_{32}$	105.1 (6)	$O_{52}P_5O_{53}$	96.6 (7)
$O_{31}P_3O_{33}$	96.1 (6)	average	100.8 (7,27,64,15)[c]
		Anion	
$F_1P_7F_4$	178.4 (13)	$F_3P_7F_6$	175.5 (14)
$F_2P_7F_5$	175.5 (14)	average	176.5 (14,13,19,3)[c]
$F_2P_7F_3$	81.1 (12)	$F_1P_7F_6$	98.9 (14)
$F_2P_7F_4$	90.4 (12)	$F_3P_7F_5$	94.9 (14)
$F_2P_7F_6$	98.7 (14)	$F_4P_7F_5$	87.7 (13)
$F_3P_7F_4$	92.8 (12)	$F_4P_7F_6$	82.7 (14)
$F_1P_7F_2$	89.7 (13)	$F_5P_7F_6$	85.1 (15)
$F_1P_7F_3$	85.7 (13)	average	90.0 (13,46,89,12)[c]
$F_1P_7F_5$	92.1 (14)		

[a] The number in parentheses following each entry is the estimated standard deviation in the last significant digit.
[b] Atoms are labeled to agree with Figure 2 and Tables III and IV.[22] [c] See ref 24.

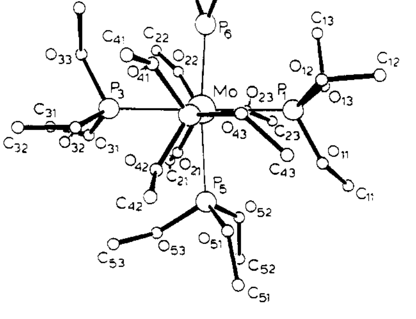

Figure 2. Perspective model (derived from an ORTEP plot) of the nonhydrogen atoms for the $\{(CH_3O)_2PMo[P(OCH_3)_3]_5{}^+\}$ cation as observed in the solid state of the hexafluorophosphate salt. All atoms are represented as open circles for purposes of clarity. The labeling scheme is described in the text[23], and the refined anisotropic thermal parameters are listed in Table IV.[22] Atom P_2 is hidden from view, and P_4 is not labeled in the drawing.

metal–ligand unit. The only anomalous ligand bond lengths and angles in **2** (Tables IX and X) involve methyl carbon atoms C_{22} and C_{23}, which are presumably disordered among (several) sites having fractional coordinates near those listed in Table III for these atoms. With every P···P contact on the molybdenum coordination sphere in **2** significantly smaller than the phosphorus van der Waals[25] diameter of 3.80 Å, this cation is clearly a sterically crowded species even though it is only six-coordinate.

The conformation of phosphite ligands in the cation appear to minimize nonbonded contacts as well as possible in this crowded coordination sphere (Figure 2). In the plane of four phosphorus atoms associated with trimethyl phosphite ligands, two of the trans phosphite ligands have nearly eclipsed methoxy group positions whereas the other two trans ligands have staggered methoxy group positions. The dimethoxyphosphino ligand is oriented in such a way as to minimize repulsions with the trimethyl phosphite ligands yet provide reasonable overlap of the phosphorus pπ orbitals with the metal d_{xz} or d_{yz} atomic orbitals; the $MoP_6O_{61}O_{62}$ least-squares mean plane[28] makes dihedral angles of 67.0 and 23.8° with those determined[27] by $MoP_1P_3P_5P_6$ and $MoP_2P_4P_5P_6$, respectively.

An unusual dynamic stereochemical feature of this molybdenum cation and of the analogous tungsten complex is apparently rapid transfer of OCH_3 groups about all phosphorus atoms in the coordination sphere. The ^{31}P NMR spectrum was not an AB_4C pattern at 25 °C but a singlet. When the solution of the complex was cooled, the single resonance for the cation broadened and then separated into three multiplets of 1:4:1 relative intensities, which were, respectively, a doublet of quintets ($J(P_{6\text{ or }5}P_{1-4})$ = 64 Hz and $J(P_5P_6)$ = 250 Hz), a triplet ($J(P_5P_{1-4}) = J(P_6P_{1-4})$ = 64 Hz), and a doublet of quintets ($J(P_{6\text{ or }5}P_{1-4})$ = 64 Hz and $J(P_5P_6)$ = 250 Hz).[8] Thus the expected AB_4C pattern was observed only below ~−50 °C (the ^{31}P NMR resonance for the hexafluorophosphate counterion was the expected septet, $J(PF)$ = 700 Hz, and was temperature-insensitive).[8] The anomaly here in the ^{31}P spectral $AB_4C \rightarrow A_6$ transformation is that the $P(OCH_3)_2$ ligand is unique; a polytopal rearrangement would have comprised an $AB_4C \rightarrow AB_5$ transformation. The NMR results can be rationalized by postulating an intramolecular OCH_3 group transfer from a phosphite phosphorus atom to the $P(OCH_3)_2$ phosphorus atom. This postulate is further supported by ^{13}C NMR data.[8] At −78 °C, the $^{13}C\{^1H\}$ spectra of $\{(CH_3O)_2PMo[P(OCH_3)_3]_5^+\}(PF_6^-)$ consisted of a resonance at δ −11.3 and a large, slightly unsymmetric resonance at δ −6.4 of relative intensities of ~1.5 and 15, which, respectively, could be ascribed to the $P(OCH_3)_2$ group ^{13}C resonance of intensity 2 and to overlapping resonances of the two types of $P(OCH_3)_3$ resonances of intensity 15. As the temperature was raised, these two resonances broadened, merged, and then sharpened into a single resonance. Estimates of E_a for the ^{13}C and ^{31}P dynamic processes were the same order of magnitude, ~12 kcal/mol.

The crystallographic data for **2** show the coordination sphere about molybdenum in the cation to be closely packed—a feature that could facilitate the postulated OCH_3 group transfer. Besides the close P···P contacts listed in Table VIII, there are several intracationic P···O contacts with separations that are near the van der Waals value[25] of 3.30 Å: $P_2\cdots O_{31}$, 3.36 Å; $P_2\cdots O_{52}$, 3.36 Å; $P_2\cdots O_{62}$, 3.47 Å; $P_4\cdots O_{32}$, 3.19 Å; $P_4\cdots O_{51}$, 3.33 Å; $P_5\cdots O_{11}$, 3.24 Å; $P_5\cdots O_{21}$, 3.29 Å; $P_6\cdots O_{12}$, 3.53 Å; $P_6\cdots O_{22}$, 3.45 Å; $P_6\cdots O_{33}$, 3.44 Å; $P_6\cdots O_{41}$, 3.44 Å. It is significant that four of these short P···O contacts involve the phosphino phosphorus atom, P_6. There are no short interion contacts in **2**.

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Supplementary Material Available: Listings of anistropic thermal parameters for nonhydrogen atoms (Table II) and bond lengths and angles involving hydrogen atoms (Table VII) in $(\eta^5\text{-}C_5H_5)Cr[PO(OCH_3)_2](CO)_2[P(OCH_3)_3]$ (**1**), anisotropic thermal parameters for nonhydrogen atoms of $\{(CH_3O)_2PMo[P(OCH_3)_3]_5^+\}(PF_6^-)$ (**2**) (Table IV), and observed and calculated structure factors from the respective final cycles of least-squares refinement (45 pages). Ordering information is given on any current masthead page.