dation via reaction 3; there is no evidence for direct $FcCH_2NMe_3^+$ oxidation or for $Fe(CN)_6^{3-}$-mediated oxidation via reaction 2. The picture is therefore like that of the $Fe(CN)_6^{4-}$–$Fe(phen)_3^{2+}$–$FcCH_2NMe_3^+$ triad (Figure 3), where the large zeolite surface cations ($Fe(phen)_3^{2+}$ or $Os(bpy)_3^{2+}$) block direct communication between $Fe(CN)_6^{3-}$ ions contained in the silane bridge and $FcCH_2NMe_3^+$ ions within the zeolite framework. Electron transfer between the zeolite surface and zeolite bulk ions (reaction 3) is nevertheless fast on the time scale of the electrochemical experiment, as evidenced by the large anodic wave near the $Os(bpy)_3^{3+/2+}$ potential. A picture consistent with the data then is oxidation of bulk $FcCH_2NMe_3^+$ ions by zeolite surface $Os(bpy)_3^{3+}$ ions; the latter are reoxidized via $Os(bpy)_3^{3+}$ ions in the silane bridge. Coverage of the zeolite surface by $Os(bpy)_3^{3+/2+}$ ions must be reasonably complete in order to block mediated oxidation via reaction 2.

Conclusions

Electrochemical data provide evidence for structural organi-

zation of molecular triads that self-assemble via ion-exchange reactions at a zeolite Y modified electrode. While the situation is complicated by ion pairing of some of these multiply charged ions, the data consistently show that electrons can be exchanged with zeolite bulk cations only via the intermediacy of redox levels of the zeolite surface ions. It is particularly interesting that rapid electron exchange between ions on either side of this zeolite surface layer does not occur; such exchange represents the short-circuiting or back-electron-transfer pathway in photochemically active molecular triads.[1-3] Experiments involving zeolite surface ions that are good photosensitizers, with donor and acceptor ions exchanged into the silane bridge and zeolite bulk sites, are presently in progress.

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Syntheses and Crystal Structures of Syn and Gauche Isomers of the Chloride-Bridged Face-Sharing Bioctahedral Molybdenum(III) Dimers [PHMe3][Mo2Cl7(PMe3)2]

F. Albert Cotton* and Rudy L. Luck

The reaction of $Mo_2Cl_4(PMe_3)_4$ and $2PhICl_2$ yields the compound $[PHMe_3][Mo_2Cl_7(PMe_3)_2]$, in which the anion is the syn conformer with respect to the arrangement of the two terminal tertiary phosphine ligands. Two crystalline forms containing this syn conformer, **1** and **2**, are reported. The equilibration of the syn and gauche conformers has been monitored by ^1H NMR spectroscopy and is found to involve phosphine dissociation. Solutions of these two forms eventually attained the statistically expected 1:2 (syn:gauche) ratio ($k_1 = 1.09 \times 10^{-4}$ s^{-1}, $k_{-1} = 5.43 \times 10^{-5}$ s^{-1} in CD$_2$Cl$_2$ at 293 K), and from such solutions single crystals of the gauche isomer were obtained. Crystal data: compound **1** (syn conformer, from CH$_2$Cl$_2$), triclinic, space group $P\bar{1}$, $a = 13.271$ (2) Å, $b = 17.855$ (3) Å, $c = 11.418$ (2) Å, $\alpha = 107.18$ (1)°, $\beta = 101.13$ (2)°, $\gamma = 93.82$ (1)°, $V = 2513.8$ (8) Å^3, $Z = 4$, $R = 0.041$ ($R_w = 0.066$) for 379 parameters and 4621 unique data having $F_o^2 > 3\sigma(F_o^2)$; compound **2** (syn conformer, from CH$_2$Cl$_2$/hexane), orthorhombic, space group $Pnma$, $a = 28.098$ (6) Å, $b = 10.140$ (1) Å, $c = 9.839$ (2) Å, $V = 2803.4$ (9) Å^3, $Z = 4$, $R = 0.079$ ($R_w = 0.103$) for 115 parameters and 1091 unique data having $F_o^2 > 3\sigma(F_o^2)$; compound **3** (gauche conformer, from acetone-d_6), monoclinic, space group $P2_1/n$, $a = 10.888$ (2) Å, $b = 20.633$ (2) Å, $c = 11.375$ (1) Å, $\beta = 106.86$ (1)°, $V = 2445.4$ (7) Å^3, $Z = 4$, $R = 0.022$ ($R_w = 0.031$) for 302 parameters and 3764 unique data having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Several edge-sharing bioctahedral complexes of molybdenum having the stoichiometry $Mo_2Cl_6(PP)_2$ (PP = bidentate tertiary phosphine) are known,[1] but analogues containing monodentate tertiary phosphines ($Mo_2Cl_6(PR_3)_4$) have not been discovered up to this time. The trimethylphosphine derivative was considered to be of great interest as it would allow a comparison with the known and structurally characterized homologues $Cr_2Cl_6(PMe_3)_4$[2] and $W_2Cl_6(PMe_3)_4$.[3] This report describes the chlorination of the quadruply bonded molybdenum dimer $Mo_2Cl_4(PMe_3)_4$.[4] This was undertaken with the goal of synthesizing $Mo_2Cl_6(PMe_3)_4$, since the homologous bidentate tertiary phosphine complexes just mentioned had been synthesized in this manner. To our surprise, this reaction resulted instead in the formation of a compound containing a face-sharing bioctahedral complex, $[PHMe_3]$-$[Mo_2Cl_7(PMe_3)_2]$, with the two terminal tertiary phosphines in a syn arrangement. This result is similar to that obtained in the reaction of $Mo_2I_4(PMe_3)_4$ and I_2, where the iodide analogue $[PHMe_3][Mo_2I_7(PMe_3)_2]$ was produced.[5]

The syn complex was found to crystallize in two different forms, triclinic and orthorhombic, depending on the conditions under which the crystals grew. Further, solutions of the syn complex slowly equilibrated with the gauche conformer, finally attaining a statistical ratio of syn:gauche equal to 1:2 over a period of 2 days. Crystals of the gauche conformer suitable for single-crystal X-ray diffraction were obtained from this acetone-d_6 solution. The addition of PMe$_3$ was found to slow down this process, indicating a dissociative mechanism for the isomerization. The single-crystal X-ray structures of each of the compounds containing the syn geometric isomer and the first structural report of a gauche conformer are reported in this paper.

Experimental Section

General Data. All manipulations were carried out under an atmosphere of argon. Solvents apart from dichloromethane were dried over sodium/potassium alloy and distilled under nitrogen before use. Dichloromethane was dried over and distilled from phosphorus pentoxide. $Mo_2Cl_4(PMe_3)_4$ was prepared from the reaction of $Mo_2(\mu-O_2CCH_3)_4$, Me$_3$SiCl, and PMe$_3$ in refluxing benzene according to similar reported preparations,[1a] and PhICl$_2$ was prepared according to a literature method.[6] The ^1H NMR spectra were recorded by using Varian XL-200 and XL-400 spectrometers. ^{31}P NMR spectra referenced to 85% H$_3$PO$_4$ were recorded at 81 MHz by using a Varian XL-200. The microanalysis was done by Galbraith Laboratories, Inc., Knoxville, TN.

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(1) (a) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 4051. (b) Canich, J. A. M.; Cotton, F. A.; Daniels, L. M.; Lewis, D. B. *Inorg. Chem.* **1987**, *26*, 4046. (c) Cotton, F. A. *Polyhedron* **1987**, *4*, 667.
(2) Cotton, F. A.; Luck, R. L. To be submitted for publication.
(3) Chisholm, M. H. Private communication.
(4) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.

(5) Cotton, F. A.; Poli, R. *Inorg. Chem.* **1987**, *26*, 3310.
(6) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* **1955**, *3*, 482.

Table I. Crystallographic Data for Compounds 1–3

	1	2	3
formula	$C_9H_{28}Cl_7P_3Mo_2$	$C_9H_{28}Cl_7P_3Mo_2$	$C_9H_{28}Cl_7P_3Mo_2$
fw	669.30	669.30	669.30
space group	$P\bar{1}$	$Pnma$	$P2_1/n$
systematic absences		$0kl, h + l \neq 2n; hk0, h \neq 2n$	$0k0, k \neq 2n; h0l, h + l \neq 2n$
a, Å	13.271 (2)	28.098 (6)	10.888 (2)
b, Å	17.855 (3)	10.140 (1)	20.633 (2)
c, Å	11.418 (2)	9.839 (2)	11.375 (1)
α, deg	107.18 (1)	90.0	90.00
β, deg	101.13 (2)	90.0	106.86 (1)
γ, deg	93.82 (1)	90.0	90.00
V, Å³	2513.8 (8)	2803.4 (9)	2445.4 (7)
Z	4	4	4
d_{calc}, g/cm³	1.768	1.586	1.818
cryst size, mm	0.1 × 0.1 × 0.4	0.4 × 0.2 × 0.4	0.3 × 0.35 × 0.15
μ(Mo Kα), cm⁻¹	19.093	17.121	19.627
data collecn instrument	Nicolet P3/F equivalent	Rigaku AFC5R Mo Kα (λ_α = 0.710 73 Å)	Enraf-Nonius CAD-4
radiation (monochromated in incident beam)			
orientation rflns: no.; range (2θ), deg	25; 20.08 < 2θ < 27.19	25; 24.0 < 2θ < 30.75	25; 28 < 2θ < 34
temp, °C	19 ± 1	19 ± 1	–80
scan method	ω–2θ	ω–2θ	ω–2θ
data collecn range, 2θ, deg	4 ≤ 2θ ≤ 45	4 ≤ 2θ ≤ 50	4 ≤ 2θ ≤ 50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6282, 4621	2637, 1091	4428, 3764
no. of params refined	379	115	302
transmission factors, %: max, min	99.9, 93.3	99.9, 65.0	99.91, 80.67
R^a	0.041	0.079	0.022
$R_w{}^b$	0.066	0.103	0.031
quality-of-fit indicator^c	1.672	2.093	1.029
largest shift/esd, final cycle	0.42	0.29	0.06
largest peak, e/Å³	0.66	1.807	0.861

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Preparation of [PHMe₃][*syn*-Mo₂Cl₇(PMe₃)₂]. PhICl₂ (171 mg, 6.2 × 10⁻⁴ mmol) was added to a solution of Mo₂Cl₄(PMe₃)₄ (200 mg, 3.1 mmol) in 15 mL of CH₂Cl₂. After the mixture was stirred for 2 h at room temperature, the clear red-brown solution was filtered and concentrated to 2 mL and hexane (15 mL) added to complete the precipitation of the red-brown [PHMe₃][*syn*-Mo₂Cl₇(PMe₃)₂]: yield 180 mg (82%); ¹H NMR (CD₂Cl₂) δ 6.9 (d, 1 H, *J* = 522 Hz, *H*PMe₃), 2.03 (d, 9 H, *J* = 12.8 Hz, (C*H₃*)₃PH), –0.607 (s, 18 H, *syn*-(C*H₃*)₃P-Mo), –0.706 (s, 18 H, *gauche*-(C*H₃*)₃P-Mo); ³¹P NMR (CH₂Cl₂) δ 82.7 (br, 2 P, Me₃*P*-Mo), 14.0 (d, 1 P, *J* = 522 Hz, H*P*Me₃). Anal. Calcd for C₉H₂₈Cl₇Mo₂: C, 16.15; H, 4.22. Found: C, 15.64; H, 4.05.

X-ray Crystallography. A suitable red crystal belonging to the triclinic system, 1, was first obtained from CH₂Cl₂ in a ³¹P NMR tube. However, we have not been able to obtain another such crystal. Crystals in the orthorhombic crystal system, 2, were obtained reproducibly by the slow diffusion of hexane into a CH₂Cl₂ solution. Red-green crystals of 3 were obtained from acetone-d_6 in a ¹H NMR tube after the equilibrium of syn and gauche conformers was attained. All relevant crystallographic information is given in Table I. In all three cases the crystals were mounted on glass fibers by using 5-min epoxy resin. Accurate unit cell parameters were obtained by means of a least-squares analysis of 25 reflections. Intensity data on each compound were then collected by utilizing the options specified in Table I and the general procedures for data collection as previously described.[7] All data sets were corrected for decay, Lorentz, and polarization effects. In addition, absorption corrections were also made by using an empirical method based on nine ψ scans (ψ = 0–360° every 10°) for χ values near 90°.[8] The heavy atoms (Mo, Cl, P) in all cases were located from a three-dimensional Patterson function. The remaining non-hydrogen atoms were found by alternating least-squares full-matrix cycles of refinement and difference Fourier maps for a cutoff ratio $F_o^2/\sigma(F_o^2)$ of 3. For this the Enraf-Nonius SDP software was employed. All of the non-hydrogen atoms were then refined anisotropically. In compound 3 all of the hydrogen atoms appeared in the final difference map and were refined. The final data are outlined in Table I. Tables II–IV list the fractional atomic coordinates and selected bond distances and angles are listed in Tables V–VII for 1–3, respectively.

Results and Discussion

Synthesis. The oxidation of Mo₂Cl₄(PMe₃)₄ with PhICl₂ in CH₂Cl₂ at room temperature produces [PHMe₃][Mo₂Cl₇(PMe₃)₂],

in which the anion is a face-sharing bioctahedral complex. The origin of the phosphonium ion remains unknown.[5] This result contrasts with the similar reaction done on the quadruply bonded molybdenum dimers bridged by bidentate tertiary phosphines where the edge-sharing bioctahedral complexes Mo₂Cl₆(PP)₂ (PP = bidentate tertiary phosphine) are obtained.[1a,b] The reason for this difference is not clear, but it may be related to the lability of the ligands on the molybdenum atom core. However, this result is similar to that found in the reaction between Mo₂I₄(PMe₃)₄ and iodine in warm toluene, where the complex [PHMe₃]-[Mo₂I₇(PMe₃)₂] was obtained.[5]

The bulk [PHMe₃][Mo₂Cl₇(PMe₃)₂] isolated from the preparative reaction in better than 80% yield appears, by NMR, to contain essentially only the syn anion. From a solution of this initial product in CH₂Cl₂, red crystals of 1 were obtained. This substance is triclinic, and the unit cell contains two each of two crystallographically independent *syn*-[Mo₂Cl₇(PMe₃)₂]⁻ ions. On the other hand, when the initial red-brown product is redissolved in CH₂Cl₂ and hexane allowed to diffuse slowly into this solution, a crystalline substance belonging to the orthorhombic system is obtained, but this, too, contains *syn*-[Mo₂Cl₇(PMe₃)₂]⁻ ions. The gauche isomer of this ion is obtained in crystalline form from a solution in acetone that has been allowed to stand at room temperature long enough to reach the equilibrium 1:2 ratio of syn to gauche isomers.

NMR Studies. The ³¹P{¹H} spectrum of 1 contains a broad multiplet at δ 82.7, which is assigned to the phosphorus atoms of the coordinated PMe₃ groups. The broadness of the peak and the downfield chemical shift are indicative of a paramagnetic component to this molecule. The fact that signals are observed indicate that this molecule is less paramagnetic than the [Mo₂I₇(PMe₃)₂]⁻ core, where no phosphorus signals were observed.[5] A singlet at δ 14, which became a broad doublet (*J* = 522 Hz) in the ³¹P-coupled ¹H experiment, can be assigned to the counterion [PHMe₃]⁺.

The ¹H NMR spectrum of this molecule is more informative. The phosphonium ion consists of a doublet at δ 6.9 (*J* = 522 Hz), which is the unique hydrogen atom, and a doublet at δ 2.03 (*J* = 12.8 Hz) due to the methyl hydrogen atoms on this group. The resonances for the methyl hydrogen atoms on the PMe₃ ligands are observed at δ –0.607 and δ –0.706 for the syn and gauche

(7) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.
(8) North, A. C. T.; Phillip, D. C.; Matthews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24A*, 351.

Table II. Positional Parameters and Their Estimated Standard Deviations for Compound **1**

atom	x	y	z	B, $Å^2$ [a]
Mo(1)	0.74015 (8)	0.08481 (6)	0.03688 (9)	2.99 (2)
Mo(2)	0.73775 (8)	0.11823 (6)	−0.1849 (1)	3.10 (2)
Cl(1)	0.7349 (3)	0.2201 (2)	0.0174 (3)	4.08 (8)
Cl(2)	0.6106 (2)	0.0227 (2)	−0.1599 (3)	3.90 (7)
Cl(3)	0.8755 (2)	0.0564 (2)	−0.0848 (3)	4.36 (8)
Cl(11)	0.8698 (3)	0.1349 (2)	0.2282 (3)	5.6 (1)
Cl(12)	0.6076 (3)	0.1053 (2)	0.1518 (3)	5.64 (9)
Cl(21)	0.8639 (3)	0.2043 (2)	−0.2246 (3)	5.67 (9)
Cl(22)	0.6000 (3)	0.1693 (2)	−0.2939 (3)	5.7 (1)
P(1)	0.7445 (3)	−0.0526 (2)	0.0543 (3)	4.07 (8)
P(2)	0.7464 (3)	0.0208 (2)	−0.3938 (3)	5.0 (1)
C(11)	0.738 (2)	−0.1292 (9)	−0.098 (2)	9.3 (6)
C(12)	0.858 (1)	−0.0662 (9)	0.157 (2)	8.4 (5)
C(13)	0.642 (2)	−0.0888 (9)	0.111 (2)	10.2 (6)
C(21)	0.661 (2)	−0.069 (1)	−0.446 (2)	13.7 (7)
C(22)	0.858 (2)	−0.014 (2)	−0.407 (2)	19 (1)
C(23)	0.740 (2)	0.063 (1)	−0.520 (2)	13.3 (9)
P(12)	0.3910 (3)	0.6171 (2)	0.1433 (3)	3.72 (8)
C(121)	0.251 (1)	0.6097 (8)	0.088 (1)	4.6 (3)
C(122)	0.458 (1)	0.6575 (8)	0.052 (1)	5.1 (4)
C(123)	0.427 (1)	0.5215 (7)	0.142 (1)	4.9 (3)
Mo(3)	0.22083 (8)	0.40243 (6)	0.36069 (9)	2.81 (2)
Mo(4)	0.25030 (8)	0.37347 (6)	0.58431 (9)	2.92 (2)
Cl(4)	0.3901 (2)	0.4405 (2)	0.5186 (3)	4.35 (8)
Cl(5)	0.1184 (2)	0.4504 (2)	0.5170 (3)	4.03 (7)
Cl(6)	0.1944 (3)	0.2699 (2)	0.3804 (3)	3.73 (7)
Cl(31)	0.3058 (3)	0.3520 (2)	0.1918 (3)	4.61 (8)
Cl(32)	0.2303 (3)	0.5316 (2)	0.3379 (3)	4.72 (8)
Cl(41)	0.3670 (3)	0.2892 (2)	0.6501 (3)	4.97 (9)
Cl(42)	0.2905 (3)	0.4710 (2)	0.7894 (3)	5.19 (9)
P(3)	0.0554 (3)	0.3606 (2)	0.1939 (3)	3.70 (8)
P(4)	0.1140 (3)	0.3086 (2)	0.6619 (3)	3.91 (8)
C(31)	0.042 (1)	0.2565 (8)	0.095 (1)	5.2 (4)
C(32)	0.045 (1)	0.4164 (9)	0.082 (1)	5.7 (4)
C(33)	−0.067 (1)	0.3700 (9)	0.249 (1)	6.0 (4)
C(41)	0.040 (2)	0.218 (1)	0.552 (2)	12.6 (6)
C(42)	0.169 (1)	0.279 (1)	0.796 (1)	8.7 (5)
C(43)	0.016 (1)	0.371 (1)	0.713 (2)	8.8 (5)
P(34)	0.5990 (3)	0.3064 (2)	0.4163 (4)	4.8 (1)
C(341)	0.720 (1)	0.270 (1)	0.461 (2)	6.7 (5)
C(342)	0.491 (1)	0.233 (1)	0.386 (2)	7.4 (5)
C(343)	0.610 (2)	0.341 (1)	0.287 (2)	10.3 (7)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Positional Parameters and Their Estimated Standard Deviations for Compound **2**

atom	x	y	z	B, $Å^2$ [a]
Mo(1)	0.15755 (8)	0.250	0.5933 (2)	4.07 (5)
Mo(2)	0.08894 (9)	0.250	0.7846 (2)	5.15 (6)
Cl(1)	0.1710 (2)	0.0803 (6)	0.4306 (5)	6.3 (1)
Cl(2)	0.0716 (2)	0.250	0.5356 (7)	5.7 (2)
Cl(3)	0.1513 (2)	0.0813 (5)	0.7702 (5)	5.6 (1)
Cl(4)	0.0309 (2)	0.0796 (7)	0.8158 (6)	9.0 (2)
P(1)	0.2458 (3)	0.250	0.627 (1)	8.3 (3)
P(2)	0.1046 (4)	0.250	1.0389 (9)	8.8 (3)
C(11)	0.290 (2)	0.250	0.480 (9)	39 (6)
C(21)	0.165 (1)	0.250	1.086 (4)	22 (3)
C(12)	0.277 (1)	0.398 (3)	0.690 (5)	17 (1)
C(22)	0.086 (2)	0.120 (5)	1.125 (3)	35 (2)
P(11)	0.0894 (4)	0.750	0.468 (1)	8.6 (3)
C(111) [b]	0.140 (1)	0.750	0.584 (4)	5.0 (9)
C(112) [b]	0.0517 (9)	0.612 (2)	0.491 (3)	5.8 (7)
C(113)	0.1157 (9)	0.750	0.322 (3)	6.4 (8)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Atoms were refined as consisting of two-thirds of (two carbons and one hydrogen) due to the disorder on the phosphonium cation.

conformers, respectively. This is at a chemical shift different from those of the *syn*- and *gauche*-[Mo$_2$I$_7$(PMe$_3$)$_2$]$^-$ anion, which are even more downfield at δ −2.18 and −2.84, respectively. This fact

Table IV. Positional Parameters and Their Estimated Standard Deviations for Compound **3**

atom	x	y	z	B, $Å^2$ [a]
Mo(1)	0.11334 (2)	0.13063 (1)	0.29392 (2)	1.406 (4)
Mo(2)	0.34236 (2)	0.13456 (1)	0.24314 (2)	1.341 (4)
Cl(1)	0.27915 (5)	0.21500 (3)	0.37520 (5)	1.88 (1)
Cl(2)	0.25123 (5)	0.03502 (3)	0.31103 (5)	1.81 (1)
Cl(3)	0.13373 (5)	0.14812 (3)	0.08624 (5)	2.17 (1)
Cl(11)	0.09800 (6)	0.10904 (3)	0.49657 (5)	2.31 (1)
Cl(12)	−0.04834 (5)	0.21363 (3)	0.25798 (6)	2.45 (1)
Cl(21)	0.54486 (5)	0.12746 (3)	0.39732 (5)	1.84 (1)
Cl(22)	0.41331 (6)	0.06547 (3)	0.10463 (5)	2.33 (1)
P(1)	−0.07742 (6)	0.05844 (3)	0.20477 (6)	2.01 (1)
P(2)	0.43723 (5)	0.22993 (3)	0.16076 (5)	1.65 (1)
C(11)	−0.1718 (3)	0.0827 (2)	0.0521 (3)	3.62 (7)
C(12)	−0.1927 (2)	0.0593 (2)	0.2914 (3)	3.20 (6)
C(13)	−0.0461 (3)	−0.0270 (2)	0.1905 (3)	4.23 (7)
C(21)	0.5768 (2)	0.2106 (1)	0.1115 (3)	2.97 (6)
C(22)	0.4936 (3)	0.2954 (1)	0.2691 (3)	3.20 (6)
C(23)	0.3283 (2)	0.2695 (1)	0.0299 (2)	2.68 (5)
P	0.44958 (6)	0.11852 (3)	0.68217 (5)	1.84 (1)
C(1)	0.4274 (2)	0.0396 (1)	0.6183 (2)	2.13 (5)
C(2)	0.6165 (3)	0.1320 (1)	0.7471 (3)	3.89 (7)
C(3)	0.3634 (3)	0.1258 (1)	0.7929 (3)	3.55 (6)
H	0.413 (2)	0.158 (1)	0.609 (2)	0.8 (6)*
H(11)	0.336 (2)	0.032 (1)	0.575 (2)	0.5 (6)*
H(12)	0.477 (3)	0.038 (2)	0.562 (3)	2.9 (8)*
H(13)	0.464 (3)	0.005 (2)	0.683 (3)	2.1 (7)*
H(21)	0.664 (4)	0.123 (2)	0.690 (4)	3.7 (9)*
H(22)	0.649 (3)	0.101 (2)	0.807 (3)	2.5 (8)*
H(23)	0.631 (4)	0.173 (2)	0.788 (4)	6 (1)*
H(31)	0.277 (4)	0.115 (2)	0.753 (4)	6 (1)*
H(32)	0.396 (3)	0.097 (1)	0.862 (3)	1.3 (6)*
H(33)	0.370 (3)	0.165 (2)	0.831 (3)	2.7 (8)*
H(111)	−0.250 (3)	0.056 (2)	0.022 (3)	1.7 (7)*
H(112)	−0.125 (3)	0.074 (1)	0.004 (3)	1.0 (6)*
H(113)	−0.190 (4)	0.132 (2)	0.057 (4)	6 (1)*
H(121)	−0.262 (3)	0.036 (2)	0.243 (3)	1.8 (7)*
H(122)	−0.160 (3)	0.037 (2)	0.371 (3)	3.6 (9)*
H(123)	−0.195 (3)	0.104 (2)	0.318 (3)	3.2 (9)*
H(131)	0.002 (3)	−0.028 (2)	0.140 (3)	3.9 (9)*
H(132)	−0.004 (3)	−0.040 (2)	0.281 (3)	3.6 (9)*
H(133)	−0.129 (3)	−0.046 (2)	0.144 (3)	2.4 (8)*
H(211)	0.602 (3)	0.245 (2)	0.075 (3)	1.9 (7)*
H(212)	0.639 (4)	0.199 (2)	0.189 (4)	5 (1)*
H(213)	0.566 (3)	0.176 (2)	0.064 (3)	1.8 (7)*
H(221)	0.530 (3)	0.325 (1)	0.230 (3)	1.2 (6)*
H(222)	0.421 (3)	0.318 (2)	0.288 (3)	2.5 (8)*
H(223)	0.540 (3)	0.278 (2)	0.336 (3)	2.9 (8)*
H(231)	0.259 (3)	0.284 (1)	0.055 (3)	0.8 (6)*
H(232)	0.369 (3)	0.303 (1)	0.005 (3)	0.9 (6)*
H(233)	0.294 (2)	0.240 (1)	−0.033 (2)	0.7 (6)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

is further evidence of a decreased paramagnetic effect. The two resonances change in intensity with time until they reach a 1:2 syn to gauche ratio (eq 1). This phenomenon has also been

$$\text{syn} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{gauche} \qquad (1)$$

observed with the iodide analogue.[5] The values of k_1 and k_{-1} have been determined to be 1.09×10^{-4} and 5.43×10^{-5} s^{-1}, respectively (supplementary material). This is about 7 times slower than for the iodide derivative. The addition of excess PMe$_3$ to a mixture of **1** in acetone-d_6 suppresses equilibration between the syn and gauche conformers for at least 1 day. This suggests that the isomerization involves a dissociative pathway in the rate-determining step. The methyl resonances are also temperature dependent and shift 1 ppm upfield as the temperature is decreased from 22 to −80 °C. This has been attributed to temperature-dependent paramagnetic effects.[5]

Structural Studies. ORTEP drawings of the structures of **1**–**3** are given in Figures 1–3, respectively. The structure of each anion

Table V. Selected Bond Lengths and Angles in Compound 1[a]

		Bond Lengths (Å)			
Mo(1)–Mo(2)	2.763 (2)	P(1)–C(13)	1.78 (2)	Mo(4)–Cl(5)	2.443 (3)
Mo(1)–Cl(1)	2.494 (3)	P(2)–C(21)	1.78 (2)	Mo(4)–Cl(6)	2.448 (3)
Mo(1)–Cl(2)	2.453 (3)	P(2)–C(22)	1.66 (3)	Mo(4)–Cl(41)	2.398 (4)
Mo(1)–Cl(3)	2.466 (4)	P(2)–C(23)	1.81 (2)	Mo(4)–Cl(42)	2.405 (3)
Mo(1)–Cl(11)	2.392 (3)	P(12)–C(121)	1.825 (13)	Mo(4)–P(4)	2.520 (4)
Mo(1)–Cl(12)	2.376 (4)	P(12)–C(122)	1.77 (2)	P(3)–C(31)	1.843 (13)
Mo(1)–P(1)	2.523 (4)	P(12)–C(123)	1.800 (14)	P(3)–C(32)	1.83 (2)
Mo(2)–Cl(1)	2.491 (3)	Mo(3)–Mo(4)	2.713 (2)	P(3)–C(33)	1.858 (15)
Mo(2)–Cl(2)	2.434 (3)	Mo(3)–Cl(4)	2.504 (3)	P(4)–C(41)	1.81 (2)
Mo(2)–Cl(3)	2.465 (4)	Mo(3)–Cl(5)	2.440 (3)	P(4)–C(42)	1.80 (2)
Mo(2)–Cl(21)	2.394 (4)	Mo(3)–Cl(6)	2.451 (3)	P(4)–C(43)	1.83 (2)
Mo(2)–Cl(22)	2.396 (4)	Mo(3)–Cl(31)	2.398 (4)	P(34)–C(341)	1.81 (2)
Mo(2)–P(2)	2.532 (4)	Mo(3)–Cl(32)	2.394 (4)	P(34)–C(342)	1.78 (2)
P(1)–C(11)	1.85 (2)	Mo(3)–P(3)	2.516 (3)	P(34)–C(343)	1.78 (2)
P(1)–C(12)	1.80 (2)	Mo(4)–Cl(4)	2.492 (4)		

		Bond Angles (deg)			
Cl(1)–Mo(1)–Cl(2)	93.4 (1)	Cl(21)–Mo(2)–P(2)	86.1 (1)	Cl(32)–Mo(3)–P(3)	89.8 (1)
Cl(1)–Mo(1)–Cl(3)	92.9 (1)	Cl(22)–Mo(2)–P(2)	88.7 (1)	Cl(4)–Mo(4)–Cl(5)	94.4 (1)
Cl(2)–Mo(1)–Cl(3)	88.1 (1)	Mo(1)–Cl(1)–Mo(2)	67.32 (8)	Cl(4)–Mo(4)–Cl(6)	93.9 (1)
Cl(11)–Mo(1)–Cl(12)	90.5 (1)	Mo(1)–Cl(2)–Mo(2)	68.86 (8)	Cl(5)–Mo(4)–Cl(6)	89.7 (1)
Cl(11)–Mo(1)–P(1)	89.5 (1)	Mo(1)–Cl(3)–Mo(2)	68.15 (9)	Cl(41)–Mo(4)–Cl(42)	92.8 (1)
Cl(12)–Mo(1)–P(1)	90.4 (1)	Cl(4)–Mo(3)–Cl(5)	94.1 (1)	Cl(41)–Mo(4)–P(4)	88.2 (1)
Cl(1)–Mo(2)–Cl(2)	93.9 (1)	Cl(4)–Mo(3)–Cl(6)	93.5 (1)	Cl(42)–Mo(4)–P(4)	86.1 (1)
Cl(1)–Mo(2)–Cl(3)	93.1 (1)	Cl(5)–Mo(3)–Cl(6)	89.7 (1)	Mo(3)–Cl(4)–Mo(4)	65.79 (8)
Cl(2)–Mo(2)–Cl(3)	88.6 (1)	Cl(31)–Mo(3)–Cl(32)	92.5 (1)	Mo(3)–Cl(5)–Mo(4)	67.50 (9)
Cl(21)–Mo(2)–Cl(22)	90.8 (1)	Cl(31)–Mo(3)–P(3)	85.6 (1)	Mo(3)–Cl(6)–Mo(4)	67.25 (7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Selected Bond Lengths and Angles in Compound 2[a]

		Bond Lengths (Å)			
Mo(1)–Mo(2)	2.694 (3)	Mo(2)–Cl(3)	2.453 (5)	P(2)–C(22)	1.65 (5)
Mo(1)–Cl(1)	2.380 (6)	Mo(2)–Cl(4)	2.396 (7)	P(11)–C(111)	1.83 (4)
Mo(1)–Cl(2)	2.482 (7)	Mo(2)–P(2)	2.54 (1)	P(11)–C(112)	1.77 (3)
Mo(1)–Cl(3)	2.447 (5)	P(1)–C(11)	1.90 (8)	P(11)–C(113)	1.62 (3)
Mo(1)–P(1)	2.501 (9)	P(1)–C(12)	1.85 (4)		
Mo(2)–Cl(2)	2.497 (7)	P(2)–C(21)	1.77 (4)		

		Bond Angles (deg)			
Cl(2)–Mo(1)–Cl(3)	95.3 (2)	Cl(2)–Mo(2)–Cl(3)	94.8 (2)	Cl(4)–Mo(2)–P(2)	89.5 (2)
Cl(3)–Mo(1)–Cl(3)′	88.7 (2)	Cl(3)–Mo(2)–Cl(3)′	88.4 (2)	Mo(1)–Cl(2)–Mo(2)	65.5 (2)
Cl(1)–Mo(1)–P(1)	86.1 (2)	Cl(4)–Mo(2)–Cl(4)′	92.3 (2)	Mo(1)–Cl(3)–Mo(2)	66.7 (2)
Cl(1)–Mo(1)–Cl(1)′	92.6 (2)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Bond Lengths and Angles in Compound 3[a]

		Bond Lengths (Å)			
Mo(1)–Mo(2)	2.7171 (3)	Mo(2)–Cl(2)	2.4964 (6)	P(2)–C(21)	1.809 (3)
Mo(1)–Cl(1)	2.4828 (6)	Mo(2)–Cl(3)	2.4623 (5)	P(2)–C(22)	1.810 (3)
Mo(1)–Cl(2)	2.4500 (6)	Mo(2)–Cl(21)	2.3889 (5)	P(2)–C(23)	1.805 (2)
Mo(1)–Cl(3)	2.4616 (6)	Mo(2)–Cl(22)	2.4102 (7)	P–C(1)	1.768 (3)
Mo(1)–Cl(11)	2.3996 (7)	Mo(2)–P(2)	2.5234 (7)	P–C(2)	1.773 (3)
Mo(1)–Cl(12)	2.4021 (6)	P(1)–C(11)	1.812 (3)	P–C(3)	1.780 (4)
Mo(1)–P(1)	2.5156 (6)	P(1)–C(12)	1.805 (3)	P–H	1.15 (3)
Mo(2)–Cl(1)	2.4649 (6)	P(1)–C(13)	1.809 (3)		

		Bond Angles (deg)			
Cl(1)–Mo(1)–Cl(2)	99.89 (2)	Cl(12)–Mo(1)–P(1)	82.81 (2)	Cl(21)–Mo(2)–P(2)	86.02 (2)
Cl(1)–Mo(1)–Cl(3)	89.80 (2)	Cl(1)–Mo(2)–Cl(2)	99.11 (2)	Cl(22)–Mo(2)–P(2)	88.55 (2)
Cl(2)–Mo(1)–Cl(3)	88.30 (2)	Cl(1)–Mo(2)–Cl(3)	90.21 (2)	Mo(1)–Cl(1)–Mo(2)	66.60 (2)
Cl(11)–Mo(1)–Cl(12)	92.52 (2)	Cl(2)–Mo(2)–Cl(3)	87.25 (2)	Mo(1)–Cl(2)–Mo(2)	66.61 (2)
Cl(11)–Mo(1)–P(1)	89.89 (2)	Cl(21)–Mo(2)–Cl(22)	92.37 (2)	Mo(1)–Cl(3)–Mo(2)	66.69 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

is that of a face-sharing bioctahedron with three bridging chlorine atoms; two terminal chlorine atoms and one trimethylphosphine ligand on each molybdenum complete the coordination spheres of the two metal centers. A reason for the different lattices in 1 and 2 may be the different phosphonium ion positions and the arrangement of the methyl groups in the trimethylphosphine ligands, which is quite evident in stereoviews, which are available as supplementary material.

However, it must be noted that for one compound to give rise to two crystalline forms under very similar conditions (and without the inclusion of any interstitial molecules of solvent in either case) is a decidedly uncommon situation. Another uncommon feature of all three of the crystals studied here is the relative looseness of packing as reflected in the volume per (non-hydrogen) atom. The rule of thumb value for this that is commonly used by crystallographers for compounds of this type is 20 Å³/atom. In compounds 1–3 we have the larger values of 30, 33, and 29 Å³/atom. An even larger value, 35.5 Å³/atom, was previously found[5] in [PHMe₃][Mo₂I₇(PMe₃)₂]. The reason for this (as previously stated[5]) appears to be the disparity between the sizes
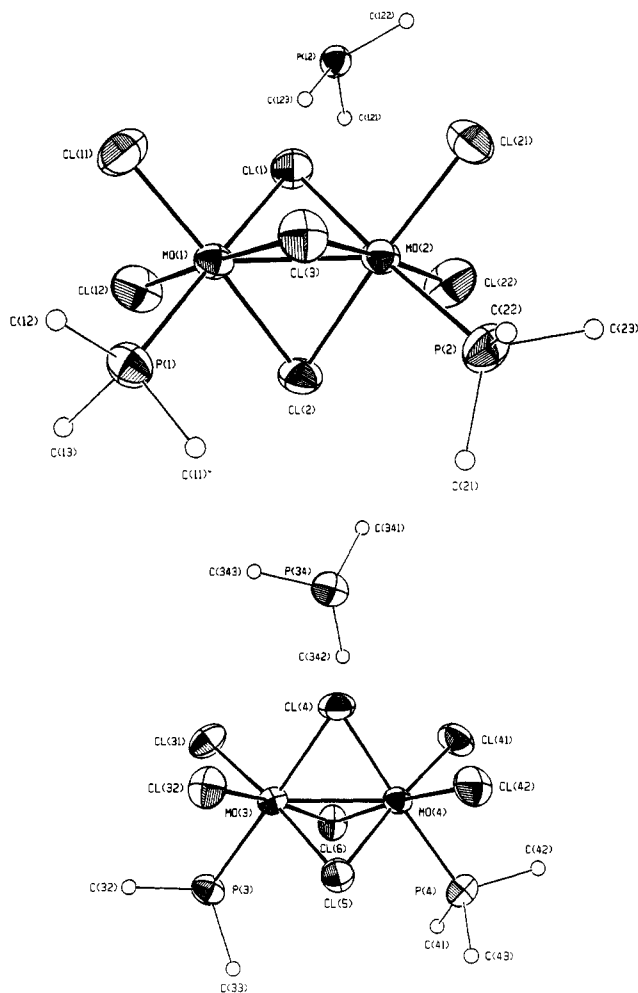
Figure 1. ORTEP drawings of the two independent formula units (**1a**, top; **1b**, bottom) in compound **1**. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. Carbon atoms are represented by spheres of arbitrary size.
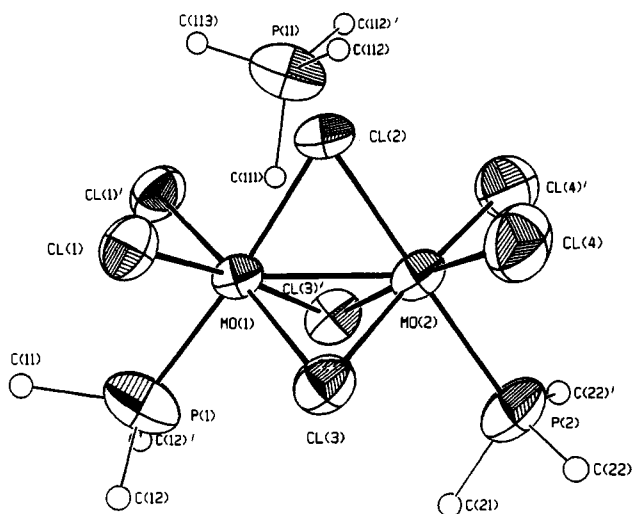

Figure 2. ORTEP drawing of the cation and anion in compound **2**. Ellipsoids and spheres are as in Figure 1.
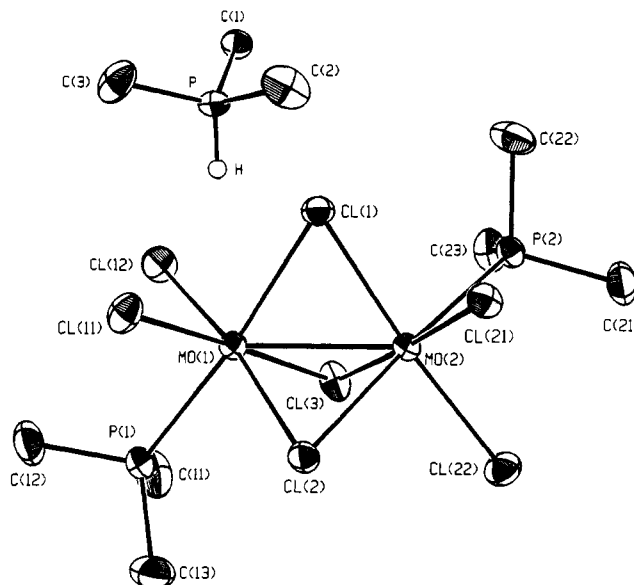

Figure 3. ORTEP drawing of the cation and anion in compound **3**. Ellipsoids and the sphere are drawn at the 50% probability level.

Table VIII. Average Dimensions of Three Syn and One Gauche [$Mo_2Cl_7(PMe_3)_2$]$^-$ Ion

dimens^{a,c}	1a	1b	2	3
Mo–Mo	2.763 (2)	2.713 (2)	2.694 (3)	2.7171 (3)
Mo–Cl$_t$	2.390 [5]	2.399 [2]	2.388 [5]	2.400 [4]
Mo–Cl$_{b,Cl}$	2.455 [7]	2.446 [3]	2.450 [2]	2.460 [3]
Mo–Cl$_{b,P}$	2.493 [2]	2.498 [8]	2.49 [1]	2.49 [1]
Mo–P	2.528 [6]	2.518 [3]	2.52 [3]	2.520 [6]
Mo–Cl$_b$–Mo	68.1 [4]	66.9 [5]	66.3 [4]	66.63 [3]
Cl$_b$–Mo–Cl$_b$	92 [1]	93 [1]	91 [1]	92 [2]
Cl$_t$–Mo–Cl$_t$	90.7 [2]	92.7 [2]	92.5 [2]	92.4 [1]
Cl$_t$–Mo–P	88.7 [9]	87.4 [9]	88 [1]	87 [2]

^{a} Distances in Å; angles in deg. ^{b} Brackets signify the variance, viz., $[(\sum \Delta_i^2)/n(n-1)]^{1/2}$. ^{c} Cl$_b$ = bridge Cl; Cl$_{b,Cl}$ = bridge Cl trans to Cl; Cl$_{b,P}$ = bridge Cl trans to P; Cl$_t$ = terminal Cl.

of the cations and the anions, so that efficient packing of the latter leaves holes that are too large for the former. This, in turn, leads to the possibility of imprecise positioning and orientation of the cations, as will be discussed below.

Let us now examine the three crystallographically distinct *syn*-[$Mo_2Cl_7(PMe_3)_2$]$^-$ ions, two of which occur in compound **1**. Tables V and VI list selected bond distances and angles for

compounds **1** and **2**. Both of the anions in **1** reside on general positions and have no crystallographically required symmetry, whereas that in **2** has a crystallographic mirror plane passing through the metal atoms, the phosphorus atoms, two carbon atoms, and one μ-Cl atom. In the case of **1** refinement of all non-hydrogen atoms proceeded straightforwardly. Despite the overlarge volumes available to them, the PHMe$_3^+$ ions showed no signs of unusual behavior. In compound **2**, on the other hand, there is at least one and perhaps a second form of disorder. The results we report present only one set of positions for the P and C atoms of the cation, but it appears likely that some cations (ca. 11%) may occupy a different site in the cavity. However, when this model (i.e., only 89% as shown in Figure 2 and Table III, plus 11% at the second site) was refined, it gave no satisfactory account of the carbon atoms of the second site nor did any significant change occur in the dimensions of the anion. Thus, we returned to the one-site, reported model. There does, however, seem to be a partial disordering of the H atom and two of the carbon atoms of this PH(CH$_3$)$_3^+$ ion, and it was so refined, as indicated in a footnote to Table III. If this disorder is not introduced, the displacement parameters diverge in ways that seem less realistic.

We turn now to compound **3**, which contains the gauche isomer. Table VII gives selected distances and angles in the anion and cation, and mean values, for various types of bonds and angles, are listed in Table VIII along with corresponding ones for the syn anions. The only closely comparable structure previously reported is that of the *gauche*-[$Mo_2Cl_7(SMe_2)_2$]$^-$ ion,[9] which is generally

(9) Boorman, P. M.; Moynihan, K. J.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1982**, 899.

quite similar but with a slightly longer Mo–Mo distance of 2.746 (9) Å compared to the present value of 2.7171 (3) Å.

When all four of the structures whose average principal dimensions are listed in Table VIII are compared, it is clear that they have for the most part very similar dimensions. The only prominent exception to this generalization is the Mo–Mo distance in the anion of **1a**, which is 2.763 (2) Å while the other three are in the range 2.694 (3)–2.7171 (3) Å. While this may appear a little surprising, it is not really inconsistent with the structure of **1** nor with what we know of face-sharing bioctahedral compounds of molybdenum(III) generally. Structural studies of the $[Mo_2Cl_9]^{3-}$ ion in at least 10 compounds with different counterions[10-13] have revealed Mo–Mo distances ranging from 2.52 to 2.82 Å. Clearly the Mo^{III}–Mo^{III} bond in this structural context is not a rigid one, and the different environments of the independent anions in **1** compress them to different extents. The difference is modest compared to the range observed for the $[Mo_2Cl_9]^{3-}$ ion.

General trends to be seen in all four structures (i.e., in the gauche as well as the syn isomer) are the following. (1) Deviations of angles from those expected for the fusion of two ideal octahedra are small and thus suggest that the Mo–Mo attraction is only moderate. For the background of this interpretation, see ref 14. The average internal Cl_b–Mo–Cl_b angles are 92 ± 1°, the external Cl_t–Mo–P and Cl_t–Mo–Cl_t angles are about 88 and 92°, respectively, and the Mo–Cl_b–Mo angles are 66.3–68.1°, which are all indicative of only slight compression along the Mo–Mo axis.

This, of course, supports the presence of some significant Mo–Mo bonding interaction, else there would be an expansion owing to the underlying Mo···Mo repulsive forces. (2) There is a small but consistent trans influence by the phosphine ligand compared to that of the Cl atom, since the Mo–$Cl_{b,P}$ distances are all 0.03–0.05 Å longer than the Mo–$Cl_{b,Cl}$ distances. (3) All Mo–$Cl_{b,Cl}$ distances are consistently about 0.05 Å longer than Mo–Cl_t distances, as is normal.

Concluding Remarks. This is the first time, to our knowledge, that both the syn and gauche isomers of a $LX_2M(\mu\text{-}X)_3MX_2L$ species have been isolated and structurally characterized. The great similarity in bond distances and angles for the isomers would suggest that bond energies and repulsive forces are about equal in the two, and that in turn is in accord with the fact that the equilibrium constant for a solution of the two isomers has the purely statistical value within experimental error. The interconversion presumably requires the loss of a tertiary phosphine ligand from one metal atom, whereupon the then five-coordinate half of the dimer can rearrange so that the reattachment of the tertiary phosphine may occur so as to form the isomeric product.

Finally, we should mention two unsolved problems raised in this work. (1) Why have we failed to obtain the product $Mo_2Cl_6(PMe_3)_4$, which was the original goal of the work? (2) What is the source of the hydrogen ion required to form the $PHMe_3^+$ cation, and why does the formation of this ion occur so easily?

Supplementary Material Available: Full tables of bond distances and angles and anisotropic displacement parameters for complexes **1–3**, stereoviews of the crystal packing and unit cells of **1–3**, and figures showing the change in the intensity of the PMe_3 resonances in the ^1H NMR spectra of complexes **1** and **3**, a plot of ln (X/X_0) vs time, and a plot of the PMe_3 ^1H NMR chemical shifts vs. T^{-1} for complexes **1** and **3** (23 pages); listings of observed and calculated structure factors for **1–3** (60 pages). Ordering information is given on any current masthead page.

(10) Saillant, R.; Jackson, R. B.; Streib, W. E.; Folting, K.; Wentworth, R. A. D. *Inorg. Chem.* **1971**, *10*, 1453.
(11) Subbotin, M. Y.; Aslanov, L. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1985**, *30*, 816; **1986**, *31*, 222.
(12) Subbotin, M. Y.; Kazin, P. E.; Aslanov, L. A.; Zelentsov, V. V. *Koord. Khim.* **1985**, *11*, 1568.
(13) Stranger, R.; Grey, I. E.; Madsen, I. C.; Smith, P. W. *J. Solid State Chem.* **1987**, *69*, 162.
(14) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

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Ligand Design for Complexation in Aqueous Solution. 1. Neutral Oxygen Donor Bearing Groups as a Means of Controlling Size-Based Selectivity for Metal Ions

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The synthesis of several novel macrocyclic ligands containing both oxygen and nitrogen donors and containing in some cases also pendent donor groups bearing one or more neutral oxygen donors is described. The protonation constants and formation constants with Ca(II), Sr(II), Ba(II), Pb(II), Zn(II), Cd(II), Cu(II), and Ni(II) are reported. The crystal structures of two complexes of the above ligands are reported, [K(BHEE-18-aneN$_2$O$_4$)]I (I) and [K(BHE-18-aneN$_2$O$_4$)]Cl (II). (The ligands BHEE-18-aneN$_2$O$_4$ and BHE-18-aneN$_2$O$_4$ are N-substituted derivatives of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, where the nitrogen substituents are respectively CH$_2$CH$_2$OCH$_2$CH$_2$OH and CH$_2$CH$_2$OH.) Compound I crystallizes in space group $P2_1/c$, with cell constants a = 8.805 (4) Å, b = 14.221 (2) Å, c = 21.957 (3) Å, β = 100.27 (2)°, Z = 4, V = 2705.16 Å^3, d_m = 1.46 g cm^{-3}, and d_c = 1.48 g cm^{-3}. The final conventional R factor was 0.054. The complex appears to be sterically crowded, with the pendent donor groups occupying the unusual trans orientation and with at least two of the oxygen donors on the pendent groups being left uncoordinated. Compound II crystallizes in space group $C2/c$, with cell constants a = 13.331 (3) Å, b = 15.716 (2) Å, c = 11.577 (4) Å, β = 117.69 (3)°, Z = 4, V = 2147.53 Å^3, d_m = 1.32 g cm^{-3}, and d_c = 1.32 g cm^{-3}. The final conventional R factor was 0.029. In contrast to compound I, II appears not to be sterically crowded and adopts the more usual cis arrangement of the pendent donor groups. Analysis of the formation constants shows how the neutral oxygen donor atom can be used to achieve metal ion size-based selectivity. The results reinforce the ligand design principle observed previously, that addition of groups bearing neutral oxygen donors increases the selectivity of a ligand for large relative to small metal ions. The control of selectivity for the large Pb(II) ion relative to the small Zn(II) ion is examined, and it is shown that the extra pair of oxygen donors in BHEE-18-aneN$_2$O$_4$, for example, leads to greatly enhanced selectivity for the large Pb(II) ion over the small Zn(II) ion, as compared with the ligand BHE-18-aneN$_2$O$_4$. The point is emphasized that oxygen donors do not have to be part of a macrocyclic ring in order to generate selectivity for large metal ions.

Introduction

The neutral oxygen donor has for some time been of considerable interest because of its occurrence in crown ethers[1] and more recently because of its occurrence as alcoholic and ethereal oxygens in side arms on ligands such as the "lariat ethers".[2,3] An important

(1) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2459.

(2) Gatto, V. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 8240.
(3) Kulstad, S.; Malmsten, L. A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 573.