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Humberto Mui, Rinaldo Poli. Preparation and structure of the dimolybdenum(III) compound hexachlorotetrakis(triethylphosphine)dimolybdenum. An anomaly in metal-metal-bonded edge-sharing bioctahedral compounds. *Inorganic Chemistry*, 1989, 28 (18), pp.3609-3612. 10.1021/ic00317a045 . hal-03544572

HAL Id: hal-03544572

<https://hal.science/hal-03544572>

Submitted on 26 Jan 2022

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**Preparation and Structure of the Dimolybdenum(III)
Compound $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$. An Anomaly in
Metal–Metal-Bonded Edge-Sharing Bioctahedral Compounds**

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Received March 21, 1989

The synthetic and structural chemistry of dinuclear transition-metal compounds containing direct metal–metal bonds has been actively investigated for over thirty years.¹ Of interest here

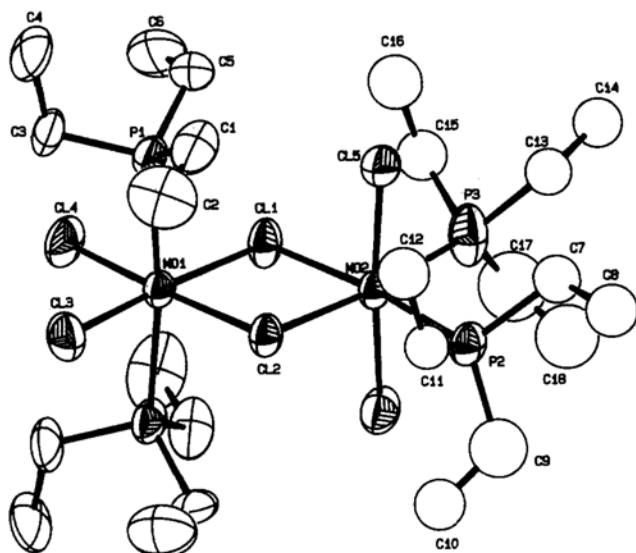
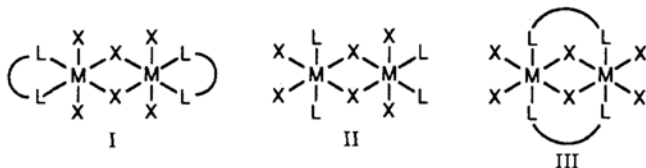


Figure 1. ORTEP view of the $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$ molecule with the atomic numbering scheme employed. Only one orientation of the disordered phosphine ligands bonding through P(2) and P(3) is shown for clarity.

are the edge-sharing bioctahedral complexes with M_2^{6+} cores, representative structures of which are illustrated in I–III ($\text{X} =$



anionic ligand; L = neutral monodentate ligand; L–L = neutral bidentate ligand).² Note that, in compounds of formula $\text{M}_2\text{X}_6\text{L}_4$, the neutral donors normally occupy axial sites on one metal center and equatorial sites on the second (type II).³ Examples of the latter include $\text{Ta}_2\text{Cl}_6(\text{PMe}_3)_4$ (d^2-d^2),⁴ $\text{Cr}_2\text{Cl}_6(\text{PEt}_3)_4$,⁵ $\text{W}_2\text{Cl}_6(\text{PEt}_3)_4$,⁶ and $\text{W}_2\text{Cl}_6\text{py}_4$ (d^3-d^3), and $\text{Ru}_2\text{Cl}_6(\text{PBu}_3)_4$ (d^5-d^5).⁸

For the group 6 derivatives the six available metal electrons can be involved in a direct metal–metal bonding of type $\sigma^2\pi^2\delta^2$ or $\sigma^2\pi^2\delta^2$, depending on the nature of the bridging ligands.⁹ $\text{W}_2\text{Cl}_6(\text{PEt}_3)_4$ is diamagnetic and exhibits a strong metal–metal interaction ($\text{W}–\text{W} = 2.7397(7) \text{ \AA}$).⁶ However, the corresponding chromium compound is paramagnetic with a nonbonding Cr–Cr separation of $3.637(2) \text{ \AA}$.⁵ The question of whether the corresponding molybdenum(III) complex would or would not have a metal–metal bond stimulated the present investigation.¹⁰ Although derivatives of formula $[\text{MoCl}_3(\text{PR}_3)_2]_n$ ($\text{R} = \text{Me}, \text{Et}$) have been mentioned briefly by Carmona et al.,¹¹ no compound with

Table I. Positional Parameters and $B(\text{eq})$ for $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$

atom	x	y	z	$B(\text{eq}), \text{ \AA}^2$
Mo(1)	0.09056 (6)	1/4	0.0928 (1)	4.09 (7)
Mo(2)	-0.06141 (6)	1/4	-0.1029 (1)	4.03 (7)
Cl(1)	0.0615 (2)	1/4	-0.1334 (4)	5.4 (2)
Cl(2)	-0.0300 (2)	1/4	0.1261 (4)	4.6 (2)
Cl(3)	0.1090 (2)	1/4	0.3135 (4)	6.4 (3)
Cl(4)	0.2045 (2)	1/4	0.0447 (5)	7.0 (3)
Cl(5)	-0.0643 (2)	0.1267 (2)	-0.1123 (3)	6.4 (2)
P(1)	0.0979 (2)	0.1158 (2)	0.0999 (4)	6.0 (2)
P(2)	-0.1811 (2)	1/4	-0.0339 (4)	5.0 (2)
P(3)	-0.0740 (3)	1/4	-0.3409 (5)	7.9 (4)
C(1)	0.0278 (7)	0.0679 (7)	0.168 (2)	8 (1)
C(2)	0.014 (1)	0.081 (1)	0.303 (2)	12 (1)
C(3)	0.1698 (7)	0.0918 (7)	0.194 (2)	8 (1)
C(4)	0.183 (1)	0.0126 (8)	0.206 (2)	13 (2)
C(5)	0.1068 (8)	0.0690 (8)	-0.049 (1)	8 (1)
C(6)	0.168 (1)	0.089 (1)	-0.122 (2)	13 (1)
C(7)	-0.234 (1)	0.195 (1)	-0.144 (2)	6.9 (7)*
C(8)	-0.306 (2)	0.191 (2)	-0.096 (3)	8.5 (8)*
C(9)	-0.222 (2)	0.336 (2)	-0.007 (4)	11 (1)*
C(10)	-0.197 (2)	0.376 (2)	0.092 (3)	8 (1)*
C(11)	-0.195 (1)	0.208 (1)	0.128 (2)	6.0 (6)*
C(12)	-0.177 (2)	0.136 (2)	0.142 (3)	8 (1)*
C(13)	-0.137 (2)	0.179 (2)	-0.393 (3)	6.7 (8)*
C(14)	-0.136 (1)	0.165 (2)	-0.540 (3)	7.5 (7)*
C(15)	0.001 (2)	0.212 (1)	-0.418 (3)	7.8 (7)*
C(16)	0.019 (2)	0.137 (2)	-0.391 (3)	9.1 (9)*
C(17)	-0.086 (3)	0.322 (3)	-0.437 (5)	15 (2)*
C(18)	-0.146 (3)	0.350 (3)	-0.424 (5)	12 (2)*

*Starred values belong to atoms whose positions were refined isotropically with a site occupancy of 0.5.

Table II. Intramolecular Distances (\AA) and Angles (deg) for $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$

Distances			
Mo(1)–Cl(1)	2.479 (4)	Mo(2)–Cl(1)	2.524 (4)
Mo(1)–Cl(2)	2.481 (4)	Mo(2)–Cl(2)	2.518 (4)
Mo(1)–Cl(3)	2.378 (5)	Mo(2)–Cl(5)	2.384 (3)
Mo(1)–Cl(4)	2.375 (5)	Mo(2)–P(2)	2.546 (4)
Mo(1)–P(1)	2.596 (3)	Mo(2)–P(3)	2.545 (6)
Angles			
Cl(1)–Mo(1)–Cl(2)	84.4 (1)	Cl(1)–Mo(2)–Cl(5)	91.07 (9)
Cl(1)–Mo(1)–Cl(3)	175.2 (2)	Cl(1)–Mo(2)–P(2)	170.6 (2)
Cl(1)–Mo(1)–Cl(4)	91.4 (2)	Cl(1)–Mo(2)–P(3)	88.4 (2)
Cl(1)–Mo(1)–P(1)	92.4 (1)	Cl(2)–Mo(2)–Cl(5)	92.7 (1)
Cl(2)–Mo(1)–Cl(3)	90.9 (2)	Cl(2)–Mo(2)–P(2)	88.0 (1)
Cl(2)–Mo(1)–Cl(4)	175.8 (2)	Cl(2)–Mo(2)–P(3)	171.1 (2)
Cl(2)–Mo(1)–P(1)	93.02 (8)	Cl(5)–Mo(2)–Cl(5)'	174.4 (2)
Cl(3)–Mo(1)–Cl(4)	93.4 (2)	Cl(5)–Mo(2)–P(2)	89.36 (9)
Cl(3)–Mo(1)–P(1)	87.8 (1)	Cl(5)–Mo(2)–P(3)	87.5 (1)
Cl(4)–Mo(1)–P(1)	87.14 (8)	P(2)–Mo(2)–P(3)	101.0 (2)
P(1)–Mo(1)–P(1)'	172.6 (2)	Mo(1)–Cl(1)–Mo(2)	96.4 (1)
Cl(1)–Mo(2)–Cl(2)	82.7 (1)	Mo(1)–Cl(2)–Mo(2)	96.5 (1)

a $\text{Mo}_2\text{Cl}_6(\text{PR}_3)_4$ stoichiometry has been structurally characterized. Molybdenum(III) dimers of type I and III, however, are well-known, and these show Mo–Mo distances in the range 2.5–2.8 \AA .²

We report here the synthesis and structural characterization of the compound $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$, the first dinuclear compound of molybdenum(III) with structure II. The key result of our structural study is that, in contrast to reported type I and type III dimolybdenum(III) complexes, $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$ does not exhibit a significant metal–metal interaction.

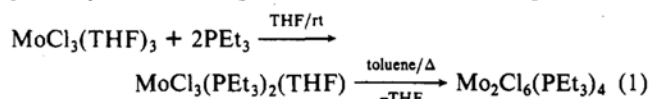
Results and Discussion

Compound $\text{Mo}_2\text{Cl}_6(\text{PEt}_3)_4$ has been obtained by reacting $\text{MoCl}_3(\text{THF})_3$ with 2 equiv of the phosphine in THF, followed by evaporation to dryness and brief reflux (ca. 10 min) of the residue in toluene. A longer thermal treatment results in partial decomposition. The compound crystallizes from the toluene so-

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- (3) However, the (d^1-d^1) zirconium(III) chloro-phosphine complexes $\text{Zr}_2\text{Cl}_6(\text{PR}_3)_4$ ($\text{R} = n\text{-Bu}, \text{Et}; \text{R}_3 = \text{Me}_2\text{Ph}$) adopt eq,eq,eq,eq rather than eq,eq,ax,ax structures. See: (a) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* 1981, 20, 1844. (b) Cotton, F. A.; Diebold, M. P.; Kibala, P. A. *Inorg. Chem.* 1988, 27, 799.
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lution upon cooling to yield well-formed, slightly air-sensitive, golden brown crystals. The molybdenum(III) mononuclear compound $\text{MoCl}_3(\text{PET}_3)_2(\text{THF})$ is probably the product of the first step. Similar compounds have been previously described.¹² During the thermal treatment in toluene, a THF molecule is probably lost, resulting in dimer formation (see eq 1). This



reactivity parallels the one recently reported by us for $\text{MoX}_3(\text{dppe})(\text{THF})$ [$\text{X} = \text{Cl}, \text{Br}$; $\text{dppe} = \text{bis}(\text{diphenylphosphino})\text{ethane}$], where the $\text{Mo}_2\text{X}_6(\text{dppe})_2$ compounds of structure I are obtained.¹³

The X-ray molecular structure of $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ is shown in Figure 1. The positional and equivalent isotropic displacement parameters are listed in Table I, and selected bond distances and angles are assembled in Table II. Like the other systems of stoichiometry $\text{M}_2\text{X}_6\text{L}_4$ listed above, this compound adopts the configuration with two axial and two equatorial neutral donors. The metal-metal separation is 3.730 (1) Å, indicative of little or no interaction between the metal centers. The lack of strong interaction is also indicated by the large $\text{Mo}(1)\text{-Cl-Mo}(2)$ angles [average 96.4 (1)°]. Among the Mo-Cl distances the following, expected trends, which are a combination of terminal vs bridging bond strength and trans influence effects, are observed: terminal [average 2.379 (5) Å] < bridging, trans to Cl [average 2.480 (4) Å] < bridging, trans to P [average 2.521 (4) Å]. For the Mo-P distances, the trans-to-P distance [2.596 (3) Å] is longer, as expected, than the trans-to-Cl distances [average 2.546 (6) Å].

Compound $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ is paramagnetic. The room-temperature magnetic susceptibility in the solid state corresponds to an effective magnetic moment of 5.05 μ_B /dimer or 3.57 μ_B /Mo atom, which is lower than the expected value for magnetically dilute Mo^{3+} centers. Either a direct metal-metal interaction or a through-the-bridge antiferromagnetic exchange could explain the reduced magnetic moment. On the basis of the long Mo-Mo distance, the latter explanation would seem to be the more logical one. Variable-temperature magnetic studies for $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ and for $\text{Cr}_2\text{Cl}_6(\text{PET}_3)_4$ are planned for the near future.¹⁴ It seems safe to conclude, however, that the reason for compound $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ not having a strong Mo-Mo bond has to do with the stabilization of the t_{2g}^3 configuration in a pseudooctahedral Mo(III) center vs the stabilization that can be attained by forming the Mo-Mo bond. The same argument can be used to rationalize the lack of bonding in the chromium compound⁵ and the strong bonding in the tungsten compound.⁶

This situation is reminiscent of the face-sharing bioctahedral group 6 $\text{M}_2\text{X}_9^{3-}$ anions and derivatives,¹⁵ where the magnetic properties range from the magnetically dilute Cr^{3+} in the Cr_2^{6+} species to the diamagnetic behavior (only small TIP) of the W_2^{6+} species, the corresponding Mo_2^{6+} species exhibiting intermediate behavior. Concerning the various Mo(III) dimers, we observe that the face-sharing bioctahedral geometry allows a closer approach of the two metals toward each other with respect to the edge-sharing bioctahedral geometry, favoring a stronger direct interaction and ultimately a further reduction of the magnetic susceptibility. In fact, the room-temperature effective magnetic moment per Mo atom in selected compounds are (Mo-Mo distance in brackets) 0.6 μ_B for $\text{Cs}_3[\text{Cl}_3\text{Mo}(\mu\text{-Cl})_3\text{MoCl}_3]$ ¹⁶ [2.655 (1) Å],¹⁷ 0.8 μ_B for $\text{Cs}_3[\text{Br}_3\text{Mo}(\mu\text{-Br})_3\text{MoBr}_3]$ ¹⁶ [2.816 (9) Å],¹⁷ and 1.29 μ_B for $\text{NMe}_4(\text{PMe}_3)_2\text{Mo}(\mu\text{-I})_3\text{MoI}_2(\text{PMe}_3)_2$ [3.021 (4) Å].¹⁸ For the edge-sharing bioctahedral $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$

molecule described here, the Mo-Mo separation is longer [3.730 (1) Å] and the room-temperature magnetic moment higher (3.57 μ_B /Mo atom).

It is interesting to observe that the $\text{Mo}_2\text{Br}_6(\text{dppe})_2$ derivative of structure I (showing a strong metal-metal interaction) can be reconverted to the mononuclear THF adduct when refluxed in THF.^{13a} This effect has been attributed to a slightly longer, and presumably weaker, Mo-Mo bond due to the larger size of the bridging bromo ligands, with respect, for instance, to the corresponding chloro-bridged dimer.¹⁹ In this respect one would predict that $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ should also easily break down to mononuclear species in a donor solvent. $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ is stable in THF at room temperature for a short period of time. Brief warming to the reflux temperature or standing at room temperature for a longer period of time causes a reaction to take place, but the product(s) of this reaction is (are) different from the $\text{MoCl}_3(\text{PET}_3)_2(\text{THF})$ precursor, as shown by UV/vis spectroscopy. The interaction of $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ with additional PET_3 also generates a change in the UV spectrum. However, $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ has been obtained in moderate yields, according to the procedure outlined in eq 1, by using a $\text{PET}_3/\text{MoCl}_3(\text{THF})_3$ ratio of 3:1. In fact, the product, including the crystal for the X-ray study, was obtained for the first time by this procedure.

It is indeed striking that such a slight change in the molecular formula (e.g. 2 mol of a bidentate ligand vs 4 mol of a monodentate one) causes such a dramatic change in the metal-metal interaction. One important difference between the various structures is the relative disposition of the neutral ligands: eq,eq,eq,eq in $\text{Mo}_2\text{Cl}_6(\text{dppe})_2$ (Mo-Mo = 2.762 (1) Å),¹⁹ ax,ax,eq,eq in $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ (Mo-Mo = 3.730 (1) Å), and ax,ax,ax,ax in $\text{Mo}_2\text{Cl}_6(\text{dppm})_2$ [Mo-Mo = 2.789 (1) Å; $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$].^{9b} Other differences are the presence of bidentate vs monodentate ligands and aryl vs alkyl groups. A detailed analysis of all the electronic and steric factors requires the structural characterization of a more extensive body of compounds, as well as theoretical calculations, possibly accompanied by detailed magnetic studies. These are ongoing in other laboratories.¹⁴

The bonding/nonbonding situation that we have described here for Mo(III) dimers of structures I/II/III is reminiscent of a similar situation encountered for rhenium, where a strong bonding interaction [$\text{Re-Re} = 2.616$ (1) Å] was observed for $\text{Re}_2\text{Cl}_6(\text{dppm})_2$, of structure III,²⁰ compared with the weak interaction [$\text{Re-Re} = 3.809$ (1) Å] in $\text{Re}_2\text{Cl}_6(\text{dppe})_2$, of structure I.²¹ Since the usual occurrence in edge-sharing bioctahedral molecules of second- and third-row transition metals is that of strong M-M bonding, the $\text{Re}_2\text{Cl}_6(\text{dppe})_2$ molecule (the only exception to this rule until the start of the present investigation) had been described as a *puzzling anomaly*.² There is no complete agreement yet as to the causes of this "anomaly".^{2,22} The two rhenium molecules mentioned above have the important difference that in one, that is the type III molecule, the two metal atoms are buttressed by the two dppm ligands. The comparison between $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ (type II, long Mo-Mo separation) and $\text{Mo}_2\text{Cl}_6(\text{dppe})_2$ (type I, short Mo-Mo separation) is even more striking in that both molecules are unbuttressed. Until an explanation for this difference is found, the $\text{Mo}_2\text{Cl}_6(\text{PET}_3)_4$ molecule can be regarded as a second *puzzling anomaly*,² as far as metal-metal bonding in edge-sharing bioctahedral compounds goes.²³

Experimental Section

All operations were carried out under an atmosphere of dinitrogen. Solvents were dehydrated by conventional methods and distilled under

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Table III. Crystal Data for Mo₂Cl₆(PEt₃)₄

formula	C ₂₄ H ₆₀ Cl ₆ Mo ₂ P ₄
fw	877.23
space group	<i>Pnma</i>
<i>a</i> , Å	20.368 (2)
<i>b</i> , Å	19.308 (2)
<i>c</i> , Å	10.6404 (7)
<i>V</i> , Å ³	4185 (1)
<i>Z</i>	4
<i>d</i> _{calc} , g/cm ³	1.39
μ(Cu Kα), cm ⁻¹	101.83
radiation (monochromated in incident beam)	Cu Kα (λ = 1.541 78 Å)
temp, °C	20
transm factors: max, min	1.000, 0.641
<i>R</i> ^a	0.052
<i>R</i> _w ^b	0.072

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|).$$

dinitrogen prior to use. Instruments used were as follows: FTIR, Nicolet 5DXC; magnetic susceptibility balance, Johnson Matthey; UV/vis, Shimadzu UV-240, X-ray diffractometer, Enraf-Nonius CAD-4. The elemental analysis was by Midwest Microlab, Indianapolis, IN. MoCl₃(THF)₃ was prepared according to the literature.²⁴ PEt₃ was purchased from Strem Chemicals and used as received.

Preparation of Mo₂Cl₆(PEt₃)₄. MoCl₃(THF)₃ (0.62 g, 1.47 mmol) was reacted with PEt₃ (0.45 mL, 3.05 mmol) in 10 mL of THF. After being stirred for 2 h, the clear yellow solution was evaporated under reduced pressure to a residue. After addition of toluene (10 mL), the resulting yellow-orange solution was refluxed for 10 min. The color of the solution turned dark pine green. Golden brown crystals of the pure product crystallized upon cooling to room temperature. Yield: 0.31 g (48%). An additional crop (0.06 g) was obtained by cooling the mother solution to -20 °C. Anal. Calcd for C₂₄H₆₀Cl₆Mo₂P₄: C, 32.9; H, 6.9; Cl, 24.2; P, 14.1. Found: C, 33.2; H, 6.9; Cl, 23.2; P, 13.5. χ_g = 11.69 × 10⁻⁶ cgsu; μ_{eff} = 5.05 μ_B (molar diamagnetic correction -480 × 10⁻⁶ cgsu).

IR (Nujol mull; cm⁻¹): 1420 m, 1280 w, 1265 m, 1045 s, 765 s, 750 sh, 735 m, 720 s. UV/vis [toluene; nm (ε/cm⁻¹ mol⁻¹ L)]: 302 (9200), 345 (6000), 370 (5500), 606 (340).

X-ray Crystallography. A single crystal was glued to the inside of a thin-walled glass capillary, which was then sealed under dinitrogen and mounted on the diffractometer. The cell determination, data collection and reduction, and semiempirical absorption correction²⁵ were routine. Systematic absences from the data indicated the space group as either *Pnma* or *Pn2₁a* (nonstandard setting of *Pna2₁*). The centrosymmetric choice was suggested by intensity statistics and was adopted for the refinement. The successful refinement shows that this was the correct choice. The structure was solved by direct methods and refined by alternate full-matrix least-squares cycles and difference Fourier maps. The two equatorial phosphine ligands [those binding through atoms P(2) and P(3)] had all the ethyl groups disordered among two symmetry-related positions. All the carbon atoms of these groups were refined at half-occupancy and were left isotropic. Hydrogen atoms were not included in the refinement. Selected crystal data are in Table III, positional and equivalent isotropic thermal parameters are listed in Table I, and selected bond distances and angles are assembled in Table II.

Acknowledgment. We thank the Department of Chemistry and Biochemistry, University of Maryland, College Park (UMCP), the UMCP General Research Board, the Camille and Henry Dreyfus Foundation (through a Distinguished New Faculty Award to R.P.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The NSF provided a portion of the funds used to purchase the X-ray diffractometer-MicroVax system (Grant CHE-84-02155). We are grateful to Prof. F. A. Cotton for helpful discussion and for disclosing to us some of his results prior to publication.

Supplementary Material Available: For Mo₂Cl₆(PEt₃)₄, full tables of crystal data, anisotropic displacement parameters, and bond distances and angles (4 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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