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A Partly Staggered Quadruple Bond in Tetrabromobis(1-diphenylphosphino-2-diphenylarsinoethane)dimolybdenum(II)

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Abstract: The crystal structure of the title compound has been determined. The arphos ligands are bridging and the As and P atoms are disordered. Each Mo atom is coordinated by two Br atoms and two P/As atoms in a trans arrangement. The two approximately square ligand atom sets are rotated away from a completely eclipsed configuration by about 30°. Alternatively stated, the rotational conformation is within about 15° of being fully staggered. The implications of this for the metal-metal bonding are discussed; briefly, the δ component of that bond, though weakened, is retained. The Mo-Mo bond length is 2.167 (4) Å. Crystallographic data follow: space group $P2_1/n$; $a = 23.387$ (9) Å, $b = 13.327$ (3) Å, $c = 16.932$ (5) Å; $\beta = 106.72$ (3)°; $Z = 4$.

Introduction

As is now well known,[2] quadruple bonds are formed between pairs of transition metal atoms such as Cr, Mo, W, Tc, and Re in a large number of compounds. It is also well known that the strength of the δ component of such bonds is dependent upon the rotational conformation in such a way that its strength is maximal for the perfectly eclipsed configuration and goes to zero for the fully staggered configuration. Two clear implications of this are that (a) no perfectly staggered structure of the X_4M-MX_4 type can have a δ bond, and (b) species of the X_4M-MX_4 type which do have quadruple bonds will tend to have rotational conformations that are as close to eclipsed as possible. Perfect eclipsing is often opposed to some extent by other forces and thus small rotations, say 1-10°, away from perfect eclipsing would not be surprising. They have in several cases been observed, and will be discussed later.

Recently, molybdenum compounds have been prepared with bidentate phosphorus and arsenic ligands whose powder patterns suggested that they are isomorphous with the markedly staggered, triply bonded compound, $Re_2Cl_4(diphos)_2$.[3,4] However, as these compounds contain molybdenum(II) and are diamagnetic, they should possess a quadruple bond. To clarify this seemingly contradictory situation and to investigate the effect of an appreciably staggered configuration on the metal-metal bond length it was clearly desirable to obtain the crystal structure of one of these species. We report here the crystal structure of $Mo_2Br_4(arphos)_2$, where arphos represents the ligand $Ph_2PCH_2CH_2AsPh_2$.

Experimental Section

The compound $Mo_2Br_4(arphos)_2$ was prepared as previously described.[5] Suitable crystals were obtained directly from the preparation. The crystals displayed no noticeable sensitivity to air and were handled with no special precautions.

X-ray Data Collection. An irregular crystal approximately 0.3 × 0.2 × 0.2 mm was selected, attached with epoxy cement to a glass fiber, and mounted on a Syntex P$\bar{1}$ automated diffractometer. All data were collected at 22 ± 2 °C using Mo Kα radiation monochromated by a graphite crystal mounted in the incident beam. Details of crystallographic procedures have been described previously.[6,7] The cell dimensions based on a least-squares fit of 15 centered reflections in the range $16 < 2\theta < 28°$ were $a = 23.387$ (9) Å, $b = 13.327$ (5) Å, $c = 16.932$ (5) Å, $\beta = 106.72$ (3)°; $V = 5054$ (5) Å^3; $Z = 4$; $d_{calcd} = 1.835$ g cm^{-3}.

A total of 6932 unique reflections were collected using the θ-2θ scan technique in the range of $0° < 2\theta \leq 45°$. Variable scan rates from 4 to 24° min^{-1} were used and the scan width extended from 0.9° below Mo Kα_1 to 0.9° above Mo Kα_2. Three standard reflections were measured after every 97 reflections and displayed only small random variations in intensity.

Solution and Refinement of the Structure. All calculations were carried out using the Enraf-Nonius structure determination package on a PDP 11/45 computer located at Molecular Structure Corp., College Station, Texas. The absorption coefficient of 53.1 cm^{-1} made an absorption correction necessary. Because of the irregular shape of the crystal an empirical correction based on the average of six sets of Ψ scans ($\Psi = 0$-360° at 10° intervals) was carried out. The maximum, minimum, and average values of the relative transmission were 1.00, 0.61, and 0.80, respectively. As in the rhenium compound[4] the systematic absences indicated space group $P2_1/n$. The structure was solved using only those 2414 reflections having $F_o^2 > 2.5\sigma(F_o^2)$.

Because of the preponderance of heavy atoms, no attempt was made to use heavy-atom techniques. Instead the initial positions for the molybdenum and bromine atoms were taken to be those of the rhenium and chlorine atoms, respectively, in $Re_2Cl_4(diphos)_2$. After three cycles of least-squares refinement the discrepancy indices were

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.373$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.477$$

The function minimized during the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w equals $4F_o^2/\sigma(F_o^2)^2$. A value of 0.07 was used for the "ignorance parameter," p, in the calculation[7] of σ.

A difference Fourier map based on this phasing displayed four strong peaks of nearly equal intensity with coordinates similar to those for the phosphorus atoms in the isomorphous rhenium compound, suggesting that the arsenic and phosphorus atoms are randomly disordered. Refinement was continued with the multiplicity of both phosphorus and arsenic atoms set at 0.5 and with all phosphorus parameters fixed and set equal to those of the corresponding arsenic atom after each least-squares cycle. No attempt was made at any time to refine the arsenic and phosphorus atoms independently.

The next two largest peaks in the difference map were clearly those of disordered molybdenum atoms again similar in position to those observed in $Re_2Cl_4(diphos)_2$. These were refined initially by allowing their multiplicities to be independent variables during least-squares refinement. After all the carbon atoms were located the method of refinement was changed. The multiplicity of Mo(2) was set equal to that of Mo(1) after each cycle and the multiplicities of Mo(3) and Mo(4) were set to one minus the multiplicity of Mo(1). Appropriate corrections were also made to the derivative of the varying multiplicity during least-squares refinement. After three cycles of such refinement with all atoms included, no atom shifted position by more than 0.001 Å and the multiplicity had converged to 0.765. The final discrepancy indices were $R_1 = 0.075$, $R_2 = 0.081$ and the final error in the estimated standard deviation in an observation of unit weight was equal to 1.402.

Results

The positional and thermal parameters for all atoms in the asymmetric unit are listed in Table I. The atomic parameters

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*X*	*Y*	*Z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mo(1)	0.3066(1)	0.2995(2)	−0.0125(2)	3.3(1)	2.4(1)	4.0(1)	0.2(1)	1.3(1)	−0.1(1)
Mo(2)	0.2496(1)	0.2026(2)	0.0346(2)	3.4(1)	2.3(1)	4.0(1)	0.0(1)	1.3(1)	0.0(1)
Mo(3)	0.2408(4)	0.2826(8)	−0.0261(6)	3.9(5)	4.3(5)	4.4(5)	0.4(5)	1.5(4)	0.2(5)
Mo(4)	0.3170(4)	0.2250(8)	0.0633(6)	3.5(4)	3.9(5)	5.6(5)	0.1(5)	1.9(4)	−0.4(5)
Br(1)	0.2603(1)	0.4659(2)	−0.0655(2)	5.4(1)	3.2(1)	5.3(1)	0.1(1)	1.5(1)	0.2(1)
Br(2)	0.4066(1)	0.2262(2)	0.0009(2)	4.2(1)	4.6(2)	6.9(2)	0.6(1)	2.4(1)	0.6(1)
Br(3)	0.2858(1)	0.1662(2)	0.1891(2)	6.1(2)	5.5(2)	4.8(1)	0.7(1)	1.7(1)	0.4(1)
Br(4)	0.1582(1)	0.1515(2)	−0.0739(2)	4.4(1)	5.2(2)	7.2(2)	−0.4(1)	0.9(1)	−1.1(2)
As(1)	0.3520(3)	0.3990(5)	0.1253(4)	4.5(3)	4.8(3)	7.1(3)	−0.8(3)	1.8(3)	−2.2(3)
As(3)	0.2785(3)	0.2240(4)	−0.1621(3)	7.3(3)	3.8(3)	4.0(3)	1.6(3)	1.0(3)	−0.2(3)
As(4)	0.2958(3)	0.0345(4)	0.0032(4)	8.0(4)	3.2(3)	6.6(3)	1.1(3)	2.8(3)	0.0(3)
As(2)	0.1924(2)	0.3468(5)	0.0857(4)	3.8(3)	5.3(3)	6.1(3)	−0.3(3)	2.4(2)	−2.1(3)
C(1)	0.291(1)	0.476(2)	0.154(2)	7.2(8)					
C(2)	0.246(1)	0.426(2)	0.176(2)	7.7(9)					
C(3)	0.306(1)	0.085(2)	−0.159(2)	8.1(9)					
C(4)	0.279(1)	0.018(2)	−0.115(2)	7.1(8)					
C(5)	0.400(1)	0.499(2)	0.098(2)	6.0(8)					
C(6)	0.380(1)	0.593(2)	0.077(2)	6.5(8)					
C(7)	0.419(1)	0.664(2)	0.060(2)	6.8(8)					
C(8)	0.477(1)	0.646(2)	0.070(2)	8.1(9)					
C(9)	0.497(1)	0.550(3)	0.087(2)	8.6(10)					
C(10)	0.459(1)	0.476(2)	0.108(2)	6.2(8)					
C(11)	0.405(1)	0.353(2)	0.224(2)	8.0(9)					
C(12)	0.427(1)	0.252(2)	0.224(2)	8.2(9)					
C(13)	0.475(2)	0.229(3)	0.299(2)	10.4(11)					
C(14)	0.491(2)	0.292(3)	0.361(2)	10.7(11)					
C(15)	0.471(2)	0.375(3)	0.363(2)	10.5(11)					
C(16)	0.426(2)	0.419(3)	0.288(2)	10.9(12)					
C(17)	0.143(1)	0.290(2)	0.143(1)	5.0(7)					
C(18)	0.155(1)	0.297(3)	0.230(2)	7.8(9)					
C(19)	0.113(1)	0.254(3)	0.264(2)	9.0(10)					
C(20)	0.064(1)	0.202(2)	0.218(2)	7.4(8)					
C(21)	0.055(1)	0.187(3)	0.134(2)	8.2(9)					
C(22)	0.097(1)	0.229(2)	0.099(2)	6.8(8)					
C(23)	0.138(1)	0.442(2)	0.025(2)	6.3(8)					
C(24)	0.113(1)	0.518(2)	0.065(2)	7.3(9)					
C(25)	0.070(1)	0.574(3)	0.012(2)	8.3(9)					
C(26)	0.050(1)	0.571(2)	−0.069(2)	8.1(9)					
C(27)	0.074(1)	0.498(3)	−0.111(2)	8.2(9)					
C(28)	0.115(1)	0.431(2)	−0.060(2)	7.1(8)					
C(29)	0.373(1)	−0.009(2)	0.053(2)	5.4(7)					
C(30)	0.410(1)	−0.050(2)	0.005(2)	8.0(9)					
C(31)	0.465(1)	−0.077(2)	0.049(2)	6.9(8)					
C(32)	0.488(1)	−0.079(2)	0.131(2)	6.8(8)					
C(33)	0.451(1)	−0.042(3)	0.179(2)	8.4(9)					
C(34)	0.394(1)	−0.008(2)	0.141(2)	7.1(8)					
C(35)	0.254(1)	−0.080(2)	0.029(2)	5.6(7)					
C(36)	0.214(1)	−0.062(2)	0.069(2)	6.9(8)					
C(37)	0.182(1)	−0.150(3)	0.090(2)	9.6(10)					
C(38)	0.198(1)	−0.238(3)	0.065(2)	9.1(10)					
C(39)	0.236(2)	−0.259(3)	0.020(2)	11.1(12)					
C(40)	0.267(1)	−0.177(3)	−0.003(2)	9.3(10)					
C(41)	0.201(1)	0.232(2)	−0.239(2)	5.7(7)					
C(42)	0.170(1)	0.316(2)	−0.240(1)	4.6(6)					
C(43)	0.109(1)	0.326(2)	−0.299(2)	7.6(9)					
C(44)	0.090(1)	0.243(2)	−0.350(2)	8.1(9)					
C(45)	0.125(2)	0.161(3)	−0.350(2)	9.9(10)					
C(46)	0.184(1)	0.155(3)	−0.295(2)	8.8(10)					
C(47)	0.327(1)	0.280(2)	−0.255(2)	5.4(7)					
C(48)	0.349(1)	0.374(2)	−0.212(2)	7.8(9)					
C(49)	0.381(1)	0.420(3)	−0.259(2)	9.2(10)					
C(50)	0.392(1)	0.363(3)	−0.322(2)	9.4(10)					
C(51)	0.374(2)	0.275(3)	−0.344(2)	12.5(13)					
C(52)	0.341(2)	0.223(3)	−0.286(2)	12.6(13)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

for the two metal atoms Mo(3) and Mo(4), in the secondary orientation of the molecule, are also included. The designations As(1)–As(4) are used for simplicity to identify the 0.5As/0.5P combination assigned to each of these sites because of the ligand disorder. The scattering factor for each is the sum of half that for P and half that for As; the positional and thermal parameters for each half-atom at each site are identical.

Because there is more than one way in which the observed

Table II. Interatomic Distances and Angles for $Mo_2(arphos)_2Br_4$ [a,b]

	Distances, Å		
Mo(1)-Mo(2)	2.167(4)	Mo(3)-Mo(4)	2.123(13)
Mo(1)-Br(1)	2.518(4)	Mo(3)-Br(1)	2.60(1)
Mo(1)-Br(2)	2.482(4)	Mo(4)-Br(2)	2.604(9)
Mo(2)-Br(3)	2.554(4)	Mo(4)-Br(3)	2.57(1)
Mo(2)-Br(4)	2.480(4)	Mo(3)-Br(4)	2.56(1)
Mo(1)-As(1)	2.628(6)	Mo(4)-As(1)	2.58(1)
Mo(2)-As(2)	2.625(6)	Mo(3)-As(2)	2.61(1)
Mo(1)-As(3)	2.627(6)	Mo(3)-As(3)	2.80(1)
Mo(2)-As(4)	2.608(6)	Mo(4)-As(4)	2.73(1)
As(1)-C(1)	1.92(3)	As(3)-C(3)	1.95(3)
As(1)-C(5)	1.88(3)	As(3)-C(41)	1.90(2)
As(1)-C(11)	1.87(3)	As(3)-C(47)	1.91(3)
As(2)-C(2)	1.98(3)	As(4)-C(4)	1.93(3)
As(2)-C(17)	1.88(2)	As(4)-C(29)	1.85(2)
As(2)-C(23)	1.88(3)	As(4)-C(35)	1.94(3)
C(1)-C(2)	1.39(3)	C(3)-C(4)	1.42(3)
C(5)-C(6)	1.36(3)	C(11)-C(12)	1.45(4)
C(6)-C(7)	1.39(3)	C(12)-C(13)	1.47(4)
C(7)-C(8)	1.36(4)	C(13)-C(14)	1.31(4)
C(8)-C(9)	1.35(4)	C(14)-C(15)	1.21(4)
C(9)-C(10)	1.44(4)	C(15)-C(16)	1.51(4)
C(10)-C(5)	1.37(3)	C(16)-C(11)	1.37(4)
C(17)-C(18)	1.42(3)	C(23)-C(24)	1.44(3)
C(18)-C(19)	1.38(4)	C(24)-C(25)	1.37(3)
C(19)-C(20)	1.38(3)	C(25)-C(26)	1.32(4)
C(20)-C(21)	1.39(3)	C(26)-C(27)	1.42(4)
C(21)-C(22)	1.41(3)	C(27)-C(28)	1.41(3)
C(22)-C(17)	1.39(3)	C(28)-C(23)	1.39(3)
C(29)-C(30)	1.46(3)	C(35)-C(36)	1.33(3)
C(30)-C(31)	1.35(3)	C(36)-C(37)	1.48(4)
C(31)-C(32)	1.34(3)	C(37)-C(38)	1.34(4)
C(32)-C(33)	1.44(4)	C(38)-C(39)	1.36(4)
C(33)-C(34)	1.38(3)	C(39)-C(40)	1.43(4)
C(34)-C(29)	1.41(3)	C(40)-C(35)	1.46(4)
C(41)-C(42)	1.34(3)	C(47)-C(48)	1.35(3)
C(42)-C(43)	1.49(3)	C(48)-C(49)	1.40(4)
C(43)-C(44)	1.40(3)	C(49)-C(50)	1.38(4)
C(44)-C(45)	1.36(4)	C(50)-C(51)	1.25(4)
C(45)-C(46)	1.43(4)	C(51)-C(52)	1.46(4)
C(46)-C(41)	1.38(3)	C(52)-C(47)	1.40(4)
	Angles, deg		
Mo(2)-Mo(1)-Br(1)	114.1(1)	Mo(4)-Mo(3)-Br(1)	110.4(4)
Mo(2)-Mo(1)-Br(2)	113.3(1)	Mo(3)-Mo(4)-Br(2)	108.5(5)
Mo(1)-Mo(2)-Br(3)	115.7(1)	Mo(3)-Mo(4)-Br(3)	108.8(4)
Mo(1)-Mo(2)-Br(4)	112.4(2)	Mo(4)-Mo(3)-Br(4)	112.4(5)
Mo(2)-Mo(1)-As(1)	96.2(2)	Mo(3)-Mo(4)-As(1)	93.9(4)
Mo(1)-Mo(2)-As(2)	96.4(2)	Mo(4)-Mo(3)-As(2)	92.9(4)
Mo(2)-Mo(1)-As(3)	96.7(2)	Mo(4)-Mo(3)-As(3)	95.0(4)
Mo(1)-Mo(2)-As(4)	95.8(2)	Mo(3)-Mo(4)-As(4)	92.6(4)
Br(1)-Mo(1)-Br(2)	132.6(1)	Br(1)-Mo(3)-Br(4)	137.0(4)
Br(1)-Mo(1)-As(1)	83.9(2)	Br(1)-Mo(3)-As(2)	91.3(3)
Br(1)-Mo(1)-As(3)	91.8(2)	Br(1)-Mo(3)-As(3)	95.0(4)
Br(2)-Mo(1)-As(1)	89.3(2)	Br(4)-Mo(3)-As(2)	90.5(3)
Br(2)-Mo(1)-As(3)	84.6(2)	Br(4)-Mo(3)-As(3)	86.4(3)
As(1)-Mo(1)-As(3)	167.0(2)	As(2)-Mo(3)-As(3)	172.1(4)
Br(3)-Mo(2)-Br(4)	131.9(2)	Br(2)-Mo(4)-Br(3)	142.5(4)
Br(3)-Mo(2)-As(2)	81.5(2)	Br(2)-Mo(4)-As(1)	87.8(3)
Br(3)-Mo(2)-As(4)	90.6(2)	Br(2)-Mo(4)-As(4)	86.3(3)
Br(4)-Mo(2)-As(2)	91.9(2)	Br(3)-Mo(4)-As(1)	94.0(3)
Br(4)-Mo(2)-As(4)	86.1(2)	Br(3)-Mo(4)-As(4)	87.7(3)
As(2)-Mo(2)-As(4)	167.5(2)	As(1)-Mo(4)-As(4)	172.4(4)
Mo(1)-As(1)-C(1)	110.7(9)	Mo(4)-As(1)-C(1)	114.2(9)
Mo(1)-As(1)-C(5)	99.6(6)	Mo(4)-As(1)-C(5)	92.0(6)
Mo(1)-As(1)-C(11)	105.0(8)	Mo(4)-As(1)-C(11)	132.8(9)
Mo(2)-As(2)-C(2)	112.2(9)	Mo(3)-As(2)-C(2)	115.23(9)
Mo(2)-As(2)-C(17)	109.1(8)	Mo(3)-As(2)-C(17)	135.0(8)
Mo(2)-As(2)-C(22)	99.4(6)	Mo(3)-As(2)-C(22)	113.6(6)
Mo(1)-As(3)-C(3)	110.4(9)	Mo(3)-As(3)-C(3)	114.8(9)
Mo(1)-As(3)-C(41)	124.4(9)	Mo(3)-As(3)-C(41)	95.0(8)
Mo(1)-As(3)-C(47)	111.3(8)	Mo(3)-As(3)-C(47)	136.4(9)
Mo(2)-As(4)-C(4)	109.8(8)	Mo(4)-As(4)-C(4)	117.0(9)
Mo(2)-As(4)-C(29)	125.6(8)	Mo(4)-As(4)-C(29)	94.1(8)
Mo(2)-As(4)-C(35)	111.3(9)	Mo(4)-As(4)-C(35)	134.4(9)

Table II (*Continued*)

As(1)-C(1)-C(2)	119(2)	As(3)-C(3)-C(4)	115(2)
As(2)-C(2)-C(1)	114(2)	As(4)-C(4)-C(3)	119(2)
As(1)-C(5)-C(6)	123(2)	As(1)-C(11)-C(12)	117(3)
As(1)-C(5)-C(10)	118(2)	As(1)-C(11)-C(16)	119(3)
C(6)-C(5)-C(10)	119(3)	C(12)-C(11)-C(16)	123(3)
C(5)-C(6)-C(7)	120(2)	C(11)-C(12)-C(13)	112(3)
C(6)-C(7)-C(8)	123(3)	C(12)-C(13)-C(14)	122(4)
C(7)-C(8)-(9)	117(3)	C(13)-C(14)-C(15)	126(4)
C(8)-C(9)-C(10)	120(3)	C(14)-C(15)-C(16)	121(4)
C(9)-C(10)-C(5)	119(3)	C(15)-C(16)-C(11)	115(3)
As(2)-C(17)-C(18)	123(2)	As(2)-C(23)-C(24)	121(2)
As(2)-C(17)-C(22)	117(2)	As(2)-C(23)-C(28)	120(2)
C(18)-C(17)-C(22)	119(3)	C(24)-C(23)-C(28)	118(3)
C(17)-C(18)-C(19)	117(3)	C(23)-C(24)-C(25)	114(3)
C(18)-C(19)-C(20)	123(3)	C(24)-C(25)-C(26)	129(3)
C(19)-C(20)-C(21)	121(3)	C(25)-C(26)-C(27)	119(3)
C(20)-C(21)-C(22)	117(3)	C(26)-C(27)-C(28)	115(3)
C(21)-C(22)-C(17)	123(3)	C(27)-C(28)-C(23)	124(3)
As(4)-C(29)-C(30)	121(2)	As(4)-C(35)-C(36)	117(2)
As(4)-C(29)-C(34)	119(2)	As(4)-C(35)-C(40)	116(2)
C(30)-C(29)-C(34)	120(3)	C(36)-C(35)-C(40)	127(3)
C(29)-C(30)-C(31)	115(2)	C(35)-C(36)-C(37)	117(3)
C(30)-C(31)-C(32)	128(3)	C(36)-C(37)-C(38)	114(3)
C(31)-C(32)-C(33)	117(3)	C(37)-C(38)-C(39)	130(4)
C(32)-C(33)-C(24)	120(3)	C(38)-C(39)-C(40)	117(4)
C(33)-C(34)-C(29)	120(3)	C(39)-C(40)-C(35)	114(3)
As(3)-C(41)-C(42)	118(2)	As(3)-C(47)-C(48)	122(2)
As(3)-C(41)-C(46)	118(2)	As(3)-C(47)-C(52)	120(3)
C(42)-C(41)-C(46)	124(3)	C(48)-C(47)-C(52)	118(3)
C(41)-C(42)-C(43)	120(2)	C(47)-C(48)-C(49)	125(3)
C(42)-C(43)-C(44)	114(3)	C(48)-C(49)-C(50)	116(3)
C(43)-C(44)-C(45)	123(3)	C(49)-C(50)-C(51)	122(4)
C(44)-C(45)-C(46)	121(3)	C(50)-C(51)-C(52)	125(4)
C(45)-C(46)-C(41)	117(3)	C(51)-C(52)-C(47)	115(4)

[a] Figures in parentheses represent the estimated standard deviation of the last significant digit. [b] All atoms designated, for simplicity, As are actually 50% As and 50% P refined with identical parameters.

disordering of the phosphorus and arsenic atoms might be interpreted, it is impossible to state what the molecular symmetry is. It is possible that in each molecule both arsenic atoms are attached to the same molybdenum atom; the molecule would then have a C_2 axis collinear with the Mo-Mo bond. Alternatively, each molybdenum atom might have one phosphorus atom and one arsenic atom attached to it; the molecule would again have a C_2 axis but it would now be perpendicular to the Mo-Mo bond. The random disorder of the P and As atoms in the crystal might result from disordering of either of these structures or from random mixing of both. The experimental data cannot discriminate among these possibilities. In effect, the disorder leads to "apparent virtual" symmetry D_2.

The metal-metal separation between the principal molybdenum atoms is 2.167 (4) Å while for the disordered pair of molybdenum atoms it is 2.123 (13) Å. The high uncertainty in the Mo(3)-Mo(4) distance makes this apparent difference problematical. Figure 1 shows the coordination around the principal molybdenum atoms as viewed down the metal-metal axis. Figure 2 provides the same view for the disordered pair. As in all ORTEP drawings in this paper the atoms are represented by 50% probability ellipsoids. Table II gives the bond distances and bond angles. Table III provides the torsional angles between the bromine and nearest arsenic/phosphorus atom bound to the other molybdenum. It is clear that the geometries for both types of molecules are nearly identical. The relationship between the two molecular orientations is illustrated in Figure 3. The ligand distances for the disordered molybdenum atoms in several cases are rather large. This suggests that the ligand positions in the disordered molecules may be slightly different than for the primary orientation. Since data were recorded only to 45° in 2θ, the resolution is insufficient to sort out such small displacements. As the

Table III. Torsional Angles

plane 1	plane 2	angle, deg
Mo(2)-Mo(1)-Br(1)	Mo(1)-Mo(2)-As(P)(2)	30.6
Mo(2)-Mo(1)-Br(2)	Mo(1)-Mo(2)-As(P)(4)	29.7
Mo(2)-Mo(1)-As(P)(1)	Mo(1)-Mo(2)-Br(3)	29.8
Mo(2)-Mo(1)-As(P)(3)	Mo(1)-Mo(2)-Br(4)	30.9
	av	30.3 ± 0.6
Mo(4)-Mo(3)-Br(1)	Mo(3)-Mo(4)-As(P)(1)	28.7
Mo(4)-Mo(3)-Br(4)	Mo(3)-Mo(4)-As(P)(4)	28.5
Mo(4)-Mo(3)-As(P)(2)	Mo(3)-Mo(4)-Br(3)	31.8
Mo(4)-Mo(3)-As(P)(3)	Mo(3)-Mo(4)-Br(2)	27.4
	av	29.1 ± 1.9

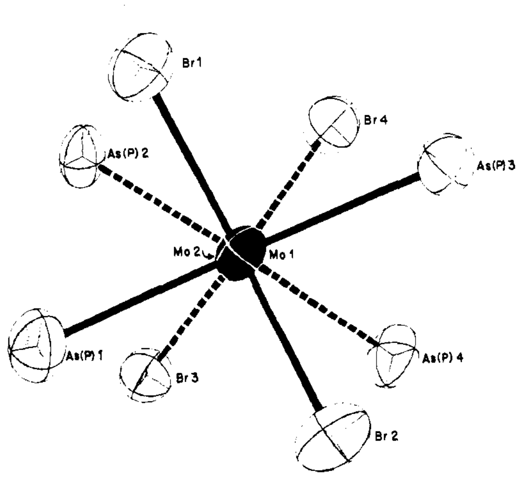

Figure 1. The coordination and rotational conformations for the principal orientation as viewed down the Mo-Mo axis. Thermal ellipsoids are drawn at the 50% probability level.

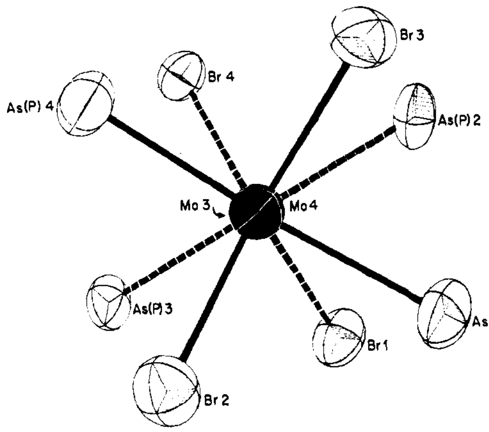

Figure 2. The coordination and rotational conformations for the secondary orientation as viewed down the Mo-Mo axis.

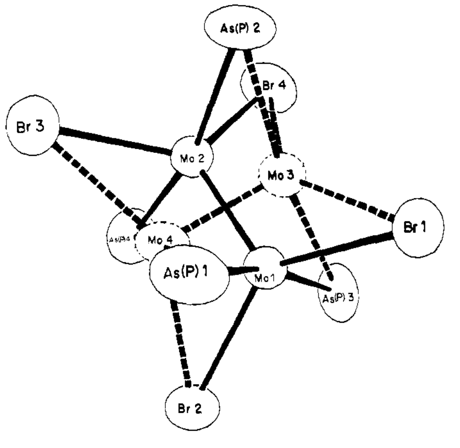

Figure 3. The relation between the two orientations of the molecule.

crystals of this compound do not diffract well at high angles in 2*θ*, it was not possible to obtain data that would give appreciably higher resolution.

A complete view of the molecule is given in Figure 4. The numbering system used is the same as that in the isomorphous $Re_2Cl_4(diphos)_2$.[4] The same type of chair conformation is found in the six-membered rings. A major difference between the two structures is in the extent of staggering. The mean torsional angle in the rhenium compound is 39° whereas it is only 30° for this molybdenum compound. Another important difference is the amount of disordering. The fractional amount of disorder was only 7% for the rhenium complex[4] while here it is 23.5%.

Discussion

In the vast majority of species with quadruple bonds, the rotational conformation in the crystalline compound is rigorously eclipsed according to the operational definition of rotational conformation that we use. That operational definition is as follows. Each of the four independent, smallest torsional angles is calculated and these are averaged algebraically. If the result is zero the conformation is eclipsed. If the result is nonzero, that value is said to be the angle of rotation away from the eclipsed configuration. This procedure and these definitions enable us to cope with cases where the cis L-M-L′ angles are not all equal but it can be perfectly well applied to those cases where they are.

The reason why the overwhelming majority of structures are perfectly eclipsed by the above definition is because there is a crystallographic symmetry element, either a center of inversion or a mirror plane either bisecting or containing the M-M axis. Regardless of how much the ML_4 unit making up half of the M_2L_8 species may deviate from having local fourfold symmetry, the average torsional angle has to be zero if one of these three crystallographic symmetry elements exists.

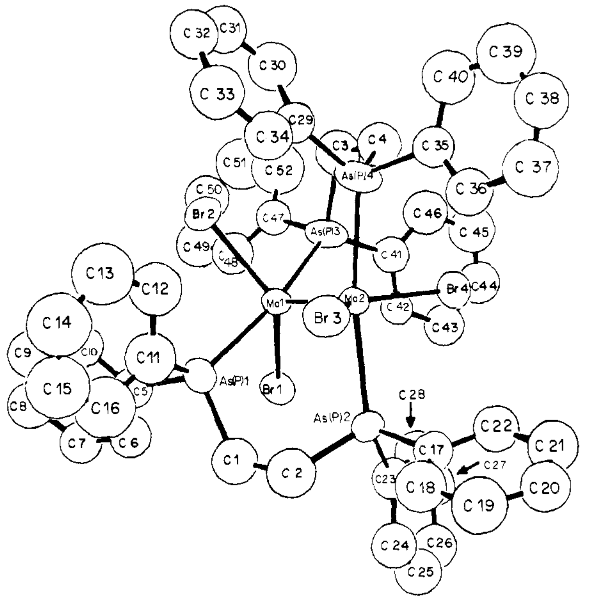

Figure 4. A view of $Mo_2Br_4(arphos)_2$. Projections of thermal ellipsoids and spheres are drawn at the 50% probability level.

The cases in which there is no crystallographic constraint that imposes the eclipsed conformation, and in which the ligands themselves do not tend strongly to impose it (as does, for example, a set of four carboxyl groups, four 2-oxopyridine groups, or the like), are few. The only two we are aware of are $Mo_2(Ph_2PCH_2PPh_2)_2(NCS)_4$,[8] where the average torsional angle is 13°, and $Re_2(PHNCPhNPh)_2Cl_4{\cdot}THF$,[9] where it is 6°. In both of these compounds the oxidation numbers of the metal atoms, the diamagnetism of the compounds, and the lengths of the M-M bonds are such that there seems no reason to question the presence of quadruple bonds. Nor is it to be expected, as we have already noted,[8] that a twist of 6° or even 13° would seriously weaken let alone destroy the *δ* bond.

However, a twist as great as 30° does require us to consider this possibility more carefully. The compound $Mo_2(arphos)_2Br_4$ is diamagnetic and the Mo-Mo bond length of 2.167 (4) Å is only ca. 0.03 Å longer than those found in the $Mo_2X_8^{4-}$ species with X = Cl (2.13-2.15 Å[2a]), X = Br (2.135 Å[10]), and X = CH_3 (2.147 Å[2a]). These features imply but do not prove that the *δ* bond has been retained despite the 30° twist angle. It is pertinent to enquire whether it is reasonable to believe that sufficient *δ* overlap could persist in this structure to stabilize a δ^2 electron configuration. To do this we must examine how the *δ* overlap varies as a function of twist angle *χ*, defined as zero for the perfectly eclipsed conformation. If we factor out those parts of the overlap integral that are independent of *χ* we are left with the following *χ*-dependent factor where *ϕ* is the angle measured in the plane perpendicular to the Mo-Mo axis.

$$\int_0^{2\pi} \sin 2\phi \sin 2(\phi + \chi)\, d\phi$$

This can be reduced as follows:

$$\int_0^{2\pi} \sin 2\phi\, [\sin 2\phi \cos 2\chi + \sin 2\chi \cos 2\phi]\, d\phi$$

$$= \cos 2\chi \int_0^{2\pi} \sin^2 2\phi\, d\phi + \sin 2\chi \int_0^{2\pi} \sin 2\phi \cos 2\phi\, d\phi$$

The last of these integrals is identically zero and the next to the last is simply the value of the overlap when the configuration is perfectly eclipsed. Hence the overlap depends on the twist angle χ according to the value of cos 2χ. For $\chi = 30°$ the δ overlap is reduced by a factor of 0.5 from its maximum value.

While it is an oversimplification to regard bond energy as a linear function of overlap, the two are related in approximately this way and thus we conclude that even for a twist of 30° the δ bond still retains about half of its maximum possible strength. It is worth pointing out that from 30 to 45° the value of cos 2χ drops sharply to zero so that a twist angle much greater than 30° would probably be inconsistent with retention of the δ bond. The value of $\chi = 39°$ found in the rhenium analogue of this structure allows only 21% of the maximum δ overlap.

The reduction by 0.5 of the δ bond strength would not be expected to affect the Mo-Mo bond distance very much since the δ component makes only a minor contribution to the total bond energy. In the case of $[Mo_2(SO_4)_4]^{4-}$ vs. $[Mo_2(SO_4)_4]^{3-}$ where the δ bond order changes from 1.0 to 0.5 the Mo-Mo distance increases by about 0.05 Å.[11] Unfortunately, there is no structure for an eclipsed $Mo_2Br_4(PR_3)_4$ molecule available for comparison with that of Mo_2Br_4(arphos). The most similar molecule available is probably $Mo_2Cl_4(SEt_2)_4$, which has an Mo-Mo distance of 2.144 (1) Å.[12] It has been reported[13] that the electronic spectra of $Mo_2Cl_4(SEt_2)_4$ and $Mo_2Cl_4(PBu_3)_4$ are very similar, so that the bond length in the latter may also be about 2.144 Å. Thus, the twisting in Mo_2Br_4(arphos)$_2$ may have caused a lengthening of the Mo-Mo bond by ca. 0.03 Å, which seems a reasonable magnitude.

Attempts to determine the Mo-Mo stretching frequency in Mo_2Br_4(arphos)$_2$ have been unsuccessful. The Raman spectrum recorded on a Cary 82 spectrometer using excitation from the argon laser line at 524.5 nm displayed no features significantly greater than the base line noise. The electronic spectra of a KBr pellet recorded at 5 K on a Cary 17D displayed no vibrational fine structure on any of the broad bands centered at about 795, 622, and 493 nm.

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Supplementary Material Available: A table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Texas A&M University; (b) Purdue University.

(2) (a) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975); (b) *Acc. Chem. Res.*, 11, 225 (1978).

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

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

(5) H. D. Glicksman and R. A. Walton, *Inorg. Chem.*, **17**, 3197 (1978).

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

(7) R. D. Adams, D. M. Collins, and F. A. Cotton, *J. Am. Chem. Soc.*, **96**, 749 (1974).

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

(9) F. A. Cotton and L. W. Shive, *Inorg. Chem.*, **14**, 2027 (1975).

(10) J. V. Brencic, I. Leban, and P. Segedin, *Z. Anorg. Allg. Chem.*, **427**, 85 (1976).

(11) F. A. Cotton, B. A. Frenz, E. Pederson, and T. R. Webb, *J. Am. Chem. Soc.*, **95**, 4431 (1973); *Inorg. Chem.*, **14**, 391 (1975).

(12) F. A. Cotton and P. E. Fanwick, unpublished work.

(13) J. San Filippo, Jr., H. J. Sniadock, and R. L. Grayson, *Inorg. Chem.*, **13**, 2121 (1974).

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cyclo-Triphosphorus and *cyclo*-Triarsenic as Ligands in "Double Sandwich" Complexes of Cobalt and Nickel

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Abstract: The reaction of white phosphorus or yellow arsenic with cobalt and nickel tetrafluoroborate in the presence of the tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos, gives a series of metal complexes each containing the novel cyclic P_3 or As_3 group. These compounds have the general formula $[M_2(D_3)(\text{triphos})_2]Y_n$ (M = Co, Ni; D = P, As; $Y^- = BF_4^-, BPh_4^-$; $n = 1, 2$). The X-ray structure determinations performed on the complexes $[Ni(P_3)(\text{triphos})_2](BPh_4)_2 \cdot 2.5(CH_3)_2CO$, $[Co,Ni(P_3)(\text{triphos})_2](BPh_4)_2 \cdot 2(CH_3)_2CO$, and $[Co_2(As_3)(\text{triphos})_2](BPh_4)_2$ have shown that the compounds are of double-sandwich structure with two molecules of triphos as external "slices". The internal layer in each complex is formed by an unprecedented *cyclo*-triphosphorus or *cyclo*-triarsenic unit acting as a 3π system which connects the two metal atoms. These double-decker $[(\text{triphos})M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(\text{triphos})]Y_n$ complexes are air stable. The number of valence electrons ranges from 31 to 34 along the series of complexes. The number of unpaired electrons, calculated on the basis of the magnetic moments, varies from zero to two electrons for the dinuclear complex cation. This is rationalized by a qualitative MO approach.

Introduction

In recent years much interest has been roused by polynuclear metal complexes having multiple-sandwich structure.[1] The ring systems acting as layers in the "sandwich" metal complexes so far described are delocalized "pure" carbocyclic groups, heterocyclic groups containing boron, nitrogen, or sulfur as heteroatoms, or borazine-type rings.

We have found two new non-carbon-containing ring systems capable of functioning as internal layers in "double sandwich" metal complexes: they are the *cyclo*-triphosphorus, η^3-P_3, and the *cyclo*-triarsenic, η^3-As_3, groups. These molecular units are capable of bridging two metal atoms in complexes and act as 3π systems. The external "slices" of such double-decker compounds are formed by two molecules of the tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos.

The complexes obtained have the general formula $[(\text{triphos})M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(\text{triphos})]Y_n$, where M = Co, Ni; D = P, As; $Y^- = BF_4^-, BPh_4^-$; $n = 1, 2$. The compounds with $n = 2$ are obtained by reaction of THF solutions of white phos-

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