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Correlation of Mo–Mo Quadruple Bond Length with Angle of Internal Rotation, Using Data for 10 Compounds

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The preparation and structural characterization of two bridged $Mo_2X_4(LL)_2$ compounds is reported, and their relevance to the relationship between Mo–Mo quadruple bond length and torsional angle is discussed. $Mo_2Br_4(dppm)_2 \cdot 2THF$ (**1**), where dppm = bis(diphenylphosphino)methane, crystallizes in space group $P2_1/n$ with a = 11.653 (2) Å, b = 17.339 (4) Å, c = 14.409 (4) Å, β = 98.07 (2)°, V = 2882 (2) Å^3, and Z = 2. There is a crystallographic center of inversion at the midpoint of the Mo–Mo bond, and the rotational conformation is eclipsed. The metal–metal bond length, 2.138 (1) Å, is identical with that in the structure of $Mo_2Cl_4(dppm)_2 \cdot 2C_3H_6O$. $Mo_2Cl_4(tdpm)_2 \cdot 2CH_2Cl_2$ (**2**), where tdpm = tris(diphenylphosphino)methane, crystallizes in space group $P\bar{1}$ with a = 15.078 (4) Å, b = 22.941 (6) Å, c = 12.380 (3) Å, α = 104.55 (2)°, β = 107.87 (2)°, γ = 92.44 (2)°, V = 3911 (4) Å^3, and Z = 2. The principal molecule possesses no crystallographic symmetry, and only two of the three phosphorus atoms of each tdpm ligand are coordinated to the molybdenum atoms. The rotational conformation is partially staggered with an average torsional angle of 20 [3]°. These new data, together with data on the bond lengths and mean torsion angles for eight other compounds of the same type, are used to show that an inverse linear relationship (correlation coefficient 0.916) exists between the Mo–Mo bond distance and cos (2χ), where χ is the angle of twist away from an eclipsed conformation.

Introduction

Compounds of the general type $Mo_2X_4(LL)_2$, where LL is a bridging bidentate phosphine ligand, provide a unique opportunity to measure the relationship between bond length and bond order since the conformational preferences of the LL ligands result in various degrees of twist about the Mo–Mo axis and thus various degrees of δ overlap in the Mo–Mo bond. Previously, the Mo–Mo bond distance in this class of compounds was shown to have a linear dependence on cos (2χ), where χ is the angle of twist away from an eclipsed conformation.[1] For several reasons, we have been motivated to characterize further examples of these complexes. The initial study involved the structural details of only three dimers, two in which X = Cl and one in which X = Br. There was some uncertainty as to whether or not a change in the halide type would affect the Mo–Mo bond length, and it was also desirable to have a much greater number of data points to establish more firmly the validity of the correlation and more accurately the slope of its line.

With the structural characterization of $Mo_2Br_4(dppm)_2 \cdot 2THF$, the bromo analogue of a previously characterized compound, $Mo_2Cl_4(dppm)_2 \cdot 2C_3H_6O$,[2] we are enabled to test the validity of comparing bromo with chloro species. We have also prepared another $Mo_2X_4(LL)_2$ compound with a three-atom bridging group similar to that of dppm but with a different rotational conformation. Neither of these new dimers contains the type of disorder commonly encountered in this class of compounds.

Experimental Section

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. Bis(diphenylphosphino)methane (dppm) and tris(diphenylphosphino)methane (tdpm) were purchased from Strem Chemicals, Inc., and used without further purification. Bromotrimethylsilane (Me_3SiBr) was obtained from Aldrich Chemical Co. and used as received. $Mo_2(O_2CCH_3)_4$[3] and $(NH_4)_5Mo_2Cl_9 \cdot H_2O$[4] were prepared according to published procedures.

Preparations. $Mo_2Br_4(dppm)_2 \cdot 2THF$ (1). Although $Mo_2Br_4(dppm)_2$ was previously prepared by another method,[5] we chose to use the following synthesis in the hope of obtaining a crystalline sample. A mixture of dppm (0.30 g, 0.76 mmol), $Mo_2(O_2CCH_3)_4$ (0.11 g, 0.25 mmol), and Me_3SiBr (0.23 mL, 1.7 mmol) was stirred and refluxed in 60 mL of THF for 12 h. A portion (10 mL) of the resulting solution was transferred to a Schlenk tube and layered with hexane to yield a nice crop of small, single crystals. The remainder of the reaction solution was pumped to dryness and the residue washed with toluene before collecting the air-stable green product.

Since no yield was determined in the above preparation, the same procedure was repeated except that the reactants were stirred but not refluxed. After 3 h of stirring, the volume of the solution was reduced under vacuum to ca. 5 mL and hexane was added to precipitate the green product. The solid was filtered off in the air, washed with 30 mL of toluene and 20 mL of hexane, and dried in vacuo; yield 67%. This is a more convenient and higher yield synthesis than the published procedure. An analogous method has been employed in the preparation of $Mo_2Cl_4(dppm)_2 \cdot 2THF$.[6]

$Mo_2Cl_4(tdpm)_2$ (2). A mixture of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ (0.29 g, 0.47 mmol) and 0.61 g (1.1 mmol) of tdpm was stirred in 35 mL of methanol for 16 h at room temperature. The resulting yellow-green solid was filtered off in the air, washed with 20 mL of methanol, and dried in vacuo; yield 74%. This product was determined to be only slightly air sensitive, decomposing after 3 days of exposure to the laboratory atmosphere.

Large, block-shaped crystals of $Mo_2Cl_4(tdpm)_2 \cdot 2CH_2Cl_2$ were grown by layering a dichloromethane solution of **2** with hexane in a Schlenk tube. These crystals immediately lost solvent upon exposure to air or mineral oil. The one selected for X-ray data collection was surrounded with a 1:3 (by volume) CH_2Cl_2/hexane mixture and sealed in a glass capillary.

X-ray Crystallography. Automated four-circle diffractometers[7] equipped with Mo Kα radiation were used to collect data on single crystals of compounds **1** and **2** at room temperature (25 ± 3 °C). Pertinent crystallographic parameters are summarized in Table I, and details of the data collection, empirical absorption corrections,[8] and computational procedures[9] are available as supplementary material. Tables II and III list atomic positional parameters, while Tables IV and V give important bond distances and angles for structures **1** and **2**, respectively. Complete tables of anisotropic thermal parameters, bond distances, bond angles, and structure factors are included in the supplementary material. Figures 1 and 2 illustrate the structures and

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

(2) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240.

(3) Brignole, A. B.; Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 81.

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(5) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 99.

(6) Green, M. L. H.; Parkin, G.; Bashkin, J.; Fail, J.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1982**, 2519.

(7) X-ray data collection for compound **1** was carried out on an Enraf-Nonius CAD-4 diffractometer at the Molecular Structure Corp., College Station, TX. Data for compound **2** were collected on a Syntex $P\bar{1}$ diffractometer at the Laboratory for Molecular Structure and Bonding, Texas A&M University.

(8) North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A 24*, 351.

(9) Crystallographic calculations for compound **1** were done with VAXSDP software on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University. Calculations for compound **2** were done with Enraf-Nonius SDP software on PDP-11/60 computer at B. A. Frenz and Associates, College Station, Texas.

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Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for Compounds **1** and **2**

compd	$Mo_2Br_4(dppm)_2\cdot 2THF$ (**1**)	$Mo_2Cl_4(tdpm)_2\cdot 2CH_2Cl_2$ (**2**)
formula	$Mo_2Br_4P_4C_{50}H_{44}\cdot 2C_4H_8O$	$Mo_2Cl_4P_6C_{74}H_{62}\cdot 2CH_2Cl_2$
fw	1424.51	1640.71
space group	$P2_1/n$	$P\bar{1}$
syst absences	$h0l$ ($h + l = 2n$), $0k0$ ($k = 2n$)	none
a, Å	11.653 (2)	15.078 (4)
b, Å	17.339 (4)	22.941 (6)
c, Å	14.409 (4)	12.380 (3)
α, deg	90	104.55 (2)
β, deg	98.07 (2)	107.87 (2)
γ, deg	90	92.44 (2)
V, Å^3	2882 (2)	3911 (4)
Z	2	2
d_{calcd}, g/cm^3	1.64	1.39
cryst size, mm	0.1 × 0.2 × 0.3	0.4 × 0.6 × 0.8
μ(Mo Kα), cm^{-1}	33.20	7.48
data collcn instrum	Enraf-Nonius CAD-4	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα	Mo Kα
no. of orientation reflcns; range (2θ), deg	25; 8–19	15; 20–30
temp, °C	25 (2)	25 (3)
scan method	ω–2θ	ω
data collcn range (2θ), deg	0–46	0–48.5
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3107	6712
no. of parameters refined	291	835
transmissn factors (max, min)	99.94, 88.15	none
R^a	0.0470	0.0635
R_w^b	0.0596	0.0864
quality of fit indicator^c	1.447	1.608
largest shift/esd, final cycle	0.02	0.67
largest peak, e/Å^3	0.96	0.93

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

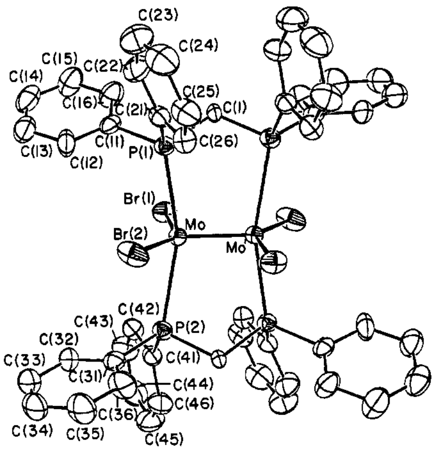

Figure 1. ORTEP view of the $Mo_2Br_4(dppm)_2$ molecule in $Mo_2Br_4(dppm)_2\cdot 2THF$ (**1**). Ellipsoids are at the 50% probability level.

atom-labeling schemes for the two complexes.

Results and Discussion

Table II. Positional and Isotropic Equivalent Thermal Parameters for $Mo_2Br_4(dppm)_2\cdot 2THF$ (1)

atom	x	y	z	B,^{a} Å^2
Mo	0.08125 (6)	0.01376 (4)	−0.02235 (5)	1.97 (1)
Br(1)	0.18504 (8)	−0.11517 (5)	−0.01541 (6)	3.12 (2)
Br(2)	0.1096 (1)	0.15705 (5)	−0.04439 (7)	4.22 (2)
P(1)	0.1928 (2)	0.0346 (1)	0.1409 (2)	2.30 (4)
P(2)	0.0186 (2)	0.0231 (1)	−0.2078 (2)	2.44 (4)
C(1)	0.1397 (6)	−0.0374 (5)	0.2191 (5)	2.4 (2)
C(11)	0.3464 (7)	0.0167 (5)	0.1446 (6)	2.7 (2)
C(12)	0.4074 (8)	0.0679 (6)	0.0934 (7)	3.8 (2)
C(13)	0.5252 (8)	0.0565 (6)	0.0907 (7)	4.1 (2)
C(14)	0.5820 (8)	−0.0052 (6)	0.1387 (8)	4.6 (2)
C(15)	0.5224 (9)	−0.0561 (7)	0.1901 (8)	5.3 (3)
C(16)	0.4024 (8)	−0.0433 (6)	0.1922 (7)	4.0 (2)
C(21)	0.1924 (7)	0.1251 (5)	0.2065 (6)	2.7 (2)
C(22)	0.2810 (8)	0.1389 (6)	0.2800 (7)	4.0 (2)
C(23)	0.276 (1)	0.2047 (6)	0.3384 (8)	5.0 (3)
C(24)	0.181 (1)	0.2527 (6)	0.3223 (7)	5.1 (3)
C(25)	0.0920 (9)	0.2397 (6)	0.2462 (7)	4.0 (2)
C(26)	0.0969 (7)	0.1742 (5)	0.1876 (6)	3.0 (2)
C(31)	0.0675 (7)	0.1078 (5)	−0.2677 (6)	2.7 (2)
C(32)	0.1756 (8)	0.1029 (6)	−0.2988 (6)	3.6 (2)
C(33)	0.2154 (9)	0.1685 (7)	−0.3424 (7)	5.0 (3)
C(34)	0.151 (1)	0.2340 (6)	−0.3563 (7)	5.2 (3)
C(35)	0.045 (1)	0.2386 (6)	−0.3258 (8)	5.5 (3)
C(36)	0.0015 (9)	0.1755 (5)	−0.2808 (7)	4.3 (2)
C(41)	0.0430 (7)	−0.0528 (5)	−0.2897 (6)	2.8 (2)
C(42)	0.1352 (8)	−0.1057 (5)	−0.2683 (6)	3.1 (2)
C(43)	0.1549 (9)	−0.1625 (6)	−0.3334 (7)	4.4 (2)
C(44)	0.086 (1)	−0.1668 (6)	−0.4197 (7)	4.9 (3)
C(45)	−0.0017 (9)	−0.1132 (7)	−0.4430 (7)	5.0 (3)
C(46)	−0.0249 (8)	−0.0557 (6)	−0.3790 (6)	4.0 (2)
O	0.7033 (9)	0.0549 (6)	0.5679 (8)	9.6 (3)*
C(2)	0.694 (1)	0.0154 (9)	0.480 (1)	8.1 (4)*
C(3)	0.599 (1)	0.0552 (9)	0.414 (1)	9.0 (4)*
C(4)	0.572 (1)	0.124 (1)	0.463 (1)	9.7 (5)*
C(5)	0.654 (1)	0.131 (1)	0.559 (1)	10.0 (5)*

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

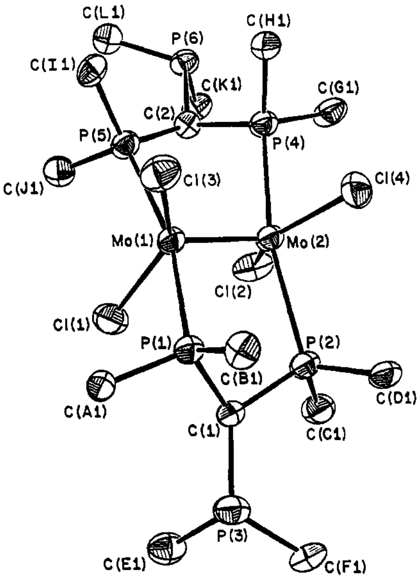

Figure 2. ORTEP view of the $Mo_2Cl_4(tdpm)_2$ molecule in $Mo_2Cl_4(tdpm)_2\cdot 2CH_2Cl_2$ (**2**). For clarity, only the phosphorus-bound carbon atom of each phenyl ring is illustrated. Ellipsoids are at the 50% probability level.

Structures. Compound 1. The principal molecule, $Mo_2Br_4(dppm)_2$, has a structure (see Figure 1) quite similar to that previously reported for $Mo_2Cl_4(dppm)_2$.[2] The dimer resides on a crystallographic inversion center and possesses virtual C_{2h} symmetry. The noncrystallographic twofold axis is coincident with the Mo–Mo axis, while the idealized mirror plane bisects the bridging ligands and is perpendicular to the Mo–Mo axis. The THF molecules occupy sites between dimers and are not bonded to them (the closest contact being 3.36 (1) Å).

Table III. Positional and Isotropic Equivalent Thermal Parameters for $Mo_2Cl_4(tdpm)_2 \cdot 2CH_2Cl_2$ (**2**)

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Mo(1)	0.22427 (6)	0.25168 (4)	0.15499 (7)	2.53 (2)	C(G2)	0.1775 (8)	0.3024 (5)	0.6293 (9)	4.8 (3)
Mo(2)	0.27913 (6)	0.24957 (4)	0.33568 (7)	2.51 (2)	C(G3)	0.209 (1)	0.3148 (6)	0.754 (1)	5.8 (4)
Cl(1)	0.3490 (2)	0.3029 (1)	0.1162 (2)	3.99 (6)	C(G4)	0.273 (1)	0.3644 (7)	0.824 (1)	6.6 (4)
Cl(2)	0.3982 (2)	0.3365 (1)	0.4348 (3)	4.18 (7)	C(G5)	0.312 (1)	0.4015 (6)	0.776 (1)	6.7 (4)
Cl(3)	0.0740 (2)	0.1916 (1)	0.0519 (2)	3.95 (7)	C(G6)	0.2854 (9)	0.3907 (5)	0.648 (1)	4.5 (3)
Cl(4)	0.1901 (2)	0.1740 (1)	0.3745 (2)	3.76 (6)	C(H1)	0.0497 (7)	0.2994 (4)	0.3815 (8)	3.2 (2)
P(1)	0.2903 (2)	0.1574 (1)	0.0670 (2)	2.74 (6)	C(H2)	0.0028 (7)	0.3378 (5)	0.452 (1)	4.3 (3)
P(2)	0.4129 (2)	0.1814 (1)	0.3133 (2)	2.80 (6)	C(H3)	−0.0960 (8)	0.3221 (6)	0.422 (1)	5.1 (3)
P(3)	0.4877 (2)	0.1109 (1)	0.0907 (2)	3.20 (6)	C(H4)	−0.1436 (9)	0.2734 (6)	0.329 (1)	5.8 (4)
P(4)	0.1763 (2)	0.3212 (1)	0.4172 (2)	2.70 (6)	C(H5)	−0.0954 (9)	0.2364 (6)	0.263 (1)	5.4 (4)
P(5)	0.1538 (2)	0.3561 (1)	0.2005 (2)	2.71 (6)	C(H6)	0.0011 (8)	0.2482 (5)	0.2888 (9)	4.1 (3)
P(6)	0.1489 (2)	0.4594 (1)	0.4475 (2)	2.93 (6)	C(I1)	0.0277 (7)	0.3507 (4)	0.1289 (8)	3.1 (2)
C(1)	0.4167 (6)	0.1662 (4)	0.1595 (8)	2.6 (2)	C(I2)	−0.0060 (8)	0.3218 (4)	0.0080 (9)	3.7 (3)
C(2)	0.1886 (6)	0.3895 (4)	0.3635 (8)	2.4 (2)	C(I3)	−0.1018 (9)	0.3199 (5)	−0.054 (1)	5.0 (3)
C(A1)	0.2836 (7)	0.1551 (5)	−0.0828 (8)	3.6 (2)	C(I4)	−0.1641 (8)	0.3476 (5)	0.004 (1)	4.4 (3)
C(A2)	0.3497 (9)	0.1857 (5)	−0.112 (1)	4.7 (3)	C(I5)	−0.1283 (8)	0.3742 (5)	0.122 (1)	4.5 (3)
C(A3)	0.3366 (9)	0.1841 (6)	−0.230 (1)	6.1 (4)	C(I6)	−0.0341 (7)	0.3758 (5)	0.1885 (9)	3.7 (3)
C(A4)	0.255 (1)	0.1542 (6)	−0.321 (1)	6.2 (4)	C(J1)	0.2022 (7)	0.4160 (4)	0.1500 (8)	3.3 (2)
C(A5)	0.185 (1)	0.1234 (7)	−0.291 (1)	6.9 (4)	C(J2)	0.1442 (9)	0.4419 (5)	0.0678 (9)	4.5 (3)
C(A6)	0.1991 (9)	0.1227 (6)	−0.173 (1)	5.0 (3)	C(J3)	0.181 (1)	0.4858 (5)	0.028 (1)	5.7 (4)
C(B1)	0.2385 (7)	0.0800 (4)	0.0487 (8)	3.2 (2)	C(J4)	0.276 (1)	0.5041 (6)	0.075 (1)	6.7 (4)
C(B2)	0.2637 (8)	0.0309 (5)	−0.0248 (9)	3.9 (3)	C(J5)	0.3386 (9)	0.4787 (6)	0.159 (1)	6.2 (4)
C(B3)	0.225 (1)	−0.0290 (6)	−0.041 (1)	5.7 (4)	C(J6)	0.2987 (8)	0.4338 (5)	0.197 (1)	4.1 (3)
C(B4)	0.164 (1)	−0.0385 (6)	0.020 (1)	7.0 (4)	C(K1)	0.2621 (7)	0.5064 (4)	0.5414 (9)	3.2 (2)
C(B5)	0.139 (1)	0.0106 (6)	0.090 (1)	6.3 (4)	C(K2)	0.3429 (8)	0.5103 (5)	0.511 (1)	4.5 (3)
C(B6)	0.1766 (8)	0.0706 (5)	0.1074 (9)	4.1 (3)	C(K3)	0.4241 (9)	0.5496 (6)	0.594 (1)	5.3 (4)
C(C1)	0.5327 (8)	0.2181 (5)	0.4029 (9)	3.7 (3)	C(K4)	0.423 (1)	0.5838 (6)	0.700 (1)	6.4 (4)
C(C2)	0.5664 (7)	0.2716 (5)	0.3860 (9)	3.9 (3)	C(K5)	0.343 (1)	0.5792 (7)	0.731 (1)	7.2 (5)
C(C3)	0.6576 (8)	0.3008 (6)	0.451 (1)	5.6 (4)	C(K6)	0.2627 (9)	0.5402 (6)	0.651 (1)	5.5 (4)
C(C4)	0.7140 (9)	0.2752 (7)	0.537 (1)	6.3 (4)	C(L1)	0.1032 (7)	0.5097 (4)	0.3534 (8)	3.2 (2)
C(C5)	0.680 (1)	0.2233 (7)	0.560 (1)	6.6 (4)	C(L2)	0.0068 (8)	0.5173 (5)	0.3378 (9)	4.2 (3)
C(C6)	0.5890 (8)	0.1926 (6)	0.492 (1)	5.1 (3)	C(L3)	−0.0351 (9)	0.5586 (5)	0.278 (1)	5.1 (3)
C(D1)	0.3993 (7)	0.1122 (5)	0.3537 (8)	3.5 (2)	C(L4)	0.018 (1)	0.5919 (5)	0.236 (1)	6.3 (3)
C(D2)	0.3928 (8)	0.0546 (5)	0.280 (1)	4.0 (3)	C(L5)	0.112 (1)	0.5860 (5)	0.251 (1)	5.7 (4)
C(D3)	0.3811 (9)	0.0022 (6)	0.321 (1)	5.1 (3)	C(L6)	0.1587 (9)	0.5429 (5)	0.311 (1)	4.6 (3)
C(D4)	0.379 (1)	0.0092 (6)	0.433 (1)	7.1 (4)	C(3)	0.055 (2)	0.840 (1)	0.261 (2)	7.6 (5)*
C(D5)	0.385 (1)	0.0685 (6)	0.509 (1)	6.2 (3)	Cl(A)	0.0491 (5)	0.7812 (3)	0.3140 (6)	8.8 (2)*
C(D6)	0.3938 (9)	0.1194 (5)	0.468 (1)	4.9 (3)	Cl(B1)	0.160 (1)	0.8684 (8)	0.262	9*
C(E1)	0.5602 (7)	0.1583 (5)	0.0446 (9)	3.6 (3)	Cl(B2)	0.167 (2)	0.886	0.299 (2)	7*
C(E2)	0.5945 (9)	0.2195 (5)	0.093 (1)	5.2 (3)	Cl(B3)	0.152 (1)	0.8486 (7)	0.222 (1)	6.3 (3)*
C(E3)	0.655 (1)	0.2498 (6)	0.053 (1)	6.3 (4)	C(4)	0.982 (2)	0.069 (1)	0.308 (2)	10.2 (8)*
C(E4)	0.689 (1)	0.2159 (7)	−0.032 (1)	9.3 (5)	Cl(C)	0.9850 (5)	0.1205 (3)	0.4394 (6)	9.8 (2)*
C(E5)	0.652 (1)	0.1556 (8)	−0.085 (2)	15.2 (5)	Cl(D1)	1.079 (1)	0.0124 (9)	0.380 (2)	11.4 (5)*
C(E6)	0.591 (1)	0.1270 (6)	−0.047 (1)	9.4 (4)	Cl(D2)	1.022 (2)	0.006 (1)	0.357 (2)	11.7 (8)*
C(F1)	0.5834 (7)	0.0909 (5)	0.203 (1)	4.1 (3)	Cl(D3)	0.977 (2)	0.014 (1)	0.286 (3)	11.0 (8)*
C(F2)	0.5775 (8)	0.0288 (5)	0.1971 (9)	5.3 (3)	C(5)	0.478 (3)	0.675 (2)	0.177 (4)	13 (1)*
C(F3)	0.6522 (9)	0.0069 (6)	0.273 (1)	6.5 (3)	Cl(E)	0.462 (1)	0.6242 (6)	0.062 (1)	8.9 (3)*
C(F4)	0.728 (1)	0.0460 (6)	0.350 (1)	7.4 (4)	Cl(F1)	0.438 (2)	0.723 (1)	0.229 (2)	8.1 (5)*
C(F5)	0.7361 (9)	0.1085 (8)	0.358 (1)	7.5 (4)	Cl(F2)	0.411 (2)	0.666 (2)	0.257 (3)	9.2 (8)*
C(F6)	0.6630 (8)	0.1329 (6)	0.285 (1)	5.2 (3)	Cl(F3)	0.480 (2)	0.687 (1)	0.280 (3)	11.7 (9)*
C(G1)	0.2177 (8)	0.3415 (5)	0.5799 (9)	3.8 (3)	Cl(G)	0.409 (1)	0.6246 (9)	0.278 (2)	7.3 (5)*

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

The dppm ligands bridge the dimetal unit in a transoid manner to form two edge-sharing five-membered rings with envelope conformations. These phosphine ligands are not, however, symmetrically bonded to the Mo–Mo unit, since the two independent Mo–Mo–P angles differ by 4.2° and the two Mo–P distances differ by 0.12 Å. A similar mode of coordination was noted in the structure of $Mo_2Cl_4(dppm)_2$.

As Figure 3 illustrates, the torsional angles about the Mo–Mo axis in compound **1** are nonzero; the two independent angles are 6.2 and 8.1°. In the chloro analogue these are 2.6 and 6.1°. However, both $Mo_2Br_4(dppm)_2$ and $Mo_2Cl_4(dppm)_2$ are centrosymmetric so that their *average* torsional angles are zero and their rotational conformations are strictly eclipsed. Most significantly, these two dimers have exactly the same Mo–Mo bond distance, 2.138 (1) Å. This is the first conclusive evidence that a change from X = Cl to X = Br in $Mo_2X_4(LL)_2$ complexes need not affect the metal–metal bond length in this class of compounds. This is in line with previous comparisons,[10]

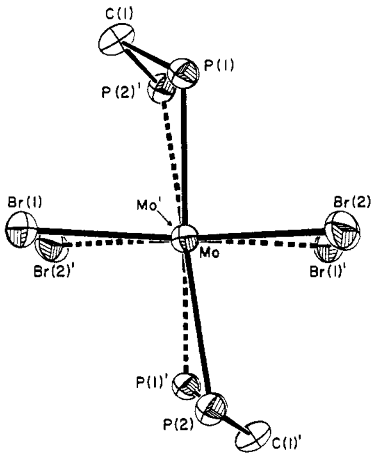

Figure 3. Central portion of the $Mo_2Br_4(dppm)_2$ molecule viewed down the Mo–Mo′ axis.

Table IV. Important Bond Distances (Å) and Angles (deg) for $Mo_2Br_4(dppm)_2 \cdot 2THF$ (**1**)

Distances			
Mo–Mo′	2.138 (1)	P(1)–C(1)	1.845 (7)
–Br(1)	2.537 (1)	–C(11)	1.810 (7)
–Br(2)	2.532 (1)	–C(21)	1.833 (7)
–P(1)	2.549 (2)	P(2)–C(1)	1.845 (7)
–P(2)	2.674 (2)	–C(31)	1.834 (7)
		–C(41)	1.816 (7)
Angles			
Mo′–Mo–Br(1)	103.24 (4)	Mo–P(1)–C(21)	124.0 (3)
–Br(2)	113.18 (5)	C(1)–P(1)–C(11)	106.4 (3)
–P(1)	96.44 (5)	–C(21)	103.8 (3)
–P(2)	100.67 (5)	C(11)–P(1)–C(21)	101.9 (3)
Br(1)–Mo–Br(2)	143.08 (4)	Mo–P(2)–C(1)	103.0 (2)
–P(1)	84.83 (5)	–C(31)	117.3 (2)
–P(2)	98.89 (5)	–C(41)	124.0 (3)
Br(2)–Mo–P(1)	85.30 (5)	C(1)–P(2)–C(31)	103.0 (3)
–P(2)	80.65 (5)	–C(41)	106.6 (3)
P(1)–Mo–P(2)	161.10 (6)	C(31)–P(2)–C(41)	100.8 (3)
Mo–P(1)–C(1)	107.2 (2)	P(1)–C(1)–P(2)	105.8 (3)
–C(11)	112.2 (2)		

Table V. Selected Bond Distances (Å) and Angles (deg) for $Mo_2Cl_4(tdpm)_2 \cdot 2CH_2Cl_2$ (**2**)

Distances			
Mo(1)–Mo(2)	2.148 (1)	P(1)–C(D1)	1.802 (9)
–Cl(1)	2.408 (2)	P(3)–C(1)	1.902 (8)
–Cl(3)	2.395 (2)	–C(E1)	1.816 (9)
–P(1)	2.553 (2)	–C(F1)	1.834 (9)
–P(5)	2.662 (2)	P(4)–C(2)	1.872 (8)
Mo(2)–Cl(2)	2.412 (2)	–C(G1)	1.84 (1)
–Cl(4)	2.378 (2)	–C(H1)	1.838 (9)
–P(2)	2.642 (2)	P(5)–C(2)	1.864 (8)
–P(4)	2.544 (2)	–C(I1)	1.818 (9)
P(1)–C(1)	1.869 (8)	–C(J1)	1.854 (9)
–C(A1)	1.813 (9)	P(6)–C(2)	1.908 (8)
–C(B1)	1.840 (9)	–C(K1)	1.849 (9)
P(2)–C(1)	1.866 (8)	–C(L1)	1.846 (9)
–C(C1)	1.84 (1)		
Angles			
Mo(2)–Mo(1)–Cl(1)	106.27 (7)	Mo(2)–P(2)–C(D1)	112.3 (3)
–Cl(3)	112.65 (7)	C(1)–P(2)–C(C1)	102.5 (4)
–P(1)	96.65 (6)	–C(D1)	111.9 (4)
–P(5)	95.77 (5)	C(C1)–P(2)–C(D1)	105.6 (4)
Cl(1)–Mo(1)–Cl(3)	140.18 (9)	C(1)–P(3)–C(E1)	103.6 (4)
–P(1)	82.38 (8)	–C(F1)	112.1 (4)
–P(5)	89.57 (8)	C(E1)–P(3)–C(F1)	97.2 (4)
Cl(3)–Mo(1)–P(1)	85.08 (8)	Mo(2)–P(4)–C(2)	104.7 (3)
–P(5)	94.54 (8)	–C(G1)	110.4 (3)
P(1)–Mo(1)–P(5)	166.69 (7)	–C(H1)	122.0 (3)
Mo(1)–Mo(2)–Cl(2)	105.88 (7)	C(2)–P(4)–C(G1)	111.1 (4)
–Cl(4)	111.68 (7)	–C(H1)	106.7 (4)
–P(2)	97.52 (6)	C(G1)–P(4)–C(H1)	101.8 (4)
–P(4)	97.70 (6)	Mo(1)–P(5)–C(2)	109.3 (3)
Cl(2)–Mo(2)–Cl(4)	141.60 (9)	–C(I1)	114.5 (3)
–P(2)	88.90 (8)	–C(J1)	113.9 (3)
–P(4)	82.91 (8)	C(2)–P(5)–C(I1)	111.9 (4)
Cl(4)–Mo(2)–P(2)	93.81 (8)	–C(J1)	103.5 (4)
–P(4)	84.45 (8)	C(I1)–P(5)–C(J1)	103.1 (4)
P(2)–Mo(2)–P(4)	164.20 (7)	C(2)–P(6)–C(K1)	102.2 (4)
Mo(1)–P(1)–C(1)	106.4 (3)	–C(L1)	111.7 (4)
–C(A1)	109.4 (3)	C(K1)–P(6)–C(L1)	98.5 (4)
–C(B1)	122.3 (3)	P(1)–C(1)–P(2)	103.6 (4)
C(1)–P(1)–C(A1)	108.8 (4)	–P(3)	113.8 (4)
–C(B1)	107.4 (4)	P(2)–C(1)–P(3)	126.4 (4)
C(A1)–P(1)–C(B1)	102.0 (4)	P(4)–C(2)–P(5)	102.6 (4)
Mo(2)–P(2)–C(1)	109.4 (3)	–P(6)	113.4 (4)
–C(C1)	114.7 (3)	P(5)–C(2)–P(6)	128.0 (4)

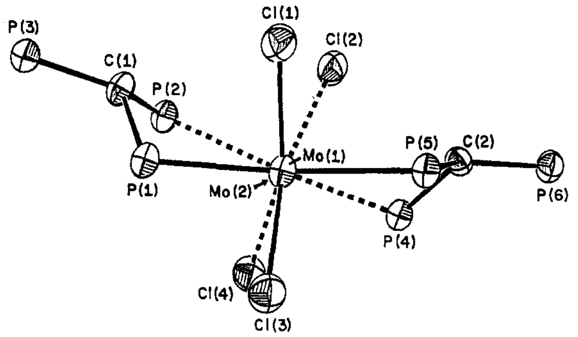

Figure 4. Central portion (including all phosphorus atoms) of the $Mo_2Cl_4(tdpm)_2$ molecule viewed down the Mo(1)–Mo(2) axis.

namely between $Mo_2Cl_8^{4-}$ and $Mo_2Br_8^{4-}$ 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 $Mo_2X_4(picoline)_4$ compounds in which the Mo–Mo distances are 2.153 (6) and 2.150 (2) Å for X = Cl and Br, respectively.

Compound 2. Figure 2 illustrates the molecular geometry and atom-labeling scheme for $Mo_2Cl_4(tdpm)_2$. For clarity, only the phosphorus-bound carbon atoms of the phenyl rings are included in this view; the phenyl carbon atoms are labeled A1–A6, B1–B6, etc., in the list of final atomic positional parameters (Table II). Three disordered CH_2Cl_2 molecules with occupancies of 0.75, 0.70, and 0.55 are present in the lattice; the closest contact between a solvent molecule and the principal molecule is 3.60 (2) Å.

The $Mo_2Cl_4(tdpm)_2$ molecule possesses no crystallographic symmetry and only C_2 idealized symmetry. The C_2 axis perpendicularly bisects the Mo–Mo bond and the two lines that can be drawn between the pairs of nongeminal chlorine atoms. Clearly, only two of the three phosphorus atoms of each tdpm ligand are coordinated to the molybdenum atoms. As in compound **1**, the bridging phosphine ligands are trans to each other and form two envelope-type five-membered rings.

It is pertinent to compare the structure of $Mo_2Cl_4(tdpm)_2$ with the structures of $Mo_2Cl_4(dppm)_2$[2] and $Mo_2Br_4(dppm)_2$ (**1**), since the tdpm and dppm ligands contain the same $Ph_2P–C–PPh_2$ bridging unit. As in the dppm compounds, the bridging ligands in **2** are not symmetrically coordinated since one of the two Mo–P distances associated with each Mo is ca. 0.1 Å longer than the other. The four Mo–Mo–P angles of **2**, however, differ by only 2°, while those of the dppm species vary 4–5°. Interestingly, the rotational conformations of $Mo_2Cl_4(dppm)_2$ and $Mo_2Br_4(dppm)_2$ are eclipsed while that of $Mo_2Cl_4(tdpm)_2$ is partially staggered. Figure 4 clearly illustrates the staggering in $Mo_2Cl_4(tdpm)_2$; the average torsional angle is 20 [3]°. Presumably, the steric bulkiness of the extra PPh_2 group in tdpm vs. dppm causes this twist about the Mo–Mo bond. The large variation of torsional angles (10.7–27.5°) in **2** and some abnormal angles about the central carbon atoms of each tdpm ligand (P(2)–C(1)–P(3) = 126.4 (4)° and P(5)–C(2)–P(6) = 128.0 (4)°) are indications that steric effects do indeed exert a profound influence upon the structure of this compound.

Dependence of Mo–Mo Bond Length on Torsional Angle. As is well-known,[11] the strength of the δ component of the Mo–Mo quadruple bond varies with cos (2χ), where χ is the angle of torsional twist away from an eclipsed conformation. With structural results for three $Mo_2X_4(LL)_2$ compounds, it was recently shown[1] that the Mo–Mo bond distance in these compounds also varies linearly with cos (2χ), χ being calculated as the algebraic average of the four smallest torsional angles about the Mo–Mo axis. Since the publication of that report, workers in this laboratory have structurally charac-

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(10) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; Table 3.1.1, p 89 and references cited therein.

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

Table VI. Summary of Metal–Metal Bond Distances and Average Torsional Angles in Structurally Characterized $Mo_2X_4(LL)_2$ Compounds

compd	Mo–Mo dist, Å	χ, deg	cos (2χ)
(A) $Mo_2Cl_4(dppm)_2 \cdot 2C_3H_6O^a$	2.138 (1)	0.0	1.0
(B) $Mo_2Br_4(dppm)_2 \cdot 2THF^b$	2.138 (1)	0.0	1.0
(C) $Mo_2Cl_4(tdpm)_2 \cdot 2CH_2Cl_2{}^b$	2.148 (1)	20 [3]^c	0.77 (7)
(D) $Mo_2Br_4(dppb)_2{}^d$	2.150 [3]^e	21.7 [2]^e	0.726 [5]
(E) $Mo_2Cl_4(dppb)_2{}^f$	2.150 (3)	24.6 [12]	0.65 (3)
(F) $Mo_2Br_4(arphos)_2{}^g$	2.167 (4)	30.3 [3]	0.491 (1)
(G) β-$Mo_2Cl_4(dppe)_2{}^h$	2.183 (3)	30.5 [5]	0.48 (2)
(H) β′-$Mo_2Cl_4(dmpe)_2{}^i$	2.168 (1)	33.8 (2)	0.381 (6)
(I) β-$Mo_2Br_4(dmpe)_2{}^i$	2.169 (2)	36.5 [3]	0.292 (10)
(J) β-$Mo_2Cl_4(dmpe)_2{}^j$	2.183 (3)	40.0 [1]	0.174 (3)

[a] Reference 2. [b] This paper. [c] A number in parentheses is an esd for a given individual values, while a number in brackets is equal to $[\Sigma_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith of n values from the arithmetic mean of the n values. [d] Reference 13. [e] Average of values for two independent dimers. [f] Reference 12. [g] Reference 11. [h] Reference 14. [i] Reference 15. [j] Reference 1.

terized several more $Mo_2X_4(LL)_2$ species. Along with **1** and **2** described above, these "new" compounds include $Mo_2X_4(dppb)_2$ (X = Cl,[12] Br;[13] dppb = 2,3-bis(diphenylphosphino)butane), β-$Mo_2Cl_4(dppe)_2$[14] (dppe = 1,2-bis(diphenylphosphino)ethane), β-$Mo_2Br_4(dmpe)_2$[15] (dmpe = 1,2-bis(dimethylphosphino)ethane), and a new form of β-$Mo_2Cl_4(dmpe)_2$.[15] We report here an updated analysis of the dependence of Mo–Mo bond length on torsional angle.

Table VI lists all of the relevant data now available, and a new plot of Mo–Mo bond distance vs. cos (2χ) is given in Figure 5. Although a straight line is drawn through the data points, the correlation coefficient of this line, −0.916, is considerably lower than that (−0.999) in the previously published plot. This suggests that still other factors, besides the angle χ, may play a role in determining the bond length. In any event, there is at least a monotonic relationship between Mo–Mo bond length and cos (2χ), and it is useful to describe it as linear. The y intercept of the plot in Figure 5 corresponds to the Mo–Mo distance in a totally staggered structure (χ = 45°), and this extrapolated value is 2.192 Å. Thus, the overall change in Mo–Mo distance on going from a full δ bond to no δ bond is 0.054 Å.

One compound, $Mo_2Cl_4(dppe)_2$, gives a data point (G) that is in particularly poor agreement with the line in Figure 5. We can find no good reason for this other than the presence of disorder that introduces inaccuracy in the Mo–Mo distance. This disorder (the presence of a second, minor Mo–Mo unit perpendicular to the main one) is also found in three other structures: $Mo_2Br_4(arphos)_2$ (F) and both forms of β-$Mo_2Cl_4(dmpe)_2$ (H, J). A plot of the six compounds that do not contain this disorder yields a line with a correlation coefficient of −0.9931 and a y intercept of 2.181 Å.

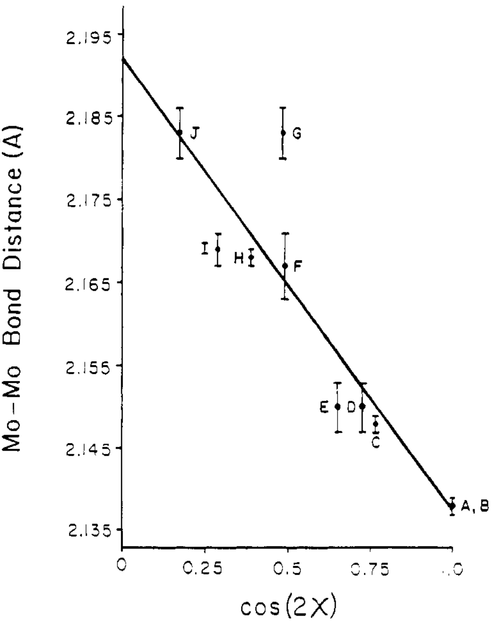

Figure 5. Plot of Mo–Mo bond length vs. the cosine of twice the torsional angle (χ) for 10 similar molybdenum dimers. Esd's for the bond lengths are represented by vertical bars. Key: A, $Mo_2Cl_4(dppm)_2 \cdot 2C_3H_6O$; B, $Mo_2Br_4(dppm)_2 \cdot 2THF$; C, $Mo_2Cl_4(tdpm)_2 \cdot 2CH_2Cl_2$; D, $Mo_2Br_4(dppb)_2$; E, $Mo_2Cl_4(dppb)_2$; F, $Mo_2Br_4(arphos)_2$; G, β-$Mo_2Cl_4(dppe)_2$; H, β′-$Mo_2Cl_4(dmpe)_2$; I, β-$Mo_2Br_4(dmpe)_2$; J, β-$Mo_2Cl_4(dmpe)_2$.

It is noteworthy that the $Mo_2X_4(LL)_2$ compounds for which LL forms a three-atom bridge have a small torsional twist, while the rest of the compounds (with four-atom bridges) all have a larger twist. This is what one would expect considering the conformational preferences of five- vs. six-membered rings. Apparently, the presence of methyl groups on the phosphorus atoms of the four-atom bridges causes more staggering than that of phenyl groups. The steric and electronic differences between methyl and phenyl groups appear to have minimal effects on Mo–Mo bond length and possibly cancel each other.

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Registry No. **1**, 92763-67-2; **2**, 92763-68-3; $Mo_2(OCCH_3)_4$, 14221-06-8; $(NH_4)_5Mo_2Cl_9$, 61583-95-7; Mo, 7439-98-7.

Supplementary Material Available: Details of the data collection and structure solution and refinement for the compounds **1** and **2** along with complete tables of anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

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(12) Agaskar, P.; Cotton, F. A., unpublished results.
(13) Agaskar, P.; Cotton, F. A., unpublished results.
(14) Agaskar, P.; Cotton, F. A. *Inorg. Chem.*, in press.
(15) Campbell, F. L.; Cotton, F. A.; Powell, G. L., submitted for publication in *Inorg. Chem.*