

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Kalamazoo College, Kalamazoo, Michigan 49007

Reaction Products of 1,2-Bis(diphenylphosphino)ethane with the Octabromodimolybdate(II) Ion

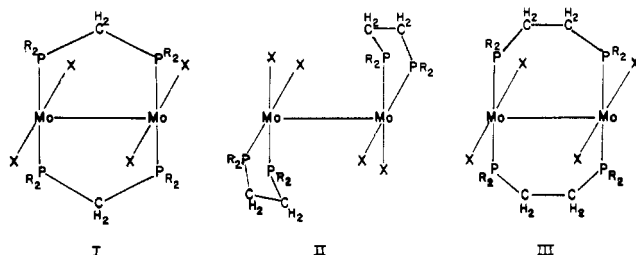
PRADYOT A. AGASKAR,^{1a} F. ALBERT COTTON,*^{1a} DANIEL R. DERRINGER,^{1b} GREGORY L. POWELL,^{1a} DAWN R. ROOT,^{1b} and THOMAS J. SMITH*^{1b}

Received November 9, 1984

Reactions of $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ with dppe ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) in alcohols yield three products, with the proportions depending on conditions: **1**, green $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$; **2**, red-brown $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$; **3**, light-brown *trans*- $\text{MoBr}_2(\text{dppe})_2$. All three solids are stable in air and soluble in dichloromethane. By the reactions just mentioned, **1** and **2** are both obtained as microcrystalline products. By reaction of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ with $(\text{CH}_3)_3\text{SiBr}$ and dppe, **2** was obtained in the form of larger crystals, but these were not of good quality and only a coarse crystallographic structure determination was made: space group $P2_1/n$, with unit cell dimensions of $a = 23.35 \text{ \AA}$, $b = 13.29 \text{ \AA}$, $c = 16.91 \text{ \AA}$, and $\beta = 106.82^\circ$, which indicate isomorphism with $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$. Compound **3** afforded good crystals directly from the reaction mixture. These are triclinic, space group $P\bar{1}$, with unit cell dimensions of $a = 10.493 (2) \text{ \AA}$, $b = 12.773 (3) \text{ \AA}$, $c = 10.331 (2) \text{ \AA}$, $\alpha = 94.78 (2)^\circ$, $\beta = 117.39 (2)^\circ$, $\gamma = 104.64 (2)^\circ$, $V = 1157 (1) \text{ \AA}^3$ and $Z = 1$. The *trans*- $\text{MoBr}_2(\text{dppe})_2$ molecule, which has a magnetic moment indicating two unpaired electrons, has inversion symmetry with $\text{Mo-Br} = 2.569 (1) \text{ \AA}$, $\text{Mo-P} = 2.516 (1)$ and $2.523 (1) \text{ \AA}$, and endocyclic P-M-P angles of $78.81 (4)^\circ$. Infrared and UV-visible spectra are reported for all compounds. The process of isomerization of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ to $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ has been studied, and a unimolecular mechanism involving internal rotation of the Mo_2 unit within the ligand cage is suggested.

Introduction

Since the first report of the preparation of $\text{Mo}_2\text{X}_4(\text{dppe})_2$ compounds by Best, Smith, and Walton,² compounds of this general type have been extensively studied³⁻⁹ to determine the interrelationship of their structural, spectroscopic, and chemical properties as well as the connections between all of these properties and the nature of the multiple Mo-Mo bonding. When the diphosphine is dpmm ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$) or another having only one carbon atom linking the phosphorus atoms, only bridged species (I) have been observed in which there are essentially eclipsed



conformations about the Mo-Mo bond.^{3,7} With other, more flexible, bis(phosphines) it is generally found that two isomers can be obtained. One, often designated α , has two chelating diphosphines (II), while the other, often designated β , has bridging diphosphines (III). Structures of type II have essentially eclipsed conformations, but those of type III display a variety of angles of internal rotation. Structures of these types have also been established for compounds of tungsten¹⁰ and rhenium.¹⁰

In the studies just cited, the halogen ligand has usually been chloride. To see whether the different steric and electronic properties of the bromide ligand would exert a significant influence on the properties of these systems, we undertook studies of reactions that were expected to give $\text{Mo}_2\text{Br}_4(\text{dppe})_2$ in one or both

of its isomeric forms. In addition to isolating these expected products, we also found that the mononuclear compound $\text{MoBr}_2(\text{dppe})_2$ can be formed when dppe reacts with the $[\text{Mo}_2\text{Br}_8]^{4-}$ ion, although no comparable reaction has been noted in the case of the chloro compounds.

Experimental Procedures

General Considerations. Literature procedures were used to prepare $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ ¹¹ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$.¹² All other reagents and solvents were obtained from commercial sources. All reactions were carried out under nitrogen atmospheres. Solvents were deoxygenated by bubbling nitrogen gas through them for 15-30 min. In reactions with $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ a wood boiling stick was placed in the flask to facilitate boiling and crystal growth. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Reactions of $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$. A. Reactions in Methanol. 1. dppe/Dimolybdenum, Mole Ratio of 2:1. Methanol (20 mL) was deoxygenated and added to $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ (0.102 g, 0.113 mmol) and dppe (0.088 g, 0.222 mmol). Within 5 min of refluxing, the initially purple suspension had turned light blue-green. After 3 h of refluxing, the mixture was cooled to room temperature and filtered, and the green microcrystalline product was washed with water, ethanol, and diethyl ether and dried under vacuum; yield 65%. Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{P}_2\text{Mo}$ ($[\text{MoBr}_2(\text{dppe})_2$]): C, 47.73; H, 3.70; Mo, 14.67. Found: C, 47.93; H, 3.85; Mo, 13.64. This product is designated $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$. On one occasion we isolated a sample of *trans*- $\text{MoBr}_2(\text{dppe})_2$.

2. Mole Ratio of 10:1. A similar procedure was employed with a 10-fold excess of dppe. After a 24-h reflux, $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ and crystals of dppe (on the boiling stick) were recovered. The green product was washed with water, ethanol, toluene, ethanol, and diethyl ether and vacuum-dried; yield 49%.

B. Reactions in Ethanol. 1. 2:1 Mole Ratio (Short Reaction Time). A 30-min reflux of $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ (0.098 g, 0.108 mmol) and dppe (0.097 g, 0.243 mmol) in ethanol (20 mL) produced $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$, yield 83%.

2. 2:1 Mole Ratio (Long Reaction Time). A mixture of $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ (0.099 g, 0.109 mmol) and dppe (0.086 g, 0.215 mmol) in ethanol (20 mL) was refluxed for 4 days, during which time a red-brown suspension was produced. The microcrystalline solid was isolated and washed with water, ethanol, and diethyl ether and dried. The bulk of this was a red-brown powder (hereafter known as $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$) while a small amount of green contaminant was evident; yield 49%. Also a small quantity of honey brown crystals, shown by X-ray crystallography to be *trans*- $\text{MoBr}_2(\text{dppe})_2$ (vide infra), was reproducibly recovered from the boiling stick; yield 7%.

3. Mole Ratio of 10:1. By a similar procedure (3-day reflux) three products were also obtained with a 10-fold excess of dppe. The bulk materials (powder) consisted of the β phase as the major product and the

- (1) (a) Texas A&M University. (b) Kalamazoo College.
- (2) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.
- (3) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240.
- (4) Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 1752.
- (5) Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 1507.
- (6) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* **1984**, *23*, 3883.
- (7) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, *23*, 4222.
- (8) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.
- (9) Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Peacock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 1851.
- (10) For complete references, see: Cole, N. F.; Cotton, F. A.; Powell, G. L.; Smith, T. J. *Inorg. Chem.* **1983**, *22*, 2618.

- (11) Brencic, J. D.; Leban, I.; Segedin, P. Z. *Angew. Chem.* **1976**, *427*, 85.
- (12) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.

α phase present in considerably smaller amount; yield 56%. The mononuclear species again appeared as a small number of crystals; yield 10%.

C. Reactions in 1-Propanol. 1. Mole Ratio of 2:1 (Short Reaction Time). A mixture of $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ (0.075 g, 0.083 mmol) and dppe (0.068 g, 0.171 mmol) in 1-propanol (20 mL) was gently warmed for 30 min, resulting in a green suspension. The green product was isolated, washed with water, ethanol, and diethyl ether, and dried. Microscopic examination revealed that the product contained a small amount of a red-brown contaminant, presumably the β form; yield 58%.

2. Mole Ratio of 2:1 (Long Reaction Time). A 4-day reflux reaction of $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$ (0.052 g, 0.057 mmol) and dppe (0.052 g, 0.131 mmol) in 1-propanol (20 mL) yielded a red-brown suspension from which a powder of the same color was isolated. This material appeared to be a pure sample of $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$, yield 55%. Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{Mo}_2$ ($[\text{MoBr}_2(\text{dppe})_n$): C, 47.73; H, 3.70; Mo, 14.67. Found: C, 46.81; H, 3.55; Mo, 14.30. Crystals of *trans*- $\text{MoBr}_2(\text{dppe})_2$ were also recovered from this reaction.

3. Mole Ratio of 10:1. A similar procedure was followed (5-day reflux) to afford a mixture of β (major product) and α (minor).

D. Conversion Reactions. 1. $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ in Methanol and 1-Propanol. A sample of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ was refluxed in methanol for 4 days; the unreacted complex was recovered upon cooling. In contrast a similar reaction in 1-propanol resulted in complete conversion to $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ in 6 h.

2. $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ and Excess dppe. Reaction of 1 mol of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ and 2 and 10 mol of dppe in ethanol for 3 days and 1 day, respectively, led to incomplete conversion to the β isomer.

Reactions of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$. A. Preparation of $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ in Bulk. $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 0.080 g, was dissolved in 10 mL of THF and a large excess, 0.250 g, of $(\text{CH}_3)_3\text{SiBr}$ was added dropwise. After about 12 h, during which stirring was continued, the solution had become deep orange. The dppe, 0.100 g, was then added, and a brown precipitate was formed. This precipitate was separated by filtration and shown to be $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ by its UV-visible spectrum, recorded in a mineral oil mull: maxima at ca. 800, 470, and 365 nm. The very pale filtrate had a similar spectrum. The yield of solid microcrystalline product was >95%.

B. Preparation of Crystalline $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$. $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 0.080 g, was dissolved in a mixture of 2 mL of THF and 8 mL of toluene, in a tube about 20 mm in diameter. The dppe, 0.100 g, was added to it, and the resulting yellow solution was covered with a layer of 5 mL of toluene. A layer of 1:4 hexane/toluene containing 0.15 g of $(\text{CH}_3)_3\text{SiBr}$ was placed over this, and the Schlenk tube was set aside so that interdiffusion could occur. Within 3 days brown crystals of $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ and some green powder (presumed to be the α isomer) were formed.

The brown crystals were examined on a diffractometer. The space group, $P2_1/n$, and unit cell dimensions, $a = 23.35 \text{ \AA}$, $b = 13.29 \text{ \AA}$, $c = 16.91 \text{ \AA}$, and $\beta = 106.82^\circ$, show that they are isomorphous with those of $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$.⁶ A complete set of data was collected, and refinement of the structure was begun. There appeared to be a considerably greater degree of disorder than in the case of the chloro compound, and the unweighted R factor could not be brought below 18.7%. Further attempts to obtain better crystals are being made. The present work, however, quite conclusively identifies the compound as the bridged (β) isomer of $\text{Mo}_2\text{Br}_4(\text{dppe})_2$.

X-ray Crystallography of $\text{MoBr}_2(\text{dppe})_2$. An orange, plate-shaped crystal was coated with epoxy cement and mounted on the end of a glass fiber with the longest dimension of the crystal approximately vertical. Data collection was carried out at room temperature on a CAD-4 diffractometer at the Molecular Structure Corp., College Station, TX. Pertinent crystallographic parameters are summarized in Table I. The $2\theta\text{-}\omega$ scan technique was used, and the scan range in ω was calculated as $(0.70 + 0.35 \tan \theta)^\circ$ with a 25% extension on either end for background determination. Three standard reflections displayed no significant variation in intensity during the 27.1 h of X-ray exposure time. Lorentz and polarization corrections¹³ were applied to the data, as was an empirical absorption correction¹⁴ based on azimuthal scans of six reflections with χ near 90° .

The structure was solved and refined in space group $P\bar{1}$. The positions of the Mo and Br atoms were determined from a three-dimensional Patterson map. The remaining atoms were located through an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were isotropically refined. Convergence of full-matrix least-

Table I. Summary of Crystal Data and Data Collection Parameters for $\text{MoBr}_2(\text{dppe})_2$

formula	$\text{MoBr}_2[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$
fw	1052.6
space group	$P\bar{1}$
a , Å	10.493 (2)
b , Å	12.773 (3)
c , Å	10.331 (2)
α , deg	94.78 (2)
β , deg	117.39 (2)
γ , deg	104.64 (2)
V , Å^3	1157 (1)
Z	1
d_{calcd} , g/cm^3	1.511
cryst size, mm	$0.08 \times 0.15 \times 0.25$
$\mu(\text{Mo K}\alpha)$, cm^{-1}	21.57
data collection instrument	Enraf-Nonius CAD-4
radiation	Mo K α (graphite monochromated), $\lambda = 0.71073 \text{ \AA}$
scan method	$2\theta\text{-}\omega$
data collection range, deg	$0 \leq 2\theta \leq 45$
no. of unique data, $F_o^2 \geq 3\sigma(F_o^2)$	2246
no. of params refined	364
R^a	0.0325
R_w^b	0.0396
quality-of-fit indicator ^c	1.1162
largest shift/esd, final cycle	0.14

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

squares refinement gave residuals of $R = 0.0325$ and $R_w = 0.0396$. The highest peak in the final difference Fourier map had a density of 0.67 e/\AA^3 . Final atomic coordinates and thermal parameters are listed in Table II. Important bond distances and angles are given in Table III.

Complete tables of anisotropic thermal parameters, all bond distances and angles, and structure factors appear as supplementary material.

Physical Measurements. Infrared spectra were recorded on a Pye Unicam SP3-300 infrared spectrophotometer by use of mineral oil mulls supported on KBr plates ($4000\text{--}400 \text{ cm}^{-1}$) and polyethylene disks ($400\text{--}200 \text{ cm}^{-1}$). Electronic absorption spectra were obtained with Perkin-Elmer Model 559 and Perkin-Elmer Lambda 3E UV-visible spectrophotometers, with solid-state spectra recorded as mulls on filter paper and solution spectra recorded with spectroscopic-grade dichloromethane in 1-cm quartz cells. Magnetic measurements were done on a Cahn/Ventron Faraday magnetic susceptibility balance utilizing Hg-Co(NCS)₂ as a calibrant. Pascal's constants were used to make diamagnetic corrections. In studies of the isomerization reaction, the plot of the natural logarithm of concentration vs. time was generated by using the statistical software package MINITAB (copyright Pennsylvania State University). The slope was taken from the line resulting from a simple linear-regression analysis.

Results and Discussion

Preparation and Characterization of $\text{Mo}_2\text{Br}_4(\text{dppe})_2$ Isomers. The reaction of tetraammonium octabromodimolybdate(II) and 1,2-bis(diphenylphosphino)ethane (dppe) in alcohol solvents yields three distinct products, the distribution of which is dependent upon preparative conditions. Reactions in methanol or short reaction times in ethanol or 1-propanol produce a green powder, $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$, while longer reactions in the latter solvents give a red-brown microcrystalline material, $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$. Extended reactions also afford crystals of orange-brown *trans*- $\text{MoBr}_2(\text{dppe})_2$ (to be discussed below) in low yield. All three compounds appear to be air stable in the solid state and exhibit fair solubility in dichloromethane. Representative results of physical measurements for these complexes are presented in Table V.

The isomeric dinuclear products, $\text{Mo}_2\text{Br}_4(\text{dppe})_2$, would naturally be presumed to be analogous to the α and β isomers previously reported for $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ and obtained by reactions of dppe with $\text{K}_4\text{Mo}_2\text{Cl}_8$ or $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$.² In the case of related tungsten compounds,¹⁵ the conclusive assignment of structures

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

(14) Computing was done on the Chemistry Department's VAX/VMS computer at Texas A&M.

(15) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 3880.

Table II. Positional Parameters and Isotropic-Equivalent Thermal Parameters for $\text{MoBr}_2(\text{dppe})_2$ ^a

atom	x	y	z	B, Å ²
Mo	0.000	0.000	0.000	1.89 (1)
Br	-0.17333 (5)	0.00041 (4)	0.11262 (5)	3.23 (1)
P(1)	0.1138 (1)	-0.1083 (1)	0.1920 (1)	2.26 (3)
P(2)	0.1926 (1)	0.1554 (1)	0.2268 (1)	2.11 (3)
C(1)	0.2392 (5)	-0.0113 (4)	0.3810 (5)	2.8 (1)
C(2)	0.2077 (5)	0.0975 (4)	0.3891 (5)	2.5 (1)
C(11)	0.2515 (5)	-0.1739 (4)	0.1896 (5)	2.6 (1)
C(12)	0.3767 (5)	-0.1067 (5)	0.1880 (6)	3.6 (1)
C(13)	0.4888 (5)	-0.1486 (6)	0.1941 (6)	4.7 (2)
C(14)	0.4745 (6)	-0.2572 (5)	0.1986 (6)	5.4 (2)
C(15)	0.3511 (6)	-0.3255 (5)	0.1983 (6)	4.6 (2)
C(16)	0.2388 (5)	-0.2846 (4)	0.1923 (5)	3.4 (1)
C(21)	-0.0175 (4)	-0.2181 (4)	0.2181 (5)	2.3 (1)
C(22)	-0.1111 (5)	-0.3135 (4)	0.1048 (5)	3.2 (1)
C(23)	-0.2085 (6)	-0.3996 (4)	0.1217 (6)	4.0 (2)
C(24)	-0.2176 (5)	-0.3920 (4)	0.2501 (6)	4.0 (1)
C(25)	-0.1291 (5)	-0.2991 (5)	0.3615 (6)	4.1 (1)
C(26)	-0.0316 (5)	-0.2111 (4)	0.3464 (5)	3.1 (1)
C(31)	0.3905 (4)	0.2032 (4)	0.2668 (5)	2.2 (1)
C(32)	0.5130 (5)	0.2051 (4)	0.4020 (5)	2.7 (1)
C(33)	0.6591 (5)	0.2369 (4)	0.4238 (6)	3.4 (1)
C(34)	0.6852 (5)	0.2680 (5)	0.3134 (6)	4.4 (2)
C(35)	0.5661 (6)	0.2695 (6)	0.1799 (6)	4.8 (2)
C(36)	0.4196 (5)	0.2365 (5)	0.1556 (5)	3.5 (1)
C(41)	0.1652 (5)	0.2869 (4)	0.2739 (5)	2.3 (1)
C(42)	0.0211 (5)	0.2969 (4)	0.2014 (5)	2.9 (1)
C(43)	-0.0010 (5)	0.3945 (4)	0.2383 (5)	3.5 (1)
C(44)	0.1149 (5)	0.4812 (4)	0.3495 (6)	3.6 (1)
C(45)	0.2598 (6)	0.4745 (4)	0.4248 (6)	4.0 (1)
C(46)	0.2833 (5)	0.3770 (4)	0.3863 (6)	3.3 (1)
H(1)	0.339 (4)	0.000 (3)	0.396 (4)	3 (1)*
H(2)	0.243 (4)	-0.044 (3)	0.460 (4)	3 (1)*
H(3)	0.280 (4)	0.150 (3)	0.479 (4)	2.0 (9)*
H(4)	0.116 (4)	0.090 (3)	0.391 (4)	1.4 (8)*
H(12)	0.391 (4)	-0.036 (3)	0.188 (4)	3 (1)*
H(13)	0.559 (4)	-0.100 (3)	0.187 (4)	3 (1)*
H(14)	0.537 (5)	-0.293 (4)	0.193 (6)	6 (1)*
H(15)	0.337 (6)	-0.402 (5)	0.202 (6)	7 (2)*
H(16)	0.159 (4)	-0.329 (4)	0.192 (5)	4 (1)*
H(22)	-0.104 (4)	-0.323 (3)	0.021 (4)	3 (1)*
H(23)	-0.264 (4)	-0.458 (3)	0.052 (4)	2.0 (9)*
H(24)	-0.280 (5)	-0.455 (4)	0.255 (5)	5 (1)*
H(25)	-0.138 (5)	-0.286 (4)	0.439 (5)	4 (1)*
H(26)	0.031 (4)	-0.147 (3)	0.423 (5)	3 (1)*
H(32)	0.503 (5)	0.187 (4)	0.481 (5)	4 (1)*
H(33)	0.718 (5)	0.236 (4)	0.501 (5)	6 (1)*
H(34)	0.758 (5)	0.273 (4)	0.319 (6)	6 (1)*
H(35)	0.579 (6)	0.292 (5)	0.102 (6)	7 (2)*
H(36)	0.327 (6)	0.215 (5)	0.047 (6)	7 (2)*
H(42)	-0.061 (4)	0.237 (3)	0.119 (4)	3 (1)*
H(43)	-0.087 (5)	0.408 (4)	0.204 (5)	4 (1)*
H(44)	0.104 (5)	0.545 (4)	0.381 (5)	4 (1)*
H(45)	0.331 (5)	0.526 (4)	0.511 (5)	5 (1)*
H(46)	0.372 (4)	0.368 (3)	0.429 (4)	2 (1)*

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

to the two isomers of $\text{W}_2\text{Cl}_4(\text{dppe})_2$ has been done by X-ray crystallography. Because of our interest in some of the structural details for β isomers we attempted to obtain a crystalline sample of brown $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ by a different preparative method, i.e., reaction of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ with $(\text{CH}_3)_3\text{SiBr}$ and dppe. This was only partially successful, giving crystals good enough to allow proof that $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ is isomorphous with $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ but not good enough to afford a complete and precise structure determination.

The infrared spectra of both green and brown $\text{Mo}_2\text{Br}_4(\text{dppe})_2$ show numerous bands indicative of the dppe ligands. The most significant differences between these spectra are in the region of C-H out-of-plane bending vibrations, 650–800 cm^{-1} . These vibrations are doubtless sensitive to the conformational differences due to the five- and six-membered rings and may also reflect

Table III. Important Bond Distances and Angles for $\text{MoBr}_2(\text{dppe})_2$

Distances (Å)			
Mo-Br	2.569 (1)	P(2)-C(2)	1.842 (5)
-P(1)	2.523 (1)	-C(31)	1.837 (5)
-P(2)	2.516 (1)	-C(41)	1.834 (5)
P(1)-C(1)	1.865 (5)	C(1)-C(2)	1.509 (7)
-C(11)	1.850 (5)		
-C(21)	1.833 (5)		
Angles (deg)			
Br-Mo-P(1)	84.32 (3)	C(11)-P(1)-C(21)	103.3 (2)
-P(2)	84.20 (3)	Mo-P(2)-C(2)	105.2 (2)
P(1)-Mo-P(2)	78.81 (4)	-C(31)	118.5 (2)
Mo-P(1)-C(1)	109.4 (2)	-C(41)	124.5 (2)
-C(11)	121.2 (2)	C(2)-P(2)-C(31)	102.9 (2)
-C(21)	117.5 (1)	-C(41)	100.4 (2)
C(1)-P(1)-C(11)	98.3 (2)	C(31)-P(2)-C(41)	102.0 (2)
-C(21)	104.3 (2)	P(1)-C(1)-C(2)	112.9 (4)

Table IV. Selected Bond Distances and Angles for Two Isoelectronic $\text{MoBr}_2(\text{dppe})_2$ Species

dist, Å, or angle, deg	$\text{MoBr}_2(\text{dppe})_2$	$[\text{TcBr}_2(\text{dppe})_2]^+$
M-Br	2.569 (1)	2.440 (1)
M-P	2.516 (1)	2.488 (1)
	2.523 (1)	2.513 (1)
Br-M-P	95.68 (3)	92.0 (1)
	95.80 (3)	94.0 (1)
P-M-P	78.81 (4)	80.8 (1)

differences in intermolecular forces in the crystals,¹⁶ since, unfortunately, they had to be recorded on mulls of these rather insoluble compounds. In the low-frequency infrared region, $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ displays a weak- to medium-intensity band at 263 cm^{-1} , which can be assigned to Mo-Br stretching. A comparison with the spectrum of $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$,² where there is a band due to Mo-Cl stretching at 340 cm^{-1} , yields a ratio of $\bar{\nu}(\text{Mo-Br})/\bar{\nu}(\text{Mo-Cl})$ of 0.73, which may be compared to the typical range¹⁷ of 0.74–0.77.

In the low-frequency infrared spectrum of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ a broad, weak band at 223 cm^{-1} seems likely to $\bar{\nu}(\text{Mo-Br})$, since it gives a $\bar{\nu}(\text{Mo-Br})/\bar{\nu}(\text{Mo-Cl})$ ratio of 0.73. The lower frequency, 223 vs. 263 cm^{-1} for the α isomer, is consistent with the expectation that since the Mo-Br bonds in the α isomer are trans to Mo-P they will be weaker than the Mo-Br bonds in the β isomer, which are trans to each other. In the case of the α and β isomers of $\text{W}_2\text{Cl}_4(\text{dppe})_2$ ¹⁵ the average W-Cl bond lengths are 2.372 (5) Å in the β isomer and 2.410 (4) Å in the α isomer. A comparable situation has been shown to exist in some similar $\text{Re}_2\text{Cl}_4\text{L}_4$ and $\text{Re}_2\text{Cl}_4(\text{LL})_2$ compounds.¹⁰

Both isomers of $\text{Mo}_2\text{Br}_4(\text{dppe})_2$ have been shown to be diamagnetic, with $\chi_g = -0.45 \times 10^{-6}$ and -0.28×10^{-6} cgsu for the α and β isomers, respectively.

In the visible region of their electronic spectra, both the α and β isomers display a prominent absorption band that we assign to the $\delta \rightarrow \delta^*$ transition. This band is substantially red shifted in $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ ($\lambda_{\text{max}} = 790$ nm in CH_2Cl_2) relative to the position for $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ ($\lambda_{\text{max}} = 687$ nm). A similar shift was seen² in the chloro analogues, i.e., 675 nm for α and 780 nm for β . This shift is to be expected since the α isomers are eclipsed whereas the β isomers have appreciable angles of twist, which weaken the δ bonds.¹⁸

The $\text{MoBr}_2(\text{dppe})_2$ Molecule. Figure 1 illustrates the complete molecular geometry and atom-labeling scheme for the non-hydrogen atoms of $\text{MoBr}_2(\text{dppe})_2$. The molecule resides on a center of inversion, and the coordination environment of the Mo atom is approximately octahedral, with the four phosphorus atoms

(16) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrophotometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; p 111.

(17) Clark, R. J. H.; Williams, C. S. *Inorg. Chem.* **1965**, *4*, 350.

(18) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.

Table V. Spectroscopic Properties of Molybdenum(II) Complexes^a

complex	IR spectra, 400–200 cm^{-1} ^b	electronic abs spectra, nm^c (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	
		solid state	soln (CH_2Cl_2)
$\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$	328 w, 268 w, sh, <u>259</u> w-m, 242 w, sh, <u>223</u> w, bd, 213 w, bd	685 s, 490 m, 410 s, sh, 379 s	~ 785 sh, ^d 687 (2180); 480 m (1060), 373 vs (5330)
$\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$	362 w, 342 w, <u>263</u> m, 248 w, sh, 242 w, sh	858 s, 820 s, sh, 700 vw, 580 m, 528 m, sh, 492 s, 392 s, sh, 375 s	790 s (1960), 636 w (780), 477 s (1480), 368 vs (5490)
<i>trans</i> - $\text{MoBr}_2(\text{dppe})_2$	376 w, 354 w, 304 w, 290 w, sh, <u>281</u> w-m, 247 w	430 s, sh, 368 s	360 vs (10030)

^a All solid-state spectra recorded as mulls. ^b $\pm 1 \text{ cm}^{-1}$; principal $\nu(\text{Mo}-\text{Br})$ underlined. ^c $\pm 2 \text{ nm}$. ^d β isomer.

Table VI. Crystal Structures of Compounds of the Type $\beta\text{-Mo}_2\text{X}_4(\text{PP})_2$ ^a

X	PP	M-M, Å	Mo-X, ^b Å	Mo-P, ^b Å	ref
Cl	$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ ^c	2.183 (3)	2.385 (7)	2.579 (8)	6
Cl	$(\text{C}_6\text{H}_5)_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{P}(\text{C}_6\text{H}_5)_2$	2.147 (3)	2.400 (8)	2.566 (8)	30
Cl	$(\text{C}_6\text{H}_5)_2\text{PCH}(\text{CH}_2)_3\text{CHP}(\text{C}_6\text{H}_5)_2$	2.159 (2)	2.399 (3)	2.574 (4)	30
Cl	$(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ ^c	2.183 (3)	2.402 (5)	2.526 (5)	5
Cl	$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2$	2.138 (1)	2.394 (1)	2.584 (1)	3
Br	$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ ^c	2.177 (8)	2.512 (8)	2.624 (14)	30
Br	$(\text{C}_6\text{H}_5)_2\text{PCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{P}(\text{C}_6\text{H}_5)_2$	2.147 (6)	2.538 (8)	2.594 (15)	30
Br	$(\text{C}_6\text{H}_5)_2\text{PCH}(\text{CH}_2)_3\text{CHP}(\text{C}_6\text{H}_5)_2$	2.155 (4)	2.541 (2)	2.586 (7)	30
Br	$(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ ^c	2.169 (2)	2.545 (2)	2.536 (5)	30
Br	$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2$	2.138 (1)	2.534 (1)	2.611 (2)	30

^a X = Cl, Br; PP = bridging bidentate diphosphine ligand. ^b Average of all crystallographically unique bonds. The highest esd in the set averaged is given in parentheses. ^c Bond lengths observed in the major orientation of the molecule.

occupying equatorial sites and the two trans bromine atoms occupying axial positions. The chelating dppe ligands define two envelope-type five-membered rings joined together by the Mo atom.

$\text{MoBr}_2(\text{dppe})_2$ is isostructural with the isoelectronic $[\text{TcBr}_2(\text{dppe})_2]^+$ cation recently characterized by Libson, Barnett, and Deutsch.¹⁹ A comparison of selected bond distances and angles in these two species is given in Table IV. The changes and relationships among these bond lengths might at first seem surprising, but they can easily be understood. There is a sharp decrease in the M-Br distance in going from Mo-Br to Tc-Br, which can be attributed to the greater electrostatic attraction of the formally 3+ ion for the Br⁻ ion. The decrease here, 0.129 (2) Å, is not matched in the M-P distances, however, which barely change, viz., 0.01–0.03 Å. This can be attributed to the facts that (a) the M-P bonds are less ionic than the M-Br bonds and hence less sensitive to the change in metal ion charge and (b) the Mo-P bonds probably have a significant M $d\pi \rightarrow \text{P } d\pi$ component that is largely lost when the charge on the metal ion increases. It is probably this π component in the Mo-P case that makes the Mo-P bond shorter than the Mo-Br bonds in $\text{MoBr}_2(\text{dppe})_2$.

The only previously reported analogues to $\text{MoBr}_2(\text{dppe})_2$ that we have found are the $\text{MoX}_2(\text{diars})_2$, X = Cl, Br, I, compounds described more than 20 years ago by Lewis, Nyholm, and Smith.²⁰ These compounds were shown to be paramagnetic with moments indicative of two unpaired electrons, and it was proposed that they have the trans structure, but there was no unequivocal proof of this.

Comparison of the Mo-Br and Mo-P bond lengths in $\text{MoBr}_2(\text{dppe})_2$ with those in binuclear, quadruply bonded compounds is also of interest. Structures are available for 10 such compounds, as listed in Table VI.

There is no significant variation in the Mo-Cl and Mo-Br distances in these compounds. The difference between the average Mo-Cl distance, 2.40 ± 0.01 Å, and the average Mo-Br distance, 2.54 ± 0.01 Å, is 0.14 ± 0.01 Å, which is about equal to the difference between the standard covalent radii of Br and Cl, 0.15 Å.

The Mo-Br distance of 2.569 (1) Å observed in $\text{MoBr}_2(\text{dppe})_2$ is not significantly different from the Mo-Br distance in the compounds listed in Table VI. This suggests that whatever in-

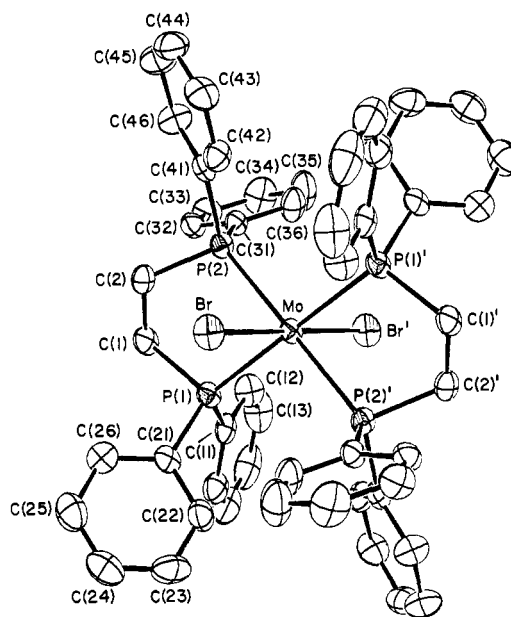


Figure 1. Molecular structure of *trans*- $\text{MoBr}_2(\text{dppe})_2$. Atoms are represented by their ellipsoids of thermal vibration at the 40% level, and the atom-labeling scheme is defined.

fluence the formation of the Mo-Mo bond has on the strength of the Mo-X bonds (e.g., because of an effect on π bonding) is slight.

The Mo-P bond lengths vary from 2.59 to 2.62 Å with a mean value of 2.60 Å in the compounds with bromo ligands on the molybdenum and phenyl substituents on the phosphorus. This is significantly greater than the mean value of 2.520 (2) Å in $\text{MoBr}_2(\text{dppe})_2$ and suggests that when the Mo atoms are engaged in the Mo-Mo π and δ bonds they have a diminished capacity to engage in Mo $d\pi \rightarrow \text{P } d\pi$ bonding.

The dominant band in the low-frequency region of the infrared spectrum of *trans*- $\text{MoBr}_2(\text{dppe})_2$ occurs at 281 cm^{-1} with a shoulder at 290 cm^{-1} ; this is presumably the antisymmetric $\nu(\text{Mo}-\text{Br})$ frequency, and it indicates that the Mo-Br bonds here are stronger and shorter than those in $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$. The electronic spectrum in both the solid state and in dichloromethane solution is featureless from 600 nm on into the near-IR region. A band is seen at 371 nm with a distinct shoulder at 450 nm in

(19) Libson, K.; Barnett, B. L.; Deutsch, E. *Inorg. Chem.* **1983**, *22*, 1695.

(20) Lewis, J.; Nyholm, R. S.; Smith, P. W. *J. Chem. Soc.* **1962**, 2592.

the solid-state spectrum, but only a single absorption at 360 nm occurs in solution. For $[\text{TcBr}_2(\text{dppe})_2]^+$ a band at 504 nm (in ethanol) was attributed to a halogen-to-metal charge-transfer process based upon the observed shift to 480 nm for this band in the case of $[\text{TcCl}_2(\text{dppe})_2]^+$ and to 454 nm for $\text{TcBr}_2(\text{dppe})_2$. It is probable that the shoulder at 450 nm in the spectrum of $\text{MoBr}_2(\text{dppe})_2$ arises from a similar LMCT transition although the origin of the higher energy band is presently unclear. The effective magnetic moment of $\text{MoBr}_2(\text{dppe})_2$ was found to be $2.8 \pm 0.4 \mu_B$; the large uncertainty is due to the small sample size (from each reaction) employed in this measurement. This value is in accord with two unpaired electrons. Moreover, μ_{eff} for $\text{MoBr}_2(\text{diars})_2$ was reported to be $2.9 \mu_B$ while $[\text{TcBr}_2(\text{dppe})_2]\text{BF}_4$ gave a value of $2.47 \mu_B$.

The circumstances under which *trans*- $\text{MoBr}_2(\text{dppe})_2$ has been recovered do not constitute an efficient preparative method for this compound. A few further observations concerning the formation of this compound are pertinent. Recovery of crystals of *trans*- $\text{MoBr}_2(\text{dppe})_2$ occurred only when reflux reactions were continued for several days. The compound is produced most reproducibly in ethanol possibly because of the higher boiling temperature relative to that of methanol and poorer solubility relative to 1-propanol. We attempted to generate greater yields of this material by resorting to 10:1 dppe: Mo_2 stoichiometry in all three alcohols. However, no appreciable increase in its production was observed. In addition, $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ was reacted with 2 mol of dppe in ethanol, but only the β complex was recovered.

Although nonredox metal-metal bond disruption of Mo(II) dimers by π -acid ligands such as carbon monoxide, isocyanides, or nitric oxide appears to be a facile process, we know of no other report of a reaction yielding a mononuclear Mo(II) species with primarily σ donors such as dppe.²¹ San Filippo and King isolated *mer*- $\text{MoX}_3(\text{py})_3$ ($X = \text{Cl}, \text{Br}$; $\text{py} = \text{pyridine}$) from the high-temperature reaction (200 °C) of $\text{Mo}_2\text{X}_4(\text{py})_4$ and py .²² In this case M-M bond cleavage is accompanied by oxidation to Mo(III). In contrast, rupture of the quadruple bond in $\text{Re}_2\text{Cl}_8^{2-}$ with dppe takes place rapidly (30 min) in acetonitrile and without oxidation.²³ The paramagnetic product, $\text{Re}_2\text{Cl}_6(\text{dppe})_2$, is a centrosymmetric dimer containing bridging chlorine atoms and chelating dppe and exhibiting a Re-Re separation of 3.8 Å.

Kinetic and Thermodynamic Relationship of the α and β Isomers. The α form of $\text{Mo}_2\text{Br}_4(\text{dppe})_2$ forms rapidly from $\text{Mo}_2\text{Br}_8^{4-}$ in all three of the alcohols used as reaction media, viz., methanol (bp 64 °C), ethanol (bp 78 °C) and 1-propanol (bp 97 °C). Although it is the only product isolated from methanol, extended refluxing results in nearly complete conversion to $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ in ethanol and complete conversion in 1-propanol (2:1 dppe: Mo_2 mole ratio). We carried out a 4-day reflux of the α isomer in methanol but recovered only unreacted α . A much shorter (6-h) reflux of α in 1-propanol resulted in complete isomerization to β . Moreover, a sample of β was refluxed in methanol for 8 days and showed no indication of isomerization to α . These results imply that the α complex is kinetically favored while the β form is more stable thermodynamically but is generated more slowly. Because α is observed initially in all three solvents, the increased boiling temperatures of ethanol and 1-propanol presumably provide sufficient thermal energy for the system to attain equilibrium. A most surprising result was the facile rearrangement of α to β in deoxygenated dichloromethane at room temperature when we attempted to record the solution electronic spectrum. Accordingly, we monitored this process spectroscopically over a 3-h period, and the results appear in Figure 2. The final spectrum in the sequence is nearly identical with that of the pure β isomer. The appearance of isosbestic points (three) is consistent with a simple isomerization. Figure 3 shows a plot of the natural logarithm of concentration of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ vs. time. From this plot we obtained a

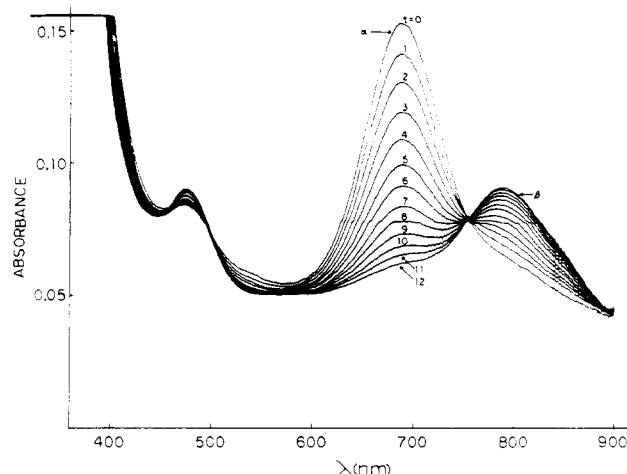


Figure 2. Electronic absorption spectra of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ (6.18×10^{-5} M) in dichloromethane solution recorded at 15-min intervals at 22 °C. The final spectrum ($t = 12$) is due primarily to $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$.

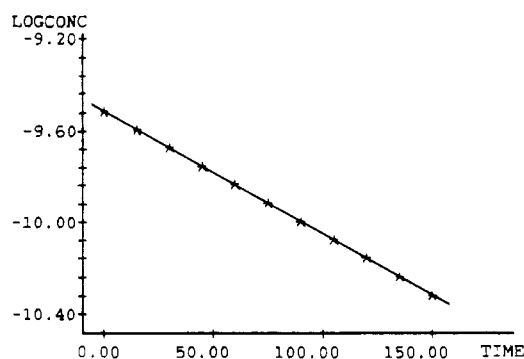


Figure 3. Plot of $\ln [\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2]$ vs. time (in min).

first-order reaction rate constant of $(7.6 \pm 1.1) \times 10^{-5} \text{ s}^{-1}$ at 22 °C. This type of rearrangement is fairly common for $\text{Mo}_2\text{X}_4(\text{LL})_2$ species ($X = \text{Cl}, \text{Br}$; $\text{LL} = \text{bidentate tertiary phosphines and arsines}$). The previously reported² isolation of $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ from $\text{Mo}_2\text{Br}_4(\text{P}(\text{C}_2\text{H}_5)_3)_4$ in methanol implies the possible occurrence of a substitution mechanism different from that which is operative in the $\text{Mo}_2\text{Br}_8^{4-}$ reaction in this medium.

Mechanism of Conversion of $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ to $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$. It has been known in a general, qualitative way that the α isomers of $\text{M}_2\text{X}_4(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$ compounds characteristically tend to rearrange to the β isomers, but these processes have not been experimentally characterized in detail²⁴ nor mechanistically discussed. In this work we have shown that $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ transforms cleanly (no intermediates; sharp isosbestic points) to $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$ by a first-order process. Since the solvent, CH_2Cl_2 , seems quite unlikely to play any intimate role in the process, we conclude that the process is truly unimolecular.

In attempting to propose a reasonable pathway for this isomerization, we begin by recalling the very common occurrence of a certain type of disorder in the crystal structures of compounds containing $[\text{M}_2\text{X}_8]^{n-}$, $\text{M}_2\text{X}_4\text{L}_4$, and $\text{M}_2\text{X}_4(\text{LL})_2$ units.²⁵ In Figure 4 we show, in a schematic way, the relevant rearrangements of an M_2 unit within an idealized cubic arrangement of ligand atoms. In (a)–(c) it is shown how the cubic set of eight X groups makes each of three orientations of the M_2 unit equally probable. In practice of course, the surroundings are not cubic (or, at least, no such case has yet been reported) and there is a major preference for one orientation, minor occupancy (5–30%) of a second one, and no observable occupancy of the third. In the $\text{M}_2\text{X}_4\text{L}_4$ case

(21) Walton, R. A. *ACS Symp. Ser.* **1981**, No. 155, 207.
 (22) San Filippo, J.; Schaefer King, M. A. *Inorg. Chem.* **1976**, *15*, 1228.
 (23) Jaeger, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

(24) R. D. Peacock, University of Glasgow, has recently conducted some thorough studies (private communication, to be submitted for publication).
 (25) For a summary, see: Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; pp 344–347.

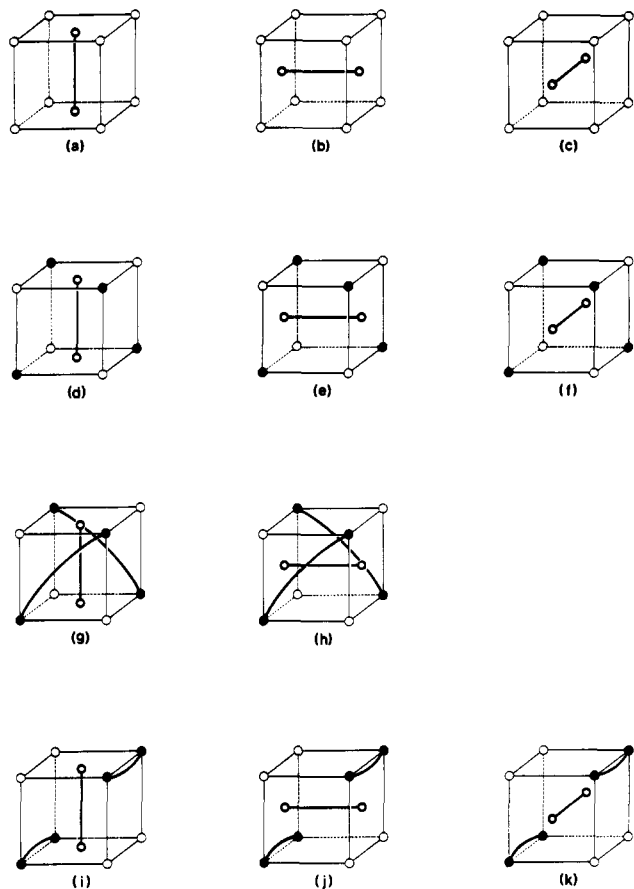


Figure 4. Schematic representations of the various orientations of the central M_2 unit within a cubic or quasi-cubic cage of eight ligand atoms.

the ideal situation shown in Figure 4d–f is actually found in Nature. In both $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ ²⁶ and $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ ²⁷ the molecules are found in cubic crystals and the three orientations of the M_2 units are equally populated. In $\text{M}_2\text{X}_4(\text{LL})_2$ molecules there are two feasible orientations of the M_2 unit within a fixed

ligand set (these are sketched *very* schematically as (g) and (h) in Figure 4) and nearly all crystalline compounds of this type show both orientations.²⁸

The common occurrence of these forms of disorder naturally raises the question of whether flipping of the metal atom pair so as to interconvert them occurs at any significant rate. At the present time we do not know; no pertinent experiment has yet been carried out.²⁸ However, it seems possible that the barriers to such flips could be low enough (below about 30 kcal mol^{-1}) to make them chemically significant. If this is true, then there is a simple pathway, not involving any blatant metal–ligand bond breaking, by which the α to β conversion could be accomplished.²⁹ This is shown schematically in Figure 4 by sketches i, j, and k. A flip of M_2 that carries either (i) or (j) to (k), followed by some relaxation of (k) to a partially staggered arrangement, would accomplish the isomerization. This seems to us to be a more attractive (and certainly more interesting) process than one in which M–P bonds are first broken, considerable excursions are made by a number of atoms, and bonds are then re-formed.

By employing the measured rate constant and assuming a value of 10^{13} for the Arrhenius preexponential factor (an appropriate value for a unimolecular reaction), one can estimate an activation energy of about 24 kcal/mol . This value is high enough that it can probably be said to exclude a pathway in which one complete bond rupture occurs, but it seems quite consistent with the internal rotation mechanism we have just described.

Acknowledgment. We are grateful to the National Science Foundation for support at TAMU and to the Research Corp. and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support at Kalamazoo College.

Registry No. $\alpha\text{-Mo}_2\text{Br}_4(\text{dppe})_2$, 96451-71-7; $\beta\text{-Mo}_2\text{Br}_4(\text{dppe})_2$, 64508-29-8; *trans*- $\text{MoBr}_2(\text{dppe})_2$, 97133-85-2; $(\text{NH}_4)_4[\text{Mo}_2\text{Br}_8]$, 61520-69-2; $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 36608-07-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, all bond distances and angles, least-squares planes for all phenyl rings, and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

(26) Cotton, F. A.; Frenz, B. A.; Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 1630.

(27) Daniels, L. M. Ph.D. Dissertation, Texas A&M University, College Station, TX, May 1984.

(28) NMR studies that might in principle afford information on a unimolecular process have been designed and are being pursued in this laboratory by P. A. Agaskar.

(29) We are grateful to Dr. Douglas Dudis for a discussion in which he persuaded us that this pathway is a realistic possibility.

(30) Unpublished results.