

Figure 3. Time-dependent electronic spectrum of a solution of the +2 cluster in 0.1 M HCl.

experiment. The paramagnetic +2 cluster cation shows very broad lines for the acetate protons centered around 16 and 20 ppm downfield while the capping group (expected at ca. 90 ppm) was not detected. This might not be considered surprising since it is a paramagnetic species. We note, however, that in the isoelectronic

$[\text{Mo}_3(\text{CCH}_3)_2(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$ ion the ^1H NMR lines are reasonably sharp² because of efficient electron relaxation. It therefore seems conceivable that the broadening observed here is caused primarily by the rapid interconversion of the +1 and +2 ions.

Electronic Spectra. Figure 3 shows the time-dependent changes in the electronic spectrum of a solution of the +2 cluster cation in 0.1 M HCl. The presence of three isosbestic points corroborates our model of a simple one-electron transfer, viz., conversion of the +2 ion and the +1 ion without intermediates. The situation is not fully understood since we have not yet identified the nature of the reductant. A likely candidate is the cluster itself, viz., oxidation of W(IV) to W(VI) accompanied by disruption of the trinuclear unit. One molecule of cluster compound could thus be used to provide the electrons necessary for the reduction of six other cluster molecules, so that there would be no drastic effect on the visible spectrum.

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Registry No. $[\text{W}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\text{Br}_2 \cdot 2\text{H}_2\text{O}$, 98990-69-3; $[\text{W}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^{2+}$, 98990-71-7; $[\text{W}_3\text{O}(\text{CCH}_3)(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$, 98990-70-6; $\text{W}(\text{CO})_4(\text{pip})_2$, 14515-95-8.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

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Steric and Electronic Factors Influencing the Structures of Bridged (β -Type) $\text{M}_2\text{Cl}_4(\text{LL})_2$ ($\text{M} = \text{Mo}, \text{Re}$) Compounds: A Refined Correlation of Bond Length with Torsion Angle

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Two compounds of the type $\beta\text{-M}_2\text{Cl}_4(\text{LL})_2$ have been prepared, where $\text{M} = \text{Mo}$ (1) and Re (2) and LL is the diphosphine ligand depe (1,2-bis(diethylphosphino)ethane, $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$). The two compounds are isomorphous, and there is an elegant form of systematic disordering due to the fact that the molecules reside on positions where the crystallographic symmetry is higher than the symmetry of an individual molecule. This has made it impossible to refine the Cl and P atoms independently. Important dimensions of the molecules are as follows: for 1, $\text{Mo-Mo} = 2.173$ (2) Å, $\text{Mo-Cl(P)} = 2.460$ (5) Å, $\angle\text{Mo-Mo-Cl(P)} = 104.1^\circ$, torsion angle $\text{Cl(P)-Mo-Mo-Cl(P)} = 42.7$ (2) $^\circ$; for 2, $\text{Re-Re} = 2.211$ (1) Å, $\text{Re-Cl(P)} = 2.395$ (7) Å, $\angle\text{Re-Re-Cl(P)} = 105.2$ (2) $^\circ$, torsion angle $\text{Cl(P)-Re-Re-Cl(P)} = 43.7$ (3) $^\circ$. Compounds 1 and 2 form tetragonal crystals in space group $I4/mmm$ with $Z = 2$ and $a = 9.494$ (4) Å, $c = 18.097$ (1) Å for 1 and $a = 9.423$ (6) Å, $c = 18.073$ (4) Å for 2. With use of data for these compounds as a guide to the magnitude of steric and inductive effects on the structures of $\text{Mo}_2\text{X}_4(\text{LL})_2$ compounds generally, the correlation between Mo-Mo bond length and $\cos 2\chi$ has been revised to yield an inverse linear function with a correlation coefficient of 0.9547. According to this new relationship, the complete loss of the δ bond is associated with an increase of 0.097 Å in the bond length.

Introduction

It is well-known that compounds containing a metal-metal quadruple bond have a preference for an eclipsed rotational conformation about the M-M bond because of the angular dependence of the δ bond. In simple, unbridged compounds of the type $\text{X}_4\text{M-MX}_4$, this tendency dominates the repulsive forces between opposed ligand atoms and fully eclipsed structures are always observed.¹ However, in compounds of the $\beta\text{-Mo}_2\text{X}_4(\text{LL})_2$ type, in which the LL ligands are 1,2-bis(diphosphino)ethanes that bridge from one metal atom to the other, there is always a rotational twist (by an angle χ) away from the fully eclipsed con-

formation ($\chi = 0^\circ$) owing to the conformational demands of the fused six-membered rings that are present in these $\beta\text{-Mo}_2\text{X}_4(\text{LL})_2$ molecules.

It has also been recognized² that the strength of the δ component of a quadruple metal-metal bond depends inversely on the angle of rotation away from the eclipsed conformation; the δ bond strength varies according to $\cos 2\chi$. Thus, for $\chi = 0^\circ$ the δ bond has its maximum strength and as χ increases the δ bond strength decreases as a linear function of $\cos 2\chi$ until at $\chi = 45^\circ$ it becomes zero. From this it would follow that the Mo-Mo bond lengths in a series of $\text{Mo}_2\text{X}_4\text{L}_4$ type compounds might be expected to vary

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(2) Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 1752.

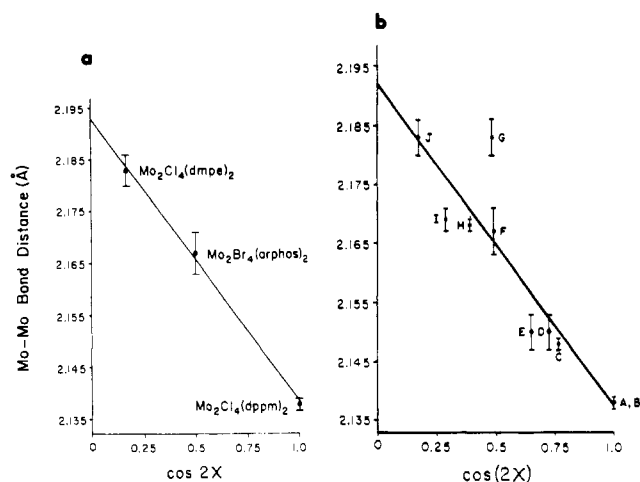


Figure 1. Earlier plots of Mo–Mo distances vs. $\cos 2\chi$: (a) original correlation using 3 compounds;³ (b) more extensive correlation employing 10 compounds.⁴ For identification of compounds, see ref 3 and 4.

linearly as a function of the strength of the δ component of the bond provided that other factors are kept constant. This would mean that, on the basis of the relationship just described between δ bonding and rotation angle χ , a plot of the Mo–Mo distance vs. $\cos 2\chi$ for a series of compounds in which the angle χ was caused to vary should be a straight line with a negative slope.

Several years ago³ we were able to test this proposition by combining available data for the compounds $Mo_2Cl_4(dppm)_2$ (where the CH_2 -bridged ligand imposes a χ value of 0°) and $Mo_2Br_4(arphos)_2$ (where a value of $\chi = 30^\circ$ was found) with new structural data for $Mo_2Cl_4(dmpe)_2$, in which we found a χ value of 40.0° . An almost perfect straight line was given by the data for these three compounds, as shown in Figure 1a.

As structural data on compounds of the β - $Mo_2X_4(LL)_2$ type continued to accumulate, we were soon able to subject the proposed relationship to a more demanding test by employing Mo–Mo distances and mean torsion angles for 10 compounds.⁴ These data gave the plot shown in Figure 1b. It is clear that while the proposed inverse linear correlation of distance with $\cos 2\chi$ is again supported, there is a fair amount of scatter; the correlation coefficient is only 0.890. In speculating upon reasons for this scatter, we recognized two factors that are likely to be most important. First, in the relatively crowded environment around the dimetal unit, the magnitude of the repulsion between the two opposing sets of ligands on adjacent metal atoms could be significant. One would expect such steric repulsion to be greatest for a completely eclipsed structure and to diminish with increasing torsional twist. Second, direct comparisons have been made between compounds containing different diphosphine ligands, some with alkyl and others with aryl substituents (methyl and phenyl groups); the effects of the dissimilar steric and electronic properties of these bridging ligands have not been taken into consideration.

Herein we report the results of an investigation into the manner in which the metal–metal interaction is affected by the two factors just mentioned above. The preparation and structural characterization of a new, triply bonded β - $Re_2Cl_4(depe)_2$ compound provides an opportunity to examine the nature of the steric repulsions and electronic influences in the absence of δ bonding. In addition, the structure of the analogous β - $Mo_2Cl_4(depe)_2$ is presented.

Experimental Section

Reaction Procedures. Unless otherwise stated, all manipulations were carried out under dry, air-free conditions with use of Schlenk and vacuum-line techniques. Solvents were dried and deoxygenated before use. In the reactions, a boiling stick made of white birch wood ("Puritan

Table I

	β - $Mo_2Cl_4(depe)_2$	β - $Re_2Cl_4(depe)_2$
formula	$Mo_2Cl_4P_4C_{20}H_{48}$	$Re_2Cl_4P_4C_{20}H_{48}$
fw	764.19	926.72
space group	$I4/mmm$	$I4/mmm$
systematic absences	$h + k + l = 2n$	$h + k + l = 2n$
a, Å	9.494 (4)	9.423 (6)
b, Å		
c, Å	18.097 (11)	18.073 (4)
α , deg		
β , deg		
γ , deg		
V, Å ³	1631 (2)	1605 (2)
Z	2	2
d_{calcd} , g/cm ³	1.519	1.918
cryst size, mm	0.29 × 0.29 × 0.37	0.22 × 0.24 × 0.26
$\mu(Mo K\alpha)$, cm ⁻¹	8.434	44.37
data collec instrument	Syntex P1	Syntex P1
radiation (monochromated in incident beam)	Mo K α , $\lambda = 0.71073$ Å	Mo K α , $\lambda = 0.71073$ Å
orientation reflcns: no., range (2θ), deg	15, 20 < 2θ < 30	15, 20 < 2θ < 31
temp, °C	25 ± 3	25 ± 3
scan method	ω -2 θ	ω -2 θ
data collec range, 2 θ , deg	5–50	5–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	330	391
no. of parameters refined	36	26
trans factors: max, min	0.98, 0.94	0.97, 0.87
R^a	0.0638	0.0436
R_w^b	0.0647	0.0445
quality of fit indicator ^c	2.143	1.471
largest shift/esd, final cycle	0.18	0.07
largest peak, e/Å ³	0.47	1.02

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

Applicator") was added to the reaction flask. These boiling sticks prevented bumping of the refluxing reaction mixture and served as agents for nucleating crystal growth.

Starting Materials. $K_4Mo_2Cl_8$ ⁵ and $(n-Bu_4N)_2Re_2Cl_8$ ⁶ were prepared by literature procedures. 1,2-Bis(diethylphosphino)ethane, depe, was purchased from Strem Chemicals, Inc., and used without further purification.

Syntheses. β - $Mo_2Cl_4(depe)_2$ (1). $K_4Mo_2Cl_8$ (0.25 g, 0.40 mmol) was placed in a flask equipped with a reflux condenser and a boiling stick. Methanol (25 mL) was added along with 2.3 mL of 0.691 M depe in toluene (1.6 mmol of depe). This mixture was refluxed for 11 h to yield a red solution and red crystalline solid. Crystals suitable for X-ray crystallographic analysis were deposited on the boiling stick while the major fraction of the product was microcrystalline. After the mixture was allowed to stand at room temperature for 10 h, the product was filtered off and washed with water (60 mL) and ethanol (50 mL); yield 0.23 g (78%). This compound was found to be slightly air-sensitive, decomposing after ca. 2 weeks of exposure to the laboratory atmosphere.

β - $Re_2Cl_4(depe)_2$ (2). A mixture of 0.20 g (0.18 mmol) of $(n-Bu_4N)_2Re_2Cl_8$, 23 mL of ethanol, and 0.69 mmol of depe (1.0 mL of 0.691 M depe in toluene) was refluxed for 10 h to yield a dark purple solid and a yellow-brown solution. As in the case of β - $Mo_2Cl_4(depe)_2$ described above, single crystals formed on a boiling stick. The air-stable product was filtered off and washed with water, ethanol, and hexane; yield 0.15 g (90%).

X-ray Crystallography. Data Collection. The crystals were coated with epoxy cement and mounted in random orientations on the ends of glass fibers. Data collection on single crystals of compounds 1 and 2 was carried out at room temperature (25 ± 3 °C) with use of an automated four-circle diffractometer (Syntex P1) equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The general procedures for geometric and intensity measurements have been fully described previously.⁷ In each case, three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. Empirical absorption corrections⁸ based on azimuthal (ψ) scans of re-

(3) Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 1507.

(4) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, *23*, 4222.

(5) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 351.

(6) Barder, T. J.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2510.

(7) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *Organomet. Chem.* **1973**, *50*, 227.

Table II. Positional Parameters and Their Estimated Standard Deviations for $\text{Mo}_2\text{Cl}_4(\text{depe})_2$ (**1**)^a

atom	x	y	z	B, Å ²
Mo	0	0	0.06003 (8)	3.86 (4)
Cl	0.1007 (6)	0.2302 (5)	0.0932 (3)	7.5 (1)
P	0.1007 (6)	0.2302 (5)	0.0932 (3)	7.5 (1)
C(1)	0.278 (3)	0.278 (3)	0.067 (2)	12 (1)
C(2)	0	0.360 (7)	0.042 (5)	28 (5)*
C(3)	0.085 (5)	0.297 (6)	0.188 (4)	22 (2)*
C(4)	0.375 (4)	0.375 (4)	0.095 (3)	17 (2)

^a Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table III. Positional Parameters and Their Estimated Standard Deviations for $\text{Re}_2\text{Cl}_4(\text{depe})_2$ (**2**)^a

atom	x	y	z	B, Å ²
Re	0	0	0.06117 (5)	3.33 (2)
Cl	0.0964 (8)	0.2256 (7)	0.0958 (4)	7.0 (2)
P	0.0964 (8)	0.2256 (7)	0.0958 (4)	7.0 (2)
C(1)	0.273 (5)	0.273 (5)	0.062 (2)	9 (1)*
C(2)	0	0.354 (5)	0.040 (3)	15 (2)*
C(3)	0.086 (7)	0.271 (7)	0.193 (1)	20 (2)*
C(4)	0.370 (6)	0.370 (6)	0.099 (4)	15 (2)*

^a Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as in Table II.

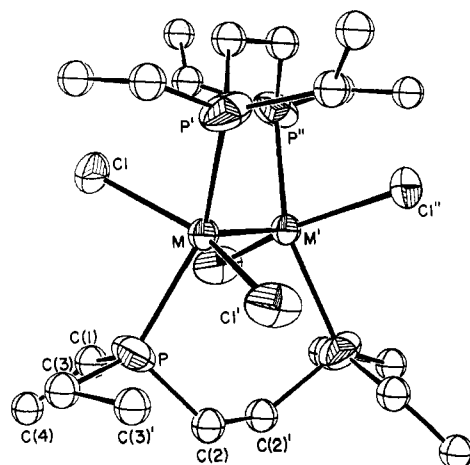
flections of Eulerian angle χ near 90° were applied to the data for compound **2**. Standard computational procedures were followed in the treatment of all X-ray data.⁹ Pertinent crystallographic parameters for both crystal structures are summarized in Table I.

Structure Solution for 1. Axial photographs and the observed systematic absence, $h + k + l \neq 2n$, for all hkl showed that the crystal was of a body-centered tetragonal type belonging to the Laue group $4/mmm$. Possible space groups were $I422$, $I4mm$, $I\bar{4}m2$, and $I4/mmm$. The Mo-Mo vector was located in a Patterson map and found to generate a disordered coordination sphere in each of the above-mentioned space groups. It was clear that at least half of the time, and possibly all of the time, chlorine and phosphorus atoms were superimposed on each other. Selection of the correct space group was accomplished by lowering the symmetry to orthorhombic and solving the structure in $I222$. This led to an arrangement of eight half-chlorine/half-phosphorus sites about each of the two Mo atoms (i.e., 16 such sites for the entire molecule). In other words, the asymmetric unit was found to consist of one Mo atom (positioned on the 2-fold axis parallel to the c axis) and four independent Cl/P sites within bonding distance from the Mo atom. The entire array possessed $4/mmm$ symmetry and thus led us to choose the space group $I4/mmm$ since it is the only one of those mentioned above that can accommodate this model.

In this space group, only one Mo atom and one Cl/P site were needed per asymmetric unit. A Cl/P atom was created and assigned a scattering factor equal to $\frac{1}{2}$ that of Cl plus $\frac{1}{2}$ that of P. After least-squares refinement of the Mo and Cl/P atoms, four independent carbon atoms were located in a difference Fourier map. In order to keep the model chemically realistic, each carbon atom was assigned an occupancy of $\frac{1}{2}$ (the multiplicity of three of the C atoms is 0.25 because they reside on special positions normally requiring occupancies of 0.5).

Conversion of the Mo and Cl/P atoms from isotropic to anisotropic led to unreasonable P-C(2) and C(2)-C(2)' bond distances. With use of the *DFIX* function of SHELX, the P-C(2) distance was constrained via an observational equation to be 1.81 (1) Å. Atoms C(2) and C(3) were refined isotropically, while all other atoms were refined anisotropically. Hydrogen atoms were omitted. Final atomic positional and isotropic equivalent displacement parameters are listed in Table II. Anisotropic displacement parameters and complete lists of bond distances and angles are available as supplementary material.

β - $\text{Re}_2\text{Cl}_4(\text{depe})_2$ (2**).** On the basis of axial photographs, systematic absences, and a Patterson map, it was suspected that the structure of **2**

**Figure 2.** Structure of the $\text{Mo}_2\text{Cl}_4(\text{depe})_2$ (**1**) and $\text{Re}_2\text{Cl}_4(\text{depe})_2$ (**2**) molecules, showing the atom labeling.**Table IV.** Selected Bond Distances and Angles in the $\text{M}_2\text{Cl}_4(\text{depe})_2$ Compounds

	M = Mo	M = Re
Bond Lengths, Å		
M-M	2.173 (2)	2.211 (1)
M-Cl	2.460 (5)	2.395 (7)
M-P	2.460 (5)	2.395 (7)
P-C(1)	1.81 (3)	1.83 (4)
P-C(2)	1.82 (6)	1.82 (4)
P-C(3)	1.84 (6)	1.81 (3)
C(2)-C(2)'	1.51 (12)	1.43 (8)
Angles, deg		
M-M-Cl	104.1 (1)	105.2 (2)
M-M-P	104.1 (1)	105.2 (2)
Cl-M-Cl	151.7 (2)	149.7 (3)
P-M-P	151.7 (2)	149.7 (3)
Cl-M-P	86.6 (2)	86.1 (2)
Cl-M-M-Cl (torsion)	41.4 (2)	42.1 (2)
P-M-M-P (torsion)	41.4 (2)	42.1 (2)

was isomorphous with that of β - $\text{Mo}_2\text{Cl}_4(\text{depe})_2$ (**1**). This suspicion was confirmed by successful refinement in space group $I4/mmm$. As in the case of structure **1**, refinement with the metal and Cl/P atoms anisotropic resulted in some unreasonable P-C and C-C bond distances. It was necessary to constrain via observational equations the P-C(2) and P-C(3) distances to be 1.81 (1) Å. Only the Re and Cl/P atoms were refined anisotropically; non-positive-definite displacement tensors resulted when the carbon atoms were converted from isotropic to anisotropic. The positional parameters and isotropic equivalent displacement parameters are listed in Table III. Anisotropic displacement parameters and complete lists of bond lengths and angles are available as supplementary material.

Results

As is apparent from Table I, these two compounds are crystallographically isomorphous. Thus it is not surprising that their molecular structures as they occur in their crystals are very similar. Figure 2 represents both and gives the common atom-numbering scheme. The atomic positional parameters and equivalent isotropic displacement parameters are listed in Tables II and III for **1** and **2**, respectively. Table IV gives important bond lengths and angles for both compounds.

The molecules of **1** and **2** have crystallographically rigorous D_2 symmetry; one 2-fold axis coincides with the M-M bond and the other two perpendicularly bisect that bond. The two six-membered rings that are fused along the M-M bond are equivalent and have a chair conformation. The molecules have almost completely staggered rotational conformations about the M-M bonds. The torsion angles are 42.7 (2)° for the molybdenum compound and 43.7 (3)° for the rhenium compound.

The crystal structures of **1** and **2** are disordered so that there are eight equivalent Cl/P sites about each metal atom, as illus-

(8) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(9) Crystallographic computations were done with either Enraf-Nonius SDP software on a PDP-11/60 computer or VAXSDP software on the VAX-11/780 computer. Certain portions of the SHELX program package were also used on the VAX.

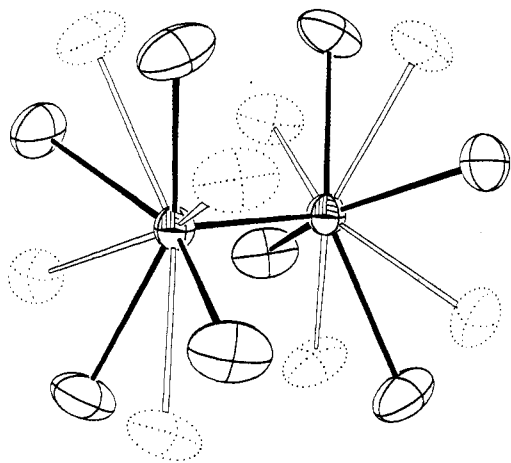


Figure 3. The set of 16 Cl/P atoms about the M_2 units in **1** and **2** as a result of the systematic disordering of the molecules on a site of $4/mmm$ symmetry in **1** and **2**. Subsets of 8 Cl/P atoms corresponding to individual molecules are indicated.

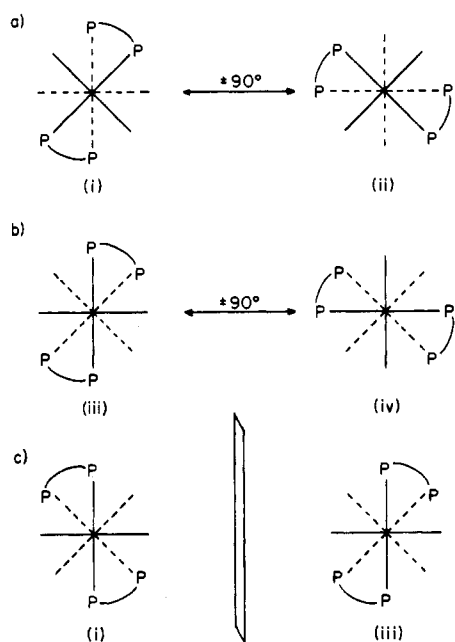


Figure 4. Schematic representations of the symmetry operations (90° rotations and mirror) that relate the several molecular orientations occurring in crystals of **1** and **2**.

trated in Figure 3. The entire disordered set of atoms can be attributed to a superposition of four orientations of a molecule of $M_2Cl_4(depe)_2$, each present one-fourth of the time. The relationship of these four orientations is schematically presented in Figure 4. The molecule illustrated in Figure 2 corresponds to orientation i in Figure 4a. As shown, orientations i and ii are related by a 90° rotation (corresponding to the crystallographic 4-fold symmetry operation) about the metal-metal axis. Orientations iii and iv are equivalent in an analogous manner. Each orientation is chiral so that i and iii, and similarly ii and iv, form an enantiomeric pair. Thus, the entire disordered set of atoms consists of two superimposed enantiomers which each take on two arrangements at right angles to one another.

A view of the complete disorder is given in Figure 5. Each of the 16 Cl/P sites is occupied by a chlorine atom 25% of the time and by a phosphorus atom 25% of the time. Similarly, the 16 equivalent positions of carbon atoms C(1), C(3), and C(4) are each occupied only one-fourth of the time. The eight sites for C(2) correspond to the carbon atom positions of the ethylene groups between the phosphorus atoms of the depe ligands and are occupied 50% of the time since they are shared by enantiomeric pairs.

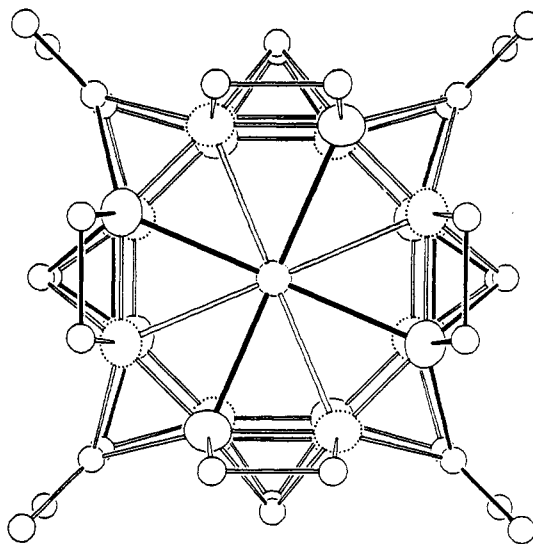
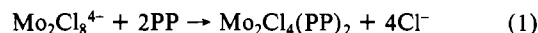


Figure 5. An ensemble of all the atomic positions that are fully (M atoms) or partially occupied in the systematic disorder model used for **1** and **2**. This ensemble has the required crystallographic $4/mmm$ (D_{4h}) symmetry. The view is down the M-M bond.

Discussion

The new β - $Mo_2X_4(PP)_2$ complex reported herein is easily prepared by the well-established ligand substitution reaction (1).



The new dirhenium complex β - $Re_2Cl_4(depe)_2$ (**2**) is prepared in excellent yield by a method analogous to reaction 1 with use of $Re_2Cl_8^{2-}$ instead of $Mo_2Cl_8^{4-}$. As has been previously observed in reactions of quadruply bonded dirhenium complexes with basic neutral ligands,^{10,11} the Re_2^{6+} core of the starting material is reduced to give a compound containing a triply bonded Re_2^{4+} core. Triply bonded **2** is structurally isomorphous with quadruply bonded **1**. This is only the third time in which analogous $Mo_2X_4(LL)_2$ and $Re_2X_4(LL)_2$ compounds have been structurally characterized.

The Distance vs. $\cos 2\chi$ Relationship. As noted in the introduction, the present work was motivated by concern over the scatter in the plot shown in Figure 1b. Of the factors considered to be the most likely causes of this, perhaps the chief one was that, in the set of 10 compounds used, some contained alkyl groups and others aryl groups as substituents on the phosphorus atoms. This type of change (from methyl to phenyl) may involve both steric and electronic factors. Insofar as there are steric factors that directly exert a force on the Mo-Mo bonds, it would seem that variations in the Mo-Mo-P and Mo-Mo-X angles might be indicative of this, whereas changes in the Mo-P and Mo-X distances might be diagnostic of electronic effects.

Table V provides a list of the pertinent angles and distances. It is to be noted that the structure of compound **1** is of no value in this respect since the disordering in the crystal denies us accurate values of the individual M-Cl and M-P angles and bond lengths. For the compounds in Table V, the Mo-Mo-P and Mo-Mo-X angles remain fairly constant throughout. In addition, the Mo-X bond lengths are essentially invariant within the chloro and bromo series of compounds. The structural similarities indicate that the steric differences between the diphosphine ligands containing methyl and phenyl groups have little to do directly with the Mo-Mo bond lengths, although of course they have an important indirect effect through their influence on the ring conformations and hence the angle χ .

On the other hand, the electronic properties of the PP ligands appear to play a significant role. It can be seen that for complexes containing Ph_2P groups the Mo-P distances are all quite similar and can be grouped together, whereas the Mo-P distances for the

(10) Cotton, F. A.; Stanley, G. G.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2099.

(11) In ref 1, Table 3.1.1, p 89, and references cited therein.

Table V. Summary of Averaged Bond Distances and Angles in β - $\text{Mo}_2\text{X}_4(\text{PP})_2$

compd	χ , deg	av Mo-P dist, Å	av Mo-X dist, Å	av Mo-Mo-P angle, deg	av Mo-Mo-X angle, deg
$\text{Mo}_2\text{Cl}_4(\text{dppm})_2 \cdot 2\text{C}_3\text{H}_6\text{O}$	0	2.58 [4]	2.394 [6]	99 [3]	106.9 [13]
$\text{Mo}_2\text{Br}_4(\text{dppm})_2 \cdot 2\text{THF}$	0	2.61 [6]	2.535 [3]	99 [2]	108 [5]
$\text{Mo}_2\text{Cl}_4(\text{tdpm})_2 \cdot 2\text{CH}_2\text{Cl}_2$	20	2.60 [3]	2.398 [8]	96.9 [4]	109 [3]
β - $\text{Mo}_2\text{Br}_4(\text{S,S-dppb})_2$	21.7	2.593 [6]	2.537 [3]	104.2 [2]	108.8 [2]
β - $\text{Mo}_2\text{Cl}_4(\text{S,S-dppb})_2 \cdot \text{THF}$	24.6	2.573 [4]	2.393 [4]	103.8 [8]	107.4 [5]
β - $\text{Mo}_2\text{Br}_4(\text{arphos})_2$	30.3	<i>a</i>	2.51 [2]	96.3 [2]	113.9 [7]
β - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$	30.5	2.579 [9]	2.386 [11]	97.1 [4]	112.3 [7]
β' - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$	33.8	2.522 (3)	2.387 (2)	96.88 (8)	111.09 (7)
β - $\text{Mo}_2\text{Br}_4(\text{dmpe})_2$	36.5	2.541 [3]	2.547 [3]	101.4 [3]	108.6 [3]
β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$	40.0	2.526 [12]	2.402 [5]	98.4 [2]	111.2 [9]

^aSince this compound contains disordered arsenic and phosphorus atoms, the average Mo-P/As distance is not included.

Me_2P -containing complexes form a separate group. The overall average Mo-P distances are 2.589 [6] and 2.530 [6] Å in the Ph_2P and Me_2P cases, respectively. The difference of 0.059 (9) Å can be attributed to the electron-donating nature of the methyl groups as against the electron-withdrawing nature of the phenyl groups. The Mo-P bonds are all primarily P→Mo σ donor bonds and are therefore stronger for the Me_2P ligands. Increased donation of electron density from the ligands to the metal atoms undoubtedly strengthens the Mo-Mo bonding in the dmpe complexes, but an a priori estimate of this effect does not seem possible. Therefore, an empirical approach has been adopted.

We have prepared the triply bonded β - $\text{Re}_2\text{Cl}_4(\text{depe})_2$ for the purpose of calibrating empirically the effect of changing Ph_2P to (alkyl) $_2\text{P}$ on the metal-metal bond length. This molecule has an essentially staggered structure ($\chi = 43.7^\circ$) and a Re-Re bond length of 2.211 (1) Å. These features may be compared to the corresponding ones in $\text{Re}_2\text{Cl}_4(\text{dppe})_2$ ¹⁰ in which we have $\chi = 34.0^\circ$ and a Re-Re distance of 2.244 (1) Å. Each of these dirhenium compounds has a triple bond based on the $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration (i.e., a net of one σ and two π bonds). In these cases no barrier to rotation is imposed and bond strength should be independent of the angle of rotation. Thus, the difference of 0.033 (2) Å in the Re-Re bond lengths should be due essentially to the different properties (steric and electronic) of the depe and dppe ligands.

We now make the reasonable assumption that both σ and π bonding in analogous β - $\text{Re}_2\text{X}_4(\text{PP})_2$ and β - $\text{Mo}_2\text{X}_4(\text{PP})_2$ molecules are sufficiently similar that the results for the triply bonded dirhenium complexes may provide guidance in the interpretation of the results obtained for the quadruply bonded dimolybdenum complexes. Assuming further that ethyl and methyl groups have similar electron-donating properties and that the change in Re-Re bond distance is due to the changes in ligand basicity and steric repulsion, the plot of Mo-Mo bond length vs. $\cos 2\chi$ has been redrawn with an increase of 0.030 Å in the Mo-Mo bond distances for the dmpe complexes (H, I, and J) as well as for the new depe β - $\text{Mo}_2\text{X}_4(\text{PP})_2$ complex (K). The result is illustrated in Figure 6. The new least-squares line has a correlation coefficient (-0.9547) that is statistically far superior to that of the previous line. This new line yields values of 2.128 and 2.225 Å for $\chi = 0$ and 45° , respectively. The overall change in Mo-Mo distance upon loss of δ bonding becomes 0.097 Å.

Since the halide ligand is also varied in the series of $\text{Mo}_2\text{X}_4(\text{PP})_2$, another possible source of error in this study is different effects between Cl and Br. However, a change from X = Cl to X = Br has little effect on the metal-metal bond length; for the $\text{Mo}_2\text{X}_4(\text{dppm})_2$ and $\text{Mo}_2\text{X}_4(\text{S,S-dppb})_2$ complexes, the chloro and bromo analogues have exactly the same Mo-Mo distances. This is in line with previous comparisons,¹¹ namely between $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2\text{Br}_8^{4-}$ ions, where distances were 2.134 (2)-2.150 (5) Å for the former and 2.135 (2) Å for the latter, and between the two $\text{Mo}_2\text{X}_4(\text{pic})_4$ compounds (pic = picoline), in which the Mo-Mo distances are 2.153 (6) and 2.150 (2) Å for X = Cl and Br, respectively. In the three $\text{Mo}_2\text{X}_4(\text{dmpe})_2$ structures a comparison between X = Cl and X = Br is complicated by significant changes in the torsion angles yet the observed Mo-Mo distances appear to be in accord with each other. On the other hand, β - Mo_2Br_4 -

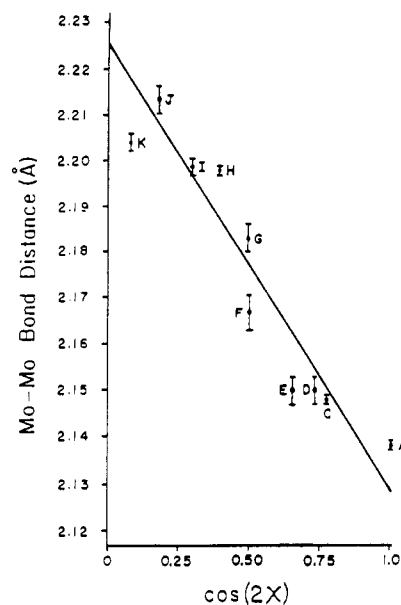


Figure 6. Plot of corrected Mo-Mo distances vs. $\cos 2\chi$. The corrections are explained in the text. Compounds are identified by the same capital letters as in Figure 1b. $\text{Mo}_2\text{Cl}_4(\text{depe})_2$ is point K.

(arphos) $_2$ and β - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ have quite different Mo-Mo bond lengths even though the arphos and dppe ligands are very similar. No reason for this is apparent other than the presence of disorder, which introduces imprecision in the determination of the metal-metal distances.

Crystallographic disorder of the Mo_2^{4+} core (the presence of a second, minor Mo-Mo unit perpendicular to the main one) was observed in β - $\text{Mo}_2\text{Br}_4(\text{arphos})_2$ and β - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, as well as in both forms of β - $\text{Mo}_2\text{Cl}_4(\text{dmpe})_2$. A different type of disorder was seen in the structure of β - $\text{Mo}_2\text{Cl}_4(\text{depe})_2$ (I). Not surprisingly, these five disordered complexes appear to have the worst fit to the line in Figure 6. However, it is generally accepted that a difference between two crystallographically determined bond distances is not significant at a level of 95% certainty unless it is greater than 3 times the sum of the estimated standard deviations (esd's) associated with each distance. In this light, the Mo-Mo bond lengths in the arphos and dppe complexes are in agreement within experimental error.

One final factor that might be considered a source of error is different intermolecular packing forces within the crystals. The previous discussion concerning the similarity of Mo-Mo-L angles and Mo-X distances should apply equally well in this case, suggesting that the impact of such forces is negligible. In this regard, the recent structural characterization¹² of a second form of β - $\text{Mo}_2\text{Cl}_4(\text{S,S-dppb})_2$ is especially important. The complex of this type used in the plots of Mo-Mo distance vs. $\cos 2\chi$ is the THF solvate, while this new compound is the tetrakis(acetonitrile)

(12) Agaskar, P.; Cotton, F. A.; Fraser, I. F.; Peacock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1851.

solvate. Mo-Mo bond lengths and average torsional angles in these two species are 2.150 (3) Å and 24.6 [5]° for the THF solvate and 2.143 (2) Å and 22.9 [3]° for the CH₃CN solvate. Since no significant change in Mo-Mo distance (0.007 ± 0.005 Å) or χ (1.7 ± 8°) is observed, the differences in packing forces between one THF molecule and four CH₃CN molecules per dimer have essentially no effect on the structural parameters of interest.

Since the assumptions and approximations made in this study have been discussed in detail, some internal consistencies are deserving of brief mention. The fact that the small increases in the Mo-Mo bond distances in β -Mo₂Cl₄(dmpe)₂, β -Mo₂Br₄(dmpe)₂, and β' -Mo₂Cl₄(dmpe)₂ all correlate with the small increases in χ is excellent support for a monotonic relationship between these two variables. The behavior of these three compounds is particularly important because the ligand dmpe is the same in all three. It is also satisfying that the observed differences in χ between analogous molybdenum and rhenium dimers may be explained by different bond multiplicities. In the M₂Cl₄(dppe)₂ case, χ = 34.0 [6]° for M = Re and 30.5 [5]° for M = Mo. The difference of 3.5° results from the absence of δ bonding (i.e., an absence of resistance to rotation) in the rhenium complex and the presence of ca. half of a δ bond in the molybdenum complex. In the Re dimer, the amount of staggering is determined entirely by the conformational preferences of the bridging moiety, while

in the Mo dimer, δ bonding resists the preferences of the PP ligands. For the M₂Cl₄(depe)₂ case, the difference in χ is smaller: 43.7 (4)° with M = Re and 42.7 (4)° with M = Mo. This is the predicted result since now the bond order of the Mo complex is ca. 3.1 or almost the same as the Re complex.

The new value, 0.097 Å, for the change in Mo-Mo bond length upon total loss of δ bonding (but without any change in atomic charges) is more consistent with other information than was the previous estimate (from Figure 1b) of ca. 0.06 Å. The best independent indications of the distance change for Mo-Mo bonds are obtained from the Franck-Condon factors in the vibrational progressions for $\delta \rightarrow \delta^*$ transitions in Mo₂(O₂CCH₃)₄ and Mo₂Cl₆⁴⁻. In both cases¹³ the result is 0.11 ± 0.01 Å.

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Registry No. 1, 99033-20-2; 2, 99033-21-3; K₄Mo₂Cl₈, 25448-39-9; (*n*-Bu₄N)₂Re₂Cl₈, 14023-10-0; Mo, 7439-98-7; Re, 7440-15-5.

Supplementary Material Available: Tables of structure factors and displacement vibration parameters and complete lists of bond lengths and angles for both compounds (14 pages). Ordering information is given on any current masthead page.

(13) Cotton, F. A. *Chem. Soc. Rev.* 1983, 12, 35.

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Vanadium(II) and Niobium(III) Edge-Sharing Bioctahedral Complexes That Contain Bis(dimethylphosphino)methane Bridges

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Two compounds, each containing bis(dimethylphosphino)methane (dmpm) bridges, have been prepared from [V₂(μ -Cl)₃(THF)₆]₂[Zn₂Cl₆] and Nb₂(μ -Cl)₂(μ -THT)Cl₄(THT)₂, respectively, and characterized completely via single-crystal X-ray studies. The vanadium compound, [VCl(dmpm)BH₄]₂ (1), is dinuclear and adopts an edge-sharing bioctahedral structure with two bridging dmpm units, two bridging chlorine atoms, and two borohydride ligands occupying axial V-V positions. The V-V distance of 3.124 (2) Å suggests that little, if any, direct metal-metal bonding occurs between the two vanadium atoms. This compound crystallizes in space group *Pbca* with the following unit cell dimensions: *a* = 12.395 (3) Å, *b* = 14.163 (3) Å, *c* = 13.858 (4) Å, *V* = 2433 (2) Å³, *Z* = 4. The niobium complex, Nb₂Cl₆(dmpm)₂ (2), also consists of two octahedra sharing an edge, with two dmpm bridges, two bridging chlorine atoms, and four terminal chlorine ligands. The Nb-Nb distance equals 2.711 (3) Å, which is consistent with a $\sigma^2\pi^2$ double bond between the two niobium atoms. For 2, crystallographic data are as follows: *P*2₁/*n*, *a* = 7.214 (3) Å, *b* = 15.468 (7) Å, *c* = 10.828 (5) Å, β = 93.6 (4)°, *V* = 1205 (2) Å³, *Z* = 2. An explanation for the different structures of the Nb₂Cl₆(dmpm)₂ and Nb₂Cl₆(dppm)₂ molecules based on a proposed mechanism of formation and solubility differences is offered.

Introduction

The ability of bis(diphenylphosphino)methane (dppm) to bridge dimeric complexes has led to its wide use in systems where a close approach of two metal atoms or retention of such unit in a reaction is desired, although it displays a number of other modes of interaction.¹ Several complexes of dppm of interest in the area of compounds with metal-metal bonds have been investigated in this laboratory.²⁻⁵ We have recently reported the synthesis and molecular structure of such complexes with group 5¹⁷ transition metals, viz. [VCl(dppm)BH₄]₂⁴ and Nb₂Cl₆(dppm)₂,⁵ both of which turned out to have structures different from those expected when their preparation was undertaken. In the former, even though the dppm molecules are bridging, no metal-metal bond between vanadium atoms was present in spite of their close proximity and seemingly favorable d³-d³ configuration. The niobium dimer contained dppm coordinating in a chelating mode, which is unusual for this ligand in dinuclear complexes. One factor

that might have been responsible for the isolation of this product was insolubility of the chelate compound relative to the desired bridged isomer. The homologue of dppm bis(dimethylphosphino)methane (dmpm) was then used in the hope that, for steric or solubility reasons, the desired bridged structure might be obtained. In this we were successful, and the first unequivocally characterized dinuclear complex of niobium or tantalum in oxidation state +3 spanned by two bidentate ligands has been obtained. To compare directly the bonding in the two diphosphinomethane derivatives, [VCl(dmpm)BH₄]₂ was also prepared and its structure is reported here.

Experimental Section

All operations were performed under an atmosphere of argon, with use of standard Schlenk techniques and a double-manifold vacuum line. Solvents were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulas and/or syringes. [V₂Cl₃(THF)₆]₂[Zn₂Cl₆]⁶ and Nb₂Cl₆(THT)₃⁷ (THT = tetrahydrothiophene) were prepared according to the literature methods. Bis(di-

(1) Puddephat, R. J. *Chem. Soc. Rev.* 1983, 99.
 (2) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
 (3) Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetric, S. M.; Walton, R. A. *J. Am. Chem. Soc.* 1984, 106, 2882.
 (4) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* 1984, 23, 4113.
 (5) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* 1983, 22, 3654.

(6) (a) Hall, V.; Schmulbach, C. D.; Soby, W. J. *Organomet. Chem.* 1981, 209, 69. (b) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. J. *Chem. Soc., Chem. Commun.* 1983, 1377. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* 1985, 24, 913.
 (7) The procedure for preparation of Nb₂Cl₆(THT)₃ has been adapted from: Templeton, J. L.; McCarley, R. E. *Inorg. Chem.* 1978, 17, 2293.