for support. We also thank Johnson-Matthey, Ltd., for a generous loan of $RhCl_3 \cdot xH_2O$. The X-ray diffractometer was purchased with funds from the National Science Foundation Grant CHE-82-05871) and the University of Texas at Austin. R.A.J. thanks the Alfred P. Sloan Foundation for a fellowship (1985–1987).

Registry No. **1**, 104114-32-1; **2**, 104114-33-2; **3**, 94645-33-7; **4**, 94645-32-6; **5**, 104114-34-3; $Rh_4(CO)_{12}$, 19584-30-6; $[Rh(COD)Cl]_2$, 12092-47-6; $[Rh(CO)_2Cl]_2$, 14523-22-9; Rh, 7440-16-6.

Supplementary Material Available: Tables of general temperature factors for **1–3**, complete tables of bond lengths and angles and least-squares planes for **2**, and a labeled ORTEP diagram of the second independent molecule for **2** (16 pages); tables of structure factors for **1–3** (88 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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Synthesis, Properties, and Structural Characterization of the Bis(dimethylphosphino)methane Complex $Mo_2(\mu\text{-dmpm})_2Cl_4$

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Received June 2, 1986

The new quadruply bonded dimolybdenum(II) compound $Mo_2(\mu\text{-dmpm})_2Cl_4$ (dmpm = bis(dimethylphosphino)methane) has been prepared by reaction of $Mo_2(O_2CCH_3)_4$ with dmpm in toluene and by reaction of $K_4Mo_2Cl_8$ with dmpm in toluene/methanol mixtures. Crystals grown from methanol are monoclinic, space group $P2_1/n$, with $a = 8.643$ (1) Å, $b = 8.893$ (1) Å, $c = 14.705$ (2) Å, $\beta = 100.02$ (1)°, $V = 1113.0$ (2) Å^3, and $Z = 2$. The crystal structure was solved and refined to residuals of $R = 0.0328$, $R_w = 0.0615$, and quality of fit 1.492. When crystals are grown by diffusion of hexane into a dichloromethane solution of $Mo_2(\mu\text{-dmpm})_2Cl_4$, a tetragonal modification is obtained, with $a = 9.063$ (15) Å, $c = 8.039$ (3) Å, $V = 660$ (3) Å^3, and $Z = 1$. This structure was solved and refined in space group $P4/mmm$, with final residuals of $R = 0.0599$, $R_w = 0.0698$, and quality of fit 1.32. The quadruple-bond distances are 2.1253 (4) and 2.134 (4) Å, respectively, in the monoclinic and tetragonal modifications. The tetragonal structure is disordered, while the monoclinic structure is not. The $^{31}P\{^1H\}$ NMR spectrum of the complex (in CH_2Cl_2) has one resonance ($\delta = -0.77$), verifying the equivalence of the four phosphorus nuclei. Electrochemical studies (by cyclic voltammetry in 0.1 M TBAH/CH_2Cl_2) reveal a reversible process at +0.49 V, an irreversible oxidation with $E_{p,a} = +1.25$ V, and an irreversible reduction with $E_{p,c} = -1.75$ V (all vs. Ag/AgCl).

Introduction

While several studies have been conducted on dinuclear compounds of the type $M_2X_4(LL)_2$ (X = halide, LL = bidentate phosphine) which contain multiple bonds between the metal atoms,[2–6] little work has yet been carried out when LL is the bis(dimethylphosphino)methane (dmpm) ligand. Recently, we found that the reactions of this ligand with $[Re_2Cl_8]^{2-}$ and with $Re_2Cl_4(P\text{-}n\text{-}Pr_3)_4$ give the novel compound $Re_2(\mu\text{-dmpm})_3Cl_4$, which contains a $Re \equiv Re$ bond and three bridging dmpm ligands.[7] This reactivity is quite different from that encountered with either dppm (dppm = $Ph_2PCH_2PPh_2$) or dmpe (dmpe = $Me_2PCH_2CH_2PMe_2$), which gave the complexes $Re_2(\mu\text{-dppm})_2Cl_4$ and $\alpha\text{-}Re_2Cl_4(dmpe)_2$, respectively.[8]

In view of this difference in reactivity between dmpm and dppm, we have investigated the reactions of dmpm with dimolybdenum(II) species. In these instances the new quadruply bonded dimolybdenum(II) compound $Mo_2(\mu\text{-dmpm})_2Cl_4$ is formed as dark blue crystals. The synthesis, characterization, and crystal structure are reported and contrasted with those of the previously reported complex $Mo_2(\mu\text{-dppm})_2Cl_4$.[4,9,10]

Experimental Section

Starting Materials. Samples of $Mo_2(O_2CCH_3)_4$[11] and $K_4Mo_2Cl_8$[12] were prepared by using procedures similar to those described in the literature. The $Me_2PCH_2PMe_2$ (dmpm) ligand was purchased from Strem Chemicals, diluted to 1.2 M in toluene, and stored under an atmosphere of dry nitrogen. Chlorotrimethylsilane was purchased from Aldrich Chemical Co. and used without further purification. Solvents used in the preparation and workup of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen with use of standard procedures.

Preparation of $Mo_2(\mu\text{-dmpm})_2Cl_4$. Method 1. A 25-mL three-neck flask was charged with 0.201 g (0.47 mmol) of $Mo_2(O_2CCH_3)_4$, 0.30 mL (2.36 mmol) of Me_3SiCl, 0.80 mL (0.96 mmol) of dmpm (1.2 M in toluene), and 15 mL of toluene. The suspension was refluxed for 1 h and then stirred for a further 4 h while it was still warm. The reaction mixture was cooled to room temperature and the blue product filtered off, washed with toluene followed by pentane, and finally vacuum-dried; yield 0.277 g (98%). Anal. Calcd for $C_{10}H_{28}Cl_4Mo_2P_4$: C, 19.82; H, 4.67; Cl, 23.40. Found: C, 20.03; H, 4.81; Cl, 23.45.

Method 2. $K_4Mo_2Cl_8$ (0.32 g, 0.50 mmol) was placed in a flask equipped with a stirring bar. A solution of 1.0 g of dmpm in 9.0 mL of toluene was prepared in a Schlenk tube, and 2.0 mL of this solution (ca. 1.5 mmol of dmpm) was added to the flask. Methanol (25 mL) was then added and, upon stirring, the mixture soon turned blue. After the mixture had been stirred for 6 h, a blue precipitate settled out of a purple solution. The blue solid was filtered off, washed with hexane, and dried in vacuo. This product was contaminated with potassium chloride; it was purified by dissolving it in CH_2Cl_2, filtering the resulting blue solution, and precipitating the solid by slow addition of hexane; yield 0.22 g (73%).

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Table I. Crystal Data for Monoclinic $Mo_2(\mu\text{-dmpm})_2Cl_4$ and Tetragonal $Mo_2(\mu\text{-dmpm})_2Cl_4 \cdot 0.5H_2O \cdot 1.25CH_3OH$

	monoclinic	tetragonal
formula	$Mo_2Cl_4P_4C_{10}H_{28}$	$Mo_2Cl_4P_4C_{11.25}O_{1.75}H_{34}$
fw	605.92	654.98
space group	$P2_1/n$	$P4/mmm$
systematic absences	$(0k0)$, $k \neq 2n$; $(h0l)$, $h + l \neq 2n$	none
a, Å	8.643 (1)	9.063 (15)
b, Å	8.893 (1)	9.063 (15)
c, Å	14.705 (2)	8.039 (3)
β, deg	100.02 (1)	90.0
V, Å^3	1113.0 (2)	660 (3)
Z	2	1
d_{calcd}, g/cm^3	1.808	1.647
cryst size, mm	0.48 × 0.41 × 0.29	0.52 × 0.21 × 0.07
μ(Mo Kα), cm^{-1}	18.5	15.7
data collecn instrument	Nicolet P3/F Equivalent	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα (λ_α = 0.71073 Å)
orientation reflecns: no.; range (2θ), deg	25; 22–35	15; 21–31
temp, °C	22–26	25 ± 3
scan method	ω–2θ	ω–2θ
data collecn range, 2θ, deg	4.0–55.0	5.0–50.0
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2235	285
no. of parameters refined	91	22
transmission factors; max, min	obsd 1.00, 0.90	obsd 1.00, 0.84
R^a	0.0328	0.0599
$R_w{}^b$	0.0615	0.0698
quality of fit indicator^c	1.492	1.32
largest shift/esd, final cycle	0.01	0.08
largest peak, e/Å^3	0.59	1.51

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$ (monoclinic form). $R_w = [\sum||F_o| - |F_c||w^{1/2}]/[\sum|F_o|w^{1/2}]$; $w = 1/[\sigma^2(|F_o|) + 0.0005F_o^2]$ (tetragonal form). [c] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

This product was shown by its physical properties to be identical with that obtained by method 1.

Method 3. A mixture comprising 0.190 g (0.30 mmol) of $K_4Mo_2Cl_8$, 0.75 mL (0.90 mmol) of dmpm (1.2 M in toluene), and 20 mL of methanol was refluxed in the presence of a pine boiling stick for 12 h. The solution was cooled very slowly, and the blue crystals of the product were collected, washed with water, ethanol, and finally diethyl ether, and then vacuum-dried; yield 0.129 g (70%). The identity of the product was confirmed by comparing its spectroscopic and electrochemical behavior with that of the product obtained by method 1.

X-ray Crystallography. Crystals were grown in two ways and proved to be different. First, some of the bulk compound obtained by preparative method 2 was dissolved in dichloromethane and a layer of hexane placed over this solution. By slow interdiffusion of the two layers, deep blue tetragonal crystals were obtained. This method of growing tetragonal crystals was consistently reproducible. The second way of obtaining single crystals was to harvest those that were to be found deposited on the boiling stick used in preparative method 3. These crystals are monoclinic.

Tetragonal Form. Geometric and intensity data were obtained from a crystal mounted on the end of a glass fiber by employing a Syntex P$\bar{1}$ automated diffractometer and utilizing standard procedures that have been described elsewhere.[13] Table I gives the important crystal data and experimental conditions. For solution and refinement of the structure standard computer codes were used.[14] Absorption corrections were made empirically by the azimuthal scan technique.[15]

Axial photographs revealed a tetragonal unit cell of Laue class 4/*mmm* with no systematic absences. These data are consistent with all of the following space groups: $P422$, $P4mm$, $P\bar{4}2m$, $P\bar{4}m2$, and $P4/mmm$. The unit cell volume implied the presence of only one molecule in the unit cell, and from the Patterson function it was evident that the Mo–Mo vector lay in the z direction. It was clear from the solution in each space group that the crystallographic symmetry imposed on the molecule was higher than the highest possible molecular symmetry (C_{2h}). We therefore anticipated a systematic disordering of the molecules with respect to their rotational orientations about the molecular Mo–Mo axis. Furthermore, the disordered pattern required by space group $P4/mmm$ appeared in all of the other space groups, which did not impose the full disorder on the molecule.

A model in which space group $P4/mmm$ was used, with the Mo atoms on the g(2×) positions and the Cl and P atoms placed on separate s(8×) positions as half-atoms, consistently refined so as to cause complete coalescence of the P and Cl atoms. We therefore employed only one s(8×) position to which we assigned $^1/_2$ P + $^1/_2$ Cl. The bridging carbon atom, C(1), was placed on an l(4×) position and the methyl carbon atom on the general (16×) u position. This model was then refined to convergence with anisotropic displacement parameters employed for Mo, Cl/P, and C(1) and an isotropic displacement parameter for C(2). The moderately large displacement parameters for C(1) and Cl/P indicate that this model may be too simple. It makes the Mo_2P_2C rings planar whereas we would expect the bridging carbon atom to be tipped out of that plane, as is always found in M_2P_2C rings when dppm is used. This tipping would in turn mean that each C(2) atom must in fact be two slightly separated half carbon atoms. However, the positional differences between the various half-atoms in a more sophisticated model would be too small to allow the separate refinement of all these half-atoms. We therefore accepted the original model as the best practical one, even though it gives large displacement parameters.

Since the molecule $Mo_2(dmpm)_2Cl_4$ lies on the line (0, 0, z), large open channels exist in the crystal at ($^1/_2$, $^1/_2$, z). We thus expected, and found, that these channels are populated in a highly (and possibly dynamically) disordered pattern by molecules of solvent. We refined no fewer than five different models for this region. The model that we report was chosen so as to provide the optimum combination of least-squares residuals and chemical credibility.

This model places a methanol molecule along ($^1/_2$, $^1/_2$, z), centered at ($^1/_2$, $^1/_2$, 0). The one crystallographically unique site defining this molecule is populated by $^1/_2$ C and $^1/_2$ O, so that the site (a special position of multiplicity $^1/_8$) is fully occupied. The second region that was modeled was centered about ($^1/_2$, $^1/_2$, $^1/_2$). An oxygen atom, assumed to be from a water molecule, resides on the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$), while a methanol molecule, treated in a fashion similar to that at ($^1/_2$, $^1/_2$, 0), occupies the inversion center. The population of the water molecule is $^1/_{32}$, which is $^1/_2$ of the site multiplicity, while the unique site defining the methanol molecule has a total population of $^1/_{32}$, which is $^1/_4$ of the site multiplicity for the ($^1/_2$, $^1/_2$, z) special position.

The foregoing model gives an overall stoichiometry of $Mo_2(dmpm)_2Cl_4 \cdot {}^1/_2H_2O \cdot {}^5/_4CH_3OH$ to the crystal. All relevant parameters reported in Table I were calculated on this basis. We realize, however, that, in a case such as this, one can arrive at slightly different answers via different paths. We draw no chemical conclusions from the results of our refinement of the disordered solvent. In particular, the bond distances in the methanol groups cannot be considered as reliable results.

The population parameters of the disordered entities were among the variable parameters in our refinement. We could achieve similar residuals with more than one combination of population and displacement parameters for these groups.

Monoclinic Form. Geometric and intensity data were taken from a crystal mounted at the end of a glass fiber, by an automated four-circle diffractometer (Nicolet P3/F Equivalent). The identification of the unit cell and the intensity data collection were conducted with routine procedures that have been described previously.[13] Axial photographs were made of the principal axes of the monoclinic cell and of the unique body and face diagonals, to verify the lattice dimensions and Laue group (2/*m*). Systematic absences from the intensity data uniquely identified the space group as $P2_1/n$. Table I lists the important crystal data and experimental parameters.

Data reduction[14] included the application of an empirical absorption correction[15] based on azimuthal scans of nine reflections with diffractometer angle χ near 90°.

The position of the unique molybdenum atom was derived from a Patterson map. Refinement of parameters for this atom gave an un-

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Table II. Positional and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for Tetragonal $Mo_2(dmpm)_2Cl_4$[a]

atom	x	y	z	B, Å^2
Mo	0.0000	0.0000	0.1327 (3)	2.65 (4)
Cl	0.2659 (5)	0.0000	0.2039 (6)	7.3 (1)
P	0.2659 (5)	0.0000	0.2039 (6)	7.3 (1)
C(1)	0.365 (4)	0.0000	0.0000	6 (1)
C(2)	0.338 (5)	0.130 (4)	0.335 (4)	11 (1)*
O(1W)	0.5000	0.5000	0.5000	13 (3)*
C(1M1)	0.5000	0.5000	0.55 (4)	13 (3)*
O(1M1)	0.5000	0.5000	0.55 (4)	13 (3)*
C(1M2)	0.5000	0.5000	0.107 (9)	22 (3)*
O(1M2)	0.5000	0.5000	0.107 (9)	22 (3)*

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

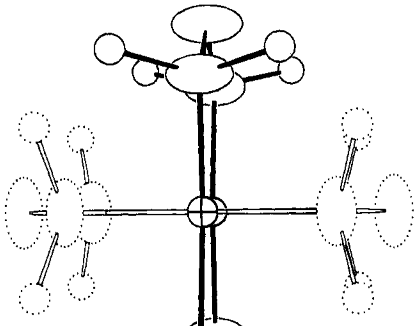

Figure 1. View of the apparent "molecule" in the tetragonal form of $Mo_2(dmpm)_2Cl_4$. See text for details.

weighted R factor of about 50%, and a difference map showed no more atoms. When the unique chlorine and phosphorus atoms—located by direct methods—were added, however, the R factor fell to ca. 15%. The structure was then developed and refined routinely with alternating difference maps and least-squares cycles. The final refinement fitted an overall scale factor and positional and anisotropic displacement parameters for 10 atoms (a total of 91 variables) to 2235 data, for a data-to-parameter ratio of 24.6:1. The final residuals are listed in Table I. The largest peak on a difference Fourier map following the refinement had a density less than 0.6 e/Å^3.

Physical Measurements. Infrared spectra were recorded from Nujol mulls between KBr plates with an IBM Instruments IR 32 Fourier transform (4000–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on an HP 8451A diode array spectrophotometer (820–350 nm). Electrochemical measurements were carried out on dichloromethane, acetonitrile, and THF solutions that contained tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to either the silver/silver chloride (Ag/AgCl) electrode or a silver quasi-reference electrode (a silver wire coated with a layer of silver chloride) at room temperature and are uncorrected for junction potentials. Voltammetric experiments were performed with a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Nicolet NT 470 spectrometer. Resonances were referenced internally to the impurity in the deuterated solvent (δ 5.35 for CD_2Cl_2).

Analytical Procedures. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

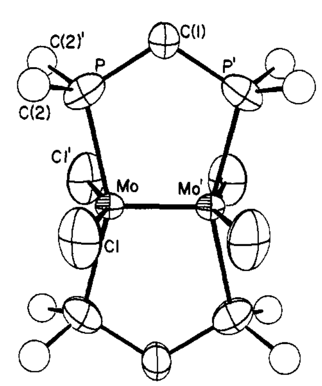

Figure 2. Molecular structure of $Mo_2(dmpm)_2Cl_4$ deduced from an X-ray crystallographic study of the tetragonal form.

Table III. Bond Lengths and Bond Angles in Tetragonal $Mo_2(dmpm)_2Cl_4$

	Bond Lengths (Å)		
Mo–Mo	2.134 (4)	P–C(1)	1.87 (2)
Mo–Cl	2.477 (4)	P–C(2)	1.71 (3)
Mo–P	2.477 (4)		
	Bond Angles (deg)		
Mo–Mo–Cl	103.4 (1)	Mo–P–C(1)	105 (1)
Mo–Mo–P	103.4 (1)	Mo–P–C(2)	121 (2)
Cl–Mo–Cl	153.3 (2)	C(1)–P–C(2)	111 (1)
P–Mo–P	153.3 (2)	P–C(1)–P	123 (2)
Cl–Mo–P	86.94 (4)		

Table IV. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for Monoclinic $Mo_2(dmpm)_2Cl_4$[a]

atom	x	y	z	B, Å^2
Mo(1)	0.10501 (3)	0.00788 (3)	−0.02806 (2)	2.208 (6)
Cl(1)	0.0893 (1)	−0.1842 (1)	−0.14439 (7)	4.22 (2)
Cl(2)	0.2532 (1)	0.2119 (1)	0.05263 (7)	3.87 (2)
P(1)	0.0097 (1)	0.1853 (1)	−0.16223 (7)	3.46 (2)
P(2)	0.2823 (1)	−0.1647 (1)	0.08368 (6)	3.24 (2)
C(1)	−0.2052 (4)	0.1692 (5)	−0.1922 (2)	3.44 (7)
C(2)	0.0764 (5)	0.1455 (7)	−0.2701 (3)	5.5 (1)
C(3)	0.0494 (8)	0.3858 (6)	−0.1431 (5)	7.1 (1)
C(4)	0.4871 (5)	−0.1070 (7)	0.1208 (3)	5.1 (1)
C(5)	0.3045 (8)	−0.3591 (6)	0.0488 (4)	6.8 (1)

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

Crystallographic Results

Tetragonal Form. This form, which was the only one known to us for several years, gave great crystallographic difficulties. As already noted in the Experimental Section, the molecule lies on a site of crystallographic D_{4h} symmetry, whereas we could not expect the molecule to have intrinsic symmetry higher than C_{2h}. Therefore, a highly disordered model had to be refined, as already explained. A view of the "molecule" so obtained is given in Figure 1. The atomic positional parameters are listed in Table II.

There are 4 equivalent $^1/_2$ Cl/$^1/_2$ P "atoms" associated with each metal atom. There are also 4 methylene carbon half-atoms and 16 methyl carbon half-atoms. It is impossible to tell from these results themselves whether the arrangement of dmpm ligands in the molecule is cis or trans, but on the basis of known contact radii it could be concluded that only a trans arrangement is possible. On this basis we obtained from the X-ray study of the tetragonal form a molecular structure shown in Figure 2 and described metrically in Table III. This structure is, of course, unsatisfactory in that it fails to define the bond lengths and angles for the Cl and P atoms independently and also because it gives planar rings, which is not at all likely to be true.

Monoclinic Form. In view of the deficiencies in the tetragonal structure just discussed, it was very fortunate that the monoclinc form became available. Here there were no unusual problems and the molecular structure was obtained straightforwardly and unambiguously. The atomic positional parameters are given in Table IV, and a view of the molecule defining the numbering scheme is shown in Figure 3. The principal bond distances and angles are listed in Table V.

Comparison of Structures. The disorder present in the tetragonal form has very little, if any, effect on our ability to measure

Table V. Selected Bond Distances and Angles and Their Estimated Standard Deviations for Monoclinic $Mo_2(\mu\text{-dmpm})_2Cl_4$[a]

Distances (Å)

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Mo(1)	Mo(1′)	2.1253 (4)	Mo(1)	P(2)	2.555 (1)	P(2)	C(1′)	1.834 (3)
Mo(1)	Cl(1)	2.405 (1)	P(1)	C(1)	1.838 (3)	P(2)	C(4)	1.833 (4)
Mo(1)	Cl(2)	2.411 (1)	P(1)	C(2)	1.815 (4)	P(2)	C(5)	1.822 (4)
Mo(1)	P(1)	2.549 (1)	P(1)	C(3)	1.828 (5)			

Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Mo(1′)	Mo(1)	Cl(1)	106.44 (3)	Cl(2)	Mo(1)	P(2)	85.85 (3)	Mo(1)	P(2)	C(1′)	107.7 (1)
Mo(1′)	Mo(1)	Cl(2)	105.97 (3)	P(1)	Mo(1)	P(2)	161.21 (3)	Mo(1)	P(2)	C(4)	117.6 (2)
Mo(1′)	Mo(1)	P(1)	99.11 (2)	Mo(1)	P(1)	C(1)	108.3 (1)	Mo(1)	P(2)	C(5)	118.0 (2)
Mo(1′)	Mo(1)	P(2)	99.67 (2)	Mo(1)	P(1)	C(2)	116.5 (2)	C(1′)	P(2)	C(4)	103.0 (2)
Cl(1)	Mo(1)	Cl(2)	147.59 (3)	Mo(1)	P(1)	C(3)	117.3 (2)	C(1′)	P(2)	C(5)	107.2 (2)
Cl(1)	Mo(1)	P(1)	85.33 (3)	C(1)	P(1)	C(2)	103.7 (2)	C(4)	P(2)	C(5)	101.9 (3)
Cl(1)	Mo(1)	P(2)	89.08 (3)	C(1)	P(1)	C(3)	105.5 (2)	P(1)	C(1)	P(2′)	107.4 (2)
Cl(2)	Mo(1)	P(1)	89.29 (3)	C(2)	P(1)	C(3)	104.2 (3)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

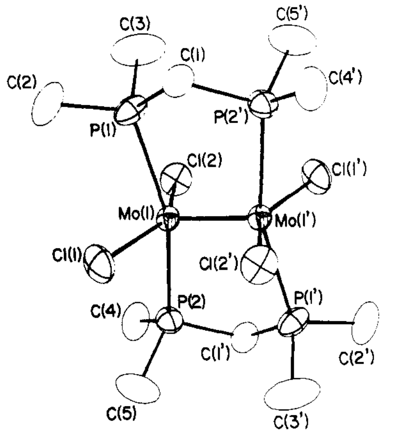

Figure 3. ORTEP plot of the molecular structure of $Mo_2(\mu\text{-dmpm})_2Cl_4$, obtained from the monoclinic form. The atom-labeling scheme is defined. All atoms are represented by their 50% probability ellipsoids. Primed and unprimed atoms are related by a crystallographic inversion center.

the Mo–Mo distance. The values obtained for the tetragonal and monoclinic cases are not different even in a statistical sense, viz., 2.134 (4) and 2.1253 (4) Å, respectively, if we consider a difference of less than 3σ to be insignificant. The big difference between the two structures in terms of bond lengths and angles, of course, has to do with the phosphorus and chlorine atoms. We see from the monoclinic form that the Mo–P and Mo–Cl distances differ by ca. 0.14 Å, whereas from the tetragonal structure we obtain only an average value, which is, interestingly, essentially equal to what we can calculate from the individual values. A similar situation pertains with regard to the Mo–Mo–P and Mo–Mo–Cl angles.

Comparison of the $Mo_2(dmpm)_2Cl_4$ Structure with Those of $M_2(dppm)_2Cl_4$ Molecules. Previous reports have described the structures of two $M_2(dppm)_2Cl_4$ molecules, namely, $Re_2(dppm)_2Cl_4$[8] and $Mo_2(dppm)_2Cl_4$.[9] The present structure closely resembles that of the latter and, like it, has an eclipsed rotational conformation. It differs markedly from $Re_2(dppm)_2Cl_4$, where there is a staggered rotational conformation.

The Mo–Mo distance in $Mo_2(dmpm)_2Cl_4$ is slightly but significantly shorter than that in $Mo_2(dppm)_2Cl_4$, namely, by 0.013 (1) Å. This may be due entirely to steric factors, but it is possible that the greater basicity of the phosphorus atoms in dmpm gives rise to this slight shortening for electronic reasons.

The major difference between the two molecules is that the dppm compound appears to be less regular because of the bulky phenyl substituents. Thus, while $Mo_2(dmpm)_2Cl_4$ has almost perfect C_{2h} symmetry, whereby pairs of Mo–Cl and Mo–P bonds as well as Mo–Mo–P and Mo–Mo–Cl angles that do not *have* to be equal effectively are equal, this is not true for $Mo_2(dppm)_2Cl_4$. Here there are considerable distortions from C_{2h} symmetry (although the inversion center is imposed crystallographically). Thus the crystallographically independent Mo–P distances differ by ca. 0.08 Å, the Mo–Mo–P angles by ca. 5°, and the Mo–Mo–Cl angles by ca. 2.5°.

Discussion

The compound $Mo_2(dmpm)_2Cl_4$ (**1**) has been obtained by the reaction of $Mo_2(O_2CCH_3)_4$ with dmpm in the presence of Me_3SiCl or by reaction of the $Mo_2Cl_8^{4-}$ ion with dmpm, as shown in the equations

$$Mo_2(O_2CCH_3)_4 + 2dmpm + 4Me_3SiCl \xrightarrow[\text{reflux}]{\text{toluene}} Mo_2(\mu\text{-dmpm})_2Cl_4 + 4Me_3SiO_2CCH_3 \quad (1)$$

$$K_4Mo_2Cl_8 + 2dmpm \rightarrow Mo_2(\mu\text{-dmpm})_2Cl_4 + 4KCl \quad (2)$$

When the second reaction was carried out as described under method 3, it afforded directly single crystals of the compound. The first reaction (as embodied in method 1) and the second reaction practiced according to method 2 gave only microcrystalline products. However, the compound is fairly soluble in dichloromethane, and when such a solution is layered with hexane, single crystals can be obtained. The compound is essentially insoluble in hexane and only slightly soluble in acetonitrile and THF. While the compound is fairly stable to air in solid form (although somewhat hygroscopic), it is very sensitive to oxygen and moisture when in solution.

The reaction of dmpm with $[Mo_2Cl_8]^{4-}$ in methanol (eq 2) contrasts with that between $[Re_2Cl_8]^{2-}$ and dmpm, from which we isolated the novel compound $Re_2(\mu\text{-dmpm})_3Cl_4$.[7] In the case of the dimolybdenum system no reduction occurs and we obtained only the bis-dmpm complex; there is no evidence for other compounds containing more equivalents of the dmpm ligand.

Spectroscopic Properties and Redox Behavior. The IR spectrum of Nujol mulls of $Mo_2(dmpm)_2Cl_4$ shows only bands associated with coordinated dmpm. The $^{31}P\{^1H\}$ NMR spectrum (200 MHz) of this complex (recorded in CH_2Cl_2) exhibits a single sharp resonance at δ −0.77 for the four equivalent phosphorus nuclei. The ^1H NMR spectrum (470 MHz) exhibits a single resonance for the methyl groups of the coordinated dmpm ligands at δ +1.51. While this figure compares well with data for other dinuclear compounds that contain dmpm bridges,[16] it is somewhat downfield from the corresponding resonance found in the 200-MHz ^1H NMR spectrum of $Mo_2(\mu\text{-dmpm})_2(OAr)_4$ (δ ca. +1), where OAr represents the 3,5-dimethylphenoxide ligand.[17] The compound exhibits its methylene resonances as a pentet located at δ +3.08 (J_{H-P} = 5.0 Hz). This is only slightly downfield from the values

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(16) See, for example: King, R. B.; Raghuveer, K. S. *Inorg. Chem.* **1984**, *23*, 2482.

(17) Kerschner, J.; Rothwell, I. P., unpublished results.

found for other dimetal complexes that contain dmpm bridges[16] but upfield from the three sets of methylene resonances found in the spectrum of the triply bonded complex $Re_2(\mu\text{-dmpm})_3Cl_4$ (δ +4.71, +4.10, and +3.95).[7] This difference may be due to a larger diamagnetic anisotropy in the triply bonded rhenium complex than in this quadruply bonded dimolybdenum compound.[2,7]

The electronic absorption spectrum of a dichloromethane solution exhibits two absorptions in the region between 350 and 820 nm, at 426 nm (ϵ = 270) and 604 nm (ϵ = 1730). The feature at 604 nm is attributed to the $\delta^2 \rightarrow (\delta\delta^*)$ transition and represents a shift to higher energy compared to the band for $Mo_2(\mu\text{-dppm})_2Cl_4$ (634 nm).[10] This energy shift correlates with an increase in the basicity of the phosphine ligand.

The electrochemical properties of **1** were examined in several solvents with use of the cyclic voltammetric technique. The compound is most soluble in dichloromethane, and solutions in this solvent, with 0.1 M TBAH as supporting electrolyte, exhibit a reversible process ($i_{p,a}/i_{p,c} \approx 1$) at +0.49 V vs. Ag/AgCl; this corresponds to a one-electron oxidation of the bulk complex. A second irreversible oxidation is observed with $E_{p,a}$ = +1.25 V vs. Ag/AgCl, and an irreversible reduction can be seen near the solvent limit with $E_{p,c}$ = −1.75 V vs. Ag/AgCl. These redox processes agree closely with those that characterize solutions of $Mo_2(\mu\text{-dppm})_2Cl_4$ in 0.1 M TBAH/CH_2Cl_2 for which we see $E_{1/2}$(ox) = +0.66 V and $E_{p,c}$ = −1.50 V vs. Ag/AgCl.[10] Although the oxidation at +0.49 V approaches electrochemical reversibility in this solvent system (ΔE_p = 110 mV at v = 200 mV/s), the cation formed is unstable chemically. Bulk electrolysis of 0.1 M TBAH/CH_2Cl_2 solutions of **1** at +0.70 V resulted in a rapid decomposition of the cation.

When either acetonitrile or THF is used as the solvent in these electrochemical measurements, the reversible oxidation observed in CH_2Cl_2 now becomes irreversible and the potentials at which the electrochemical processes occur are shifted. In 0.1 M TBAH/CH_3CN, one irreversible oxidation is observed at $E_{p,a}$ = +0.31 V vs. Ag/AgCl and an irreversible reduction at $E_{p,c}$ = −1.52 V vs. Ag/AgCl. In 0.2 M TBAH/THF solutions these processes shift to more positive potentials at $E_{p,a}$ = +0.45 V and $E_{1/2}$ = −1.50 V vs. a silver quasi reference electrode. Note that the process at −1.50 V looks reasonably reversible provided a switching potential of ca. −1.75 V is used. However, when the measurements are extended to ca. −2.5 V, product waves are seen at $E_{p,c}$ = −1.90 and −2.20 V and the $i_{p,c}/i_{p,a}$ ratio for a couple at −1.50 V is now much greater than unity.[18,19]

Acknowledgment. Support from the National Science Foundation (Grant No. CHE 85-06702 to R.A.W. and Grant No. CHE-8514588 to F.A.C.) is gratefully acknowledged. We also thank Professor I. P. Rothwell for making the results cited in ref 17 available to us.

Registry No. $Mo_2(\mu\text{-dmpm})_2Cl_4\cdot{}^1/_2H_2O\cdot{}^5/_4CH_3OH$, 104092-00-4; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $K_4Mo_2Cl_8$, 25448-39-9; Mo, 7439-98-7.

Supplementary Material Available: Tables of anisotropic displacement parameters for both structures and a table of torsion angles for the monoclinic structure (3 pages); tables of observed and calculated structure factors for both structures (14 pages). Ordering information is given on any current masthead page.

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(18) Under our experimental conditions the ferrocenium/ferrocene couple has $E_{1/2}$ = 0.47 V vs. the Ag/AgCl and silver quasi reference electrodes in 0.1 M TBAH/CH_2Cl_2 and 0.2 M TBAH/THF, respectively.

(19) We note that the cyclic voltammogram of $Mo_2(\mu\text{-dmpm})_2Cl_4$ in THF is quite different from that of $Mo_2(\mu\text{-dmpm})_2(OAr)_4$ (OAr = 3,5-dimethylphenoxide).[17] This aryloxide complex exhibits two reversible processes corresponding to oxidations at $E_{1/2}$ = +0.10 and −0.40 V vs. a silver quasi reference electrode. Two reductions are also observed, the first with $E_{1/2}$ = −1.40 V and the second with $E_{p,c}$ = −2.00 V vs. the silver quasi reference electrode. This apparently reflects the strong π-donor capability of alkoxide ligands and the consequent electron-rich nature of the metal centers.

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Solid-State Structure and Solution Equilibria of Cyano(triethylphosphine)gold(I)

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Received January 30, 1986

The solid-state structure and solution equilibria of cyano(triethylphosphine)gold have been investigated. Et_3PAuCN crystallizes in the orthorhombic lattice *Pbca* with a = 6.6711 (7) Å, b = 15.002 (1) Å, c = 19.439 (2) Å, and Z = 8. The Au–P distance is 228.8 (5) pm, and the Au–C distance is 197 (2) pm. ∠CAuP = 176.6 (6)°. The structure was refined to R = 0.061. The ^{197}Au Mössbauer parameters are IS = 4.69 mm/s and QS = 9.56 mm/s, consistent with a linear, two-coordinate structure. IR and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR studies show that in solution Et_3PAuCN disproportionates to form $Au(CN)_2^-$ and $(Et_3P)_2Au^+$. The equilibrium constant for the disproportionation of Et_3PAuCN is solvent-dependent: K_{eq} = 0.06 ($CDCl_3$), 0.13 (C_6D_6), and 0.88 (CH_3OD). The solution chemistry of Ph_3PAuCN was also studied by ^{31}P and ^{13}C NMR. At 297 K Ph_3PAuCN is in rapid equilibrium with $(Ph_3P)_2Au^+$ and $Au(CN)_2^-$, but at 200 K resonances for all three species are observed. These results suggest that, in some cases, the disproportionation of LAuX complexes may be masked by rapid ligand exchange.

Introduction

Gold(I) has a strong but not exclusive tendency to form linear two-coordinate complexes, LAuX, where L is a neutral Lewis base (e.g. phosphine, thioether, etc.) and X is an aryl or alkyl group, halide, or pseudohalide.[1-3] These complexes are usually formulated as neutral complexes, LAuX, but since gold(I) is generally labile, there exists the possibility of ligand scrambling to form the symmetrically substituted complexes AuL_2^+ and AuX_2^-. Indeed, (tetrahydrothiophene)gold iodide in the solid state contains the ions $[Au(THF)_2^+][AuI_2^-]$ linked by weak gold–gold interactions,[4] and anionic cyano(thiolato)gold(I) complexes, $RSAuCN^-$, in aqueous solution are in equilibrium with substantial concentrations of $Au(CN)_2^-$ and $Au(SR)_2^-$.[5] Similar ligand-scrambling reactions may significantly alter the solution chemistry of gold(I) complexes such as the new antiarthritic drug auranofin, which is a (phosphine)gold(I) thiolate. Since ^{31}P and ^{13}C NMR can probe each ligand directly, R_3PAuCN complexes are useful model systems for examining the ligand-scrambling reactions of gold(I) complexes. Therefore, we have undertaken a detailed study of the

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