Complexes Containing Heteronuclear and Homonuclear Quadruple Bonds. Preparation and Characterization of $MoWCl_4(dmpm)_2$ and $Mo_2X_4(dmpm)_2$ (X = Br, I)

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The quadruply bonded heterobimetallic complex $MoWCl_4(dmpm)_2$ (**1**) and the homobimetallic complexes $Mo_2X_4(dmpm)_2$ (X = Br (**2**), I, (**3**)) were synthesized and their structures determined. The crystals of compound **1** exhibit the typical disorder for heteronuclear systems, namely, the random orientation of the M–M′ vector, with each metal atom appearing as 50% Mo and 50% W. The structural refinement in the space group P4 resulted in lower residuals, with $R = 0.048$ and $R_W = 0.067$, than in the space group *P4/m*. For complexes **2** and **3**, crystals obtained from THF solutions are monoclinic, with space groups $P2_1/c$ and $P2_1/n$ for **2** and **3**, respectively. The quadruple bond distances are 2.193(2), 2.1271(8), and 2.132(2) Å for **1**, **2**, and **3**, respectively. In addition, each complex has been characterized using UV–visible, $^{31}P\{^1H\}$ NMR, and ^1H NMR spectroscopies. The average magnetic anisotropy of the Mo–Mo quadruple bond in complexes **2** and **3** has been calculated from ^1H NMR data as -4450×10^{-36} m^3 molecule^{-1}. The crystal structures of complexes **1–3** are fully described, and their crystallographic data are as follows: (**1**) space group *P*4 with $a = b = 9.083(2)$ Å, $c = 8.092(2)$ Å, $V = 667.5(5)$ Å^3, and $Z = 2$; (**2**) space group $P2_1/n$ with $a = 8.694(1)$ Å, $b = 8.695(2)$ Å, $c = 15.369(2)$ Å, $\beta = 100.70(1)°$, $V = 1141.6(6)$ Å^3, and $Z = 2$; (**3**) space group $P2_1/c$ with $a = 9.076(2)$ Å, $b = 16.813(7)$ Å, $c = 16.654(5)$ Å, $\beta = 102.4(1)°$, $V = 2481(4)$ Å^3, and $Z = 4$.

Introduction

Complexes of the type $MM'X_4(LL)_2$ (M, M′ = Mo, W; X = Cl, Br, I; LL = bidentate phosphine) that contain M–M′ homonuclear and heteronuclear quadruple bonds are interesting subjects for structural and spectroscopic studies.[2] Such complexes tend to adopt an eclipsed conformation which allows for maximum δ overlap. Steric repulsions, however, often cause the molecule to twist about the M–M′ axis away from the eclipsed geometry. An extensive study carried out recently on a series of $Mo_2X_4(LL)_2$ complexes with a torsion angle, χ, varying from 0 to 69.4°, revealed that the ground state remains $^1A_{1g}$ (δ^2) even at $\chi = 45°$, where the $^3A_{2u}$ ($\delta\delta^*$) state lies 1230 cm^{-1} higher in energy.[3] Only a few complexes containing a heteronuclear quadruple bond have been synthesized and structurally characterized.[4,5]

The present work is an interesting extension of the earlier studies on $MM'X_4(LL)_2$ type compounds. The structural and spectroscopic properties of the compounds $MoWCl_4(dmpm)_2$ (**1**), $Mo_2Br_4(dmpm)_2$ (**2**), and $Mo_2I_4(dmpm)_2$ (**3**) are reported and compared with those of $Mo_2Cl_4(dmpm)_2$,[5] as well as other similar homonuclear and heteronuclear compounds. Complexes **2** and **3** also afford an excellent opportunity to study the magnetic anisotropy of the Mo–Mo quadruple bond. Studies have already been carried out on similar dimolybdenum systems that contain phosphines with phenyl groups, which may also influence the chemical shift of the test protons.[6–8]

Experimental Section

All syntheses, manipulations and spectroscopic studies were carried out under an atmosphere of argon or nitrogen unless otherwise specified. Standard Schlenk and vacuum line techniques were used. Commercial grade solvents were dried and deoxygenated by refluxing at least 24 h over appropriate reagents and freshly distilled prior to use. THF, benzene, toluene, and hexanes were purified by distillation from potassium/sodium benzophenone ketyl, dichloromethane was purified from phosphorus pentoxide, and methanol was purified from magnesium methoxide.

Bis(dimethylphosphino)methane (dmpm) was purchased from Strem Chemicals and diluted to either a 1 M solution in toluene or a 1.5 M solution in hexanes. Trimethylbromosilane and trimethyliodosilane were purchased from Aldrich Inc. and used as received. $Mo_2(O_2CCH_3)_4$[9] and $Mo_2(O_2CCF_3)_4$[10] were prepared according to published procedures.

The UV/vis data of compounds **1** and **2** were measured in CH_2Cl_2 on a Cary 17-D spectrometer, whereas the UV/vis data of compound **3** were recorded in CH_2Cl_2 on a Hitachi U-2000 spectrometer. The ^1H NMR data were obtained on a Varian XL-200 spectrometer for **1** and **2** (200 MHz) and a Varian Gemini-300 for **3** (300 MHz). $^{31}P\{^1H\}$ NMR spectra (80.96 MHz) were recorded on a Varian XL-200 spectrometer, and the $^{31}P\{^1H\}$ NMR chemical shifts were referenced externally and are reported relative to 85% H_3PO_4. Elemental analyses were performed by Galbraith Laboratories, Inc.

The preparation of $MoWCl_4(dmpm)_2$ (**1**) has been previously reported.[4]

Preparation of $Mo_2Br_4(dmpm)_2$ (2). $Mo_2(O_2CCF_3)_4$ (0.20 g, 0.31 mmol) was dissolved in 20 mL of THF in a 50-mL three-neck flask equipped with a reflux condenser. A 1.47 M hexane solution of dmpm (0.50 mL, 0.74 mmol) was added, and the color of the THF solution changed from yellow to rose. The rose color turned to blue upon addition of 0.50 mL of Me_3SiBr (4.7 mmol), and a blue solid began to precipitate. This mixture was stirred at room temperature for 18 h and refluxed for an additional 2 h to give a blue solid and a blue solution. The solid was filtered, washed with hexanes, and vacuum-dried overnight. Yield: 90–95%. UV/vis spectrum in CH_2Cl_2: 630, 440, 345 nm. $^{31}P\{^1H\}$ NMR

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spectrum in THF/C_6D_6: −3.35 ppm (singlet). ^1H NMR spectrum in CD_2Cl_2: 3.12 (2H, pentet), 1.60 ppm (12H, multiplet).

Crystals of **2** were obtained by slow diffusion of a benzene/hexane (1:10) mixture into a THF solution of the solid. The compound is soluble in many organic solvents other than hydrocarbons. The solid is stable in air for short periods but solutions must be protected.

Preparation of $Mo_2I_4(dmpm)_2$ (3). Method 1. $Mo_2(O_2CCF_3)_4$ (0.20 g, 0.31 mmol) was dissolved in 20 mL of THF in a 50-mL three-neck flask equipped with a reflux condenser. A 1.47 M hexane solution of dmpm (0.50 mL, 0.74 mmol) was added and stirred for 5 min, after which time 0.50 mL of Me_3SiI (3.6 mmol) was added. The solution color gradually became green with the concomitant formation of a green precipitate. The reaction mixture was stirred at room temperature for 10 h and refluxed for an additional 3 h to give a dark green solid and a green solution. The solid was filtered, washed with hexanes, and vacuum-dried overnight. Yield: 90-97%. Anal. Calcd for $Mo_2I_4P_4C_{10}H_{28}$: C, 12.36; H, 2.90. Found: C, 12.85; H, 2.58. UV/vis spectrum in CH_2Cl_2: 700, 465, 415 nm. $^{31}P\{^1H\}$ NMR spectrum THF/C_6D_6: −7.04 ppm (singlet). ^1H NMR spectrum in CD_2Cl_2: 3.23 (2H, pentet), 1.77 ppm (12H, multiplet).

Dark block-shaped crystals were obtained by slow diffusion of a benzene/hexanes (1:10) mixture into a THF solution of the product. The general properties of this compound are similar to those of **2**.

Method 2. In a standard reaction, a solution of $Mo_2(O_2CCH_3)_4$ (0.13 g, 0.30 mmol) in 10 mL of MeOH was reacted with 0.60 mL of a 1 M toluene solution of dmpm (0.60 mmol) and 0.20 mL of Me_3SiI (1.4 mmol). An immediate color change from yellow to red ensued with the gradual precipitation of a green solid with no further change after the reaction was heated and stirred for three hours. The green solid was filtered, washed with MeOH and dried under reduced pressure. Yield: 70%.

When THF was used as the solvent instead of MeOH, the reaction mixture produced a green solution and a bright pink solid in the same time period. This pink solid was identified as *cis*-$Mo_2I_2(O_2CCH_3)_2(dmpm)_2$; a detailed synthesis, structure determination and spectroscopic studies concerning this compound will be reported elsewhere.[11]

Crystals of **3** were obtained by slow diffusion of hexanes into the THF filtrate.

X-ray Crystallography

General Procedures. Single-crystal diffraction experiments were conducted on Rigaku AFC5R or Siemens P3/V automated diffractometers using Mo Kα or Cu Kα radiation. Routine unit cell identification and intensity data collection procedures were followed utilizing the options specified in Table I and general procedures previously described.[12] Lattice dimensions and Laue symmetry were verified using axial photographs. Three standard reflections were measured during data collections to monitor any intensity and crystal orientation changes.

The structures of **1**, **2**, and **3** were determined by a general procedure that has been fully described elsewhere.[12] Data reduction was carried out by standard methods with the use of well-established computational procedures.[13] In each case, one octant of data was collected. The computations for compounds **1** and **2** were done with Enraf-Nonius SDP and SHELX-76 software on the VAX computer, whereas the computations for **3** were carried out using the TEXSAN software package.[14] Structure factors were obtained after a Lorentz and polarization correction. Empirical absorption corrections based on azimuthal (ψ) scans of reflections with Eulerian angle χ near 90° were applied to the data of compounds **1** and **2**.[15] For compound **3**, the program DIFABS was used to correct for absorption after all non-hydrogen atoms had been located and isotropically refined.[16] Pertinent crystallographic information for the three structures is given in Table I. Tables II–IV list the positional and thermal parameters for complexes **1**, **2** and **3**, respectively. Table V lists the important bond distances and angles for each of the structures. Tables of anisotropic thermal parameters and complete tables of bond distances, bond angles, and torsion angles along the Mo–Mo and Mo–W bonds are available as supplementary material.

Table I. Crystallographic Data and Data Collection Parameters for 1–3

	1	2	3
formula	$WMoCl_4P_4C_{10}H_{28}$	$Mo_2Br_4P_4C_{10}H_{28}$	$Mo_2I_4P_4C_{10}H_{28}$
fw	693.83	783.75	971.72
space group (No.)	*P*4 (75)	$P2_1/n$ (14)	$P2_1/c$ (14)
a, Å	9.083(2)	8.694(1)	9.076(2)
b, Å	9.083(2)	8.695(2)	16.813(7)
c, Å	8.092(2)	15.369(2)	16.654(5)
α, deg	(90)	(90)	(90)
β, deg	(90)	100.70(1)	102.4(4)
γ, deg	(90)	(90)	(90)
V, $Å^3$	667.5(5)	1141.6(6)	2481(4)
Z	1	2	4
ρ_{calcd}, g/cm^{-3}	3.450	2.280	2.601
μ(Mo Kα or Cu Kα), cm^{-1}	358.63	201.645	61.634
λ, Å	1.541 84	1.541 84	0.710 73
T, °C	23 ± 2	20 ± 2	−90 ± 2
transm coeff	1.00, 0.61	1.00, 0.43	1.00, 0.79
R;[a] R_w[b]	0.048; 0.067	0.056; 0.079	0.061; 0.085
quality-of-fit indicator[c]	1.78	2.306	2.54
largest peak, $e^-/Å^3$	1.23	0.902	2.50

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

Table II. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $MoWCl_4(dmpm)_2$ (1)

atom	*x*	*y*	*z*	B_{eq},[a] $Å^2$
MW(1)[b]	0.000	0.000	0.1356(2)	3.35(5)
MW(2)[b]	0.000	0.000	−0.1356(2)	3.63(6)
Cl(1)	0.247(1)	0.010(2)	0.216(2)	4.8(2)
Cl(2)	0.251(2)	0.033(2)	−0.206(2)	6.1(2)
P(1)	0.273(2)	0.018(1)	0.178(2)	4.2(2)
P(2)	0.287(2)	0.018(2)	−0.191(2)	5.6(2)
C(1)	0.375(3)	−0.050(3)	−0.003(4)	5.0(2)
C(11)	0.348(3)	−0.083(4)	0.353(3)	5.4(2)
C(12)	0.317(4)	0.211(3)	0.193(4)	8.0(2)
C(21)	0.344(5)	−0.118(5)	−0.348(5)	14.4(2)
C(22)	0.356(3)	0.195(3)	−0.244(4)	5.8(2)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}$. [b] Hybrid metal atom composed of 50% Mo and 50% W.

Table III. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_2Br_4(dmpm)_2$ (2)

atom	*x*	*y*	*z*	B_{eq},[a] $Å^2$
Mo(1)	0.39494(6)	−0.00878(6)	0.02576(3)	1.53(1)
Br(1)	0.4010(1)	0.1950(1)	0.14084(6)	4.21(2)
Br(2)	0.2413(1)	−0.2268(1)	−0.05274(6)	3.48(2)
P(1)	0.2159(2)	0.1554(2)	−0.0855(1)	2.85(4)
P(2)	0.4924(3)	−0.1801(3)	0.1561(2)	3.53(4)
C(1)	0.296(1)	0.156(1)	−0.1877(6)	3.3(2)
C(2)	0.013(1)	0.097(2)	−0.1229(7)	5.1(3)
C(3)	0.691(2)	0.150(1)	0.443(1)	7.5(4)
C(4)	0.460(2)	−0.379(1)	0.143(1)	8.3(3)
C(5)	0.578(1)	0.140(2)	0.7407(6)	6.8(3)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}$.

Compound 1. Block-shaped single crystals of $MoWCl_4(dmpm)_2$ were obtained as previously described.[4] A crystal with dimensions of 0.40 × 0.35 × 0.20 mm was coated with a thin layer of epoxy cement and mounted on the tip of a glass fiber. The single-crystal diffraction experiment was

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Table IV. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $Mo_2I_4(dmpm)_2$ (3)

atom	x	y	z	B_{eq},[a] Å^2
I(1)	1.0045(2)	0.10003(8)	1.39768(8)	2.79(7)
I(2)	0.5978(2)	0.3121(1)	1.4027(1)	3.79(7)
I(3)	0.9826(2)	0.13982(8)	1.16755(8)	2.28(6)
I(4)	0.4968(2)	0.3034(1)	1.1528(1)	4.02(8)
Mo(1)	0.7872(2)	0.2119(1)	1.3456(1)	1.44(7)
Mo(2)	0.7489(2)	0.2166(1)	1.2148(1)	1.53(7)
P(1)	0.5958(6)	0.0878(3)	1.1767(4)	2.5(2)
P(2)	0.6056(7)	0.0995(3)	1.3539(4)	3.2(3)
P(3)	0.9046(7)	0.3396(3)	1.2085(3)	2.5(2)
P(4)	1.0004(7)	0.3163(3)	1.3873(3)	2.4(2)
C(1)	0.613(2)	0.030(1)	1.272(1)	2.5(9)
C(2)	0.655(3)	0.020(1)	1.106(2)	4(1)
C(3)	0.399(3)	0.093(2)	1.129(2)	4(1)
C(4)	0.640(4)	0.040(2)	1.445(2)	6(2)
C(5)	0.408(3)	0.128(2)	1.337(2)	5(1)
C(6)	1.066(3)	0.338(1)	1.294(2)	4(1)
C(7)	0.808(3)	0.435(1)	1.217(2)	4(1)
C(8)	0.978(3)	0.356(1)	1.118(2)	3.8(5)*
C(9)	1.173(3)	0.290(1)	1.458(1)	4(1)
C(10)	0.957(3)	0.412(1)	1.425(2)	4(1)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}$ Starred values denote atoms that were refined isotropically.

Table V. Comparison of Important Dimensions (Å, deg) between $Mo_2X_4(dmpm)_2$ (X = Cl, Br, I) and $MoWCl_4(dpmp)_2$

	$Mo_2Cl_4(dmpm)_2^{intl}$				
bond or angle	mono- clinic	tetra- gonal	$MoWCl_4$ $(dmpm)_2$	Mo_2Br_4 $(dmpm)_2$	Mo_2I_4 $(dmpm)_2$
M–M′	2.1253(4)	2.134(4)	2.193(2)	2.1271(8)	2.132(2)
M–P (av)	2.552(1)	2.477(4)	2.58(1)	2.522(2)	2.556(6)
M–X (av)	2.408(1)	2.477(4)	2.35(1)	2.497(1)	2.728(3)
X–M–X (av)	147.59(3)	153.3(2)	150.0(5)	145.09(4)	141.56(9)
P–M–P (av)	161.21(3)	153.3(2)	162.2(5)	161.31(8)	162.3(2)
M–M–P (av)	99.39(2)	103.4(1)	98.9(4)	99.35(6)	98.7(1)
M–M–X (av)	106.71(3)	103.4(1)	105.0(5)	107.46(3)	109.2(1)
torsional	0		~0	0	11.4

conducted using a Rigaku AFC5R with Cu Kα radiation. Crystal quality was verified by means of a rotation photograph and reflections suitable for indexing were found using the automatic search routine. A least-squares analysis of the setting angles of 25 reflections provided accurate unit cell parameters (Table I). Axial photographs verified the lattice dimensions but failed to unambiguously identify the Laue symmetry. Three standard reflections were measured every hour during data collection and displayed no systematic variation in intensity.

There were nine possible space groups for **1**, as the axial photograph had failed to positively identify the Laue class as either $4/m$ or $4/mmm$ and there were no systematic absences. A suitable solution was found in space group $P4/m$ (No. 83) with the heavy-atom positions that were derived from a three dimensional Patterson function. Hybrid atoms composed of 50% Mo and 50% W were placed at the metal atom positions in the initial stages of the refinement. The positions of all remaining non-hydrogen atoms were found using a series of full-matrix refinements followed by difference Fourier syntheses. These were initially refined with isotropic thermal parameters, then allowed to converge anisotropically.

In $P4/m$, the metal atom positions of the dinuclear unit coincide with a crystallographic 4-fold axis, a symmetry element that is not present in the molecule itself. The phosphorus and chlorine atoms, then, must necessarily be disordered about this 4-fold axis. Initially, the chlorine and phosphorus atoms were assigned identical coordinates, each with half occupancy. This disorder was then modeled by restraining the phosphorus and chlorine atoms at fixed distances from the metal atom positions (MW–P = 2.55(5) Å, MW–Cl = 2.35 (5) Å). This model was allowed to refine to convergence with isotropic thermal parameters. Finally, the restraints on the phosphorus and chlorine atoms were released, and the model was allowed to freely refine to convergence with anisotropic thermal parameters. No attempt was made to locate the hydrogen atoms, and the final Fourier map revealed only one peak above 1 e/Å^3, located in the vicinity of MW(1). Because both the initial refinement of the hybrid metal atom composition and the $^{31}P\{^1H\}$ NMR spectrum failed to indicate the presence of $Mo_2Cl_4(dmpm)_2$, the hybrid metal atom composition was fixed at precisely 50% Mo and 50% W in the final refinement. These refinements led to final residuals of $R = 0.06$ and $R_W = 0.08$.

The structure was also solved in space group $P4$, allowing for torsion about the M–M′ vector. Refinement in $P4$ indicated that the molecule is slightly twisted and produced lower residuals of $R = 0.048$ and $R_W = 0.067$. The final refinement factors after convergence are listed in Table I, and positional and thermal parameters are given in Table II.

Compound 2. A blue crystal with dimensions of 0.30 × 0.20 × 0.10 mm was coated with epoxy cement and mounted on the tip of a quartz fiber. Diffraction data were collected at 20 °C on a Rigaku AFC5R diffractometer using Cu Kα radiation. The space group $P2_1/n$ was determined from systematic absences in the data. One independent Mo atom of the dinuclear skeleton and its coordinated atoms were determined from a three dimensional Patterson function. The use of alternating difference Fourier maps and least-squares refinements gave the positions of all the remaining non-hydrogen atoms. The final refinement included positional and anisotropic displacements for 10 atoms (a total of 91 variables) for 1879 data and a data-to-parameter ratio of 20.6. The final residuals are listed in Table I. The largest peak in the final difference Fourier map was 0.9 e/Å^3.

Compound 3. A green crystal of dimensions 0.20 × 0.26 × 0.15 mm was mounted with silicon grease on the tip of a glass fiber and immediately placed in a stream of cold nitrogen at $T = -90$ °C. Intensity data were collected on a Nicolet P3/F diffractometer equipped with graphite-monochromated Mo Kα radiation, which had been upgraded to a Siemens P3/V. An accurate cell was determined from 25 reflections ranging from 15 to 25° in 2θ. Data collection was carried out with a ω–2θ scan motion in the range 4–50° for 2θ values. Three standard reflections measured every 150 reflections revealed negligible decay. After averaging of equivalent reflections, 3623 unique data remained.

The positions of the heavy atoms were determined by the direct methods program MITHRIL.[17] A series of full-matrix least-squares refinements followed by difference Fourier maps revealed the positions of all other non-hydrogen atoms. The program DIFABS was used to correct for absorption after all non-hydrogen atoms had been located and isotropically refined. The final cycle included anisotropic refinement for all atoms except C(8). The final refinement factors are listed in Table I.

Results and Discussion

Structure and Bonding. Two types of structures, namely the monoclinic and tetragonal forms, had been previously observed in the structure determination of $Mo_2Cl_4(dmpm)_2$.[5] The space group $P4/mmm$ was used to describe the tetragonal form, in which the molecule resides on a site of crystallographic D_{4h} symmetry. For crystals of $MoWCl_4(dmpm)_2$ (**1**), only the tetragonal form was observed. A suitable solution was found in the space group $P4/m$ and the refinement led to the final residuals of $R = 0.06$ and $R_W = 0.08$. Refinements in the space group $P4$, however, resulted in a better final agreement ($R = 0.048$ and $R_W = 0.067$), due account having been taken of the polar character of the space group. Some important metric parameters obtained using space group $P4$ are listed in Table V. As the crystals of **1** exhibited the usual type of disorder for heteronuclear systems, namely the randomly disordered direction of the M–M′ vectors, the metal to ligand bond distances are actually averages of Mo–L and W–L (L = Cl, P) distances. Due to this enforced averaging, only the metal–metal bond length and the overall conformation of the compound can be considered accurate. The Mo–W distance, 2.193(2) Å, is significantly longer than the Mo–Mo length, 2.134(4) Å, in the tetragonal form of its homonuclear analogue. Figure 1 displays an ORTEP diagram of compound **1** projected along the Mo–W axis. The torsion angle P(1)–MW(1)–MW(2)–P(2) is only 0.35°, indicating an effectively eclipsed conformation.

Crystals of **2** conformed to the space group $P2_1/n$ with two molecules per unit cell; thus, the molecule resides on a crystallographic inversion center. Figure 2 depicts one molecule in its

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(17) Gilmore, G. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

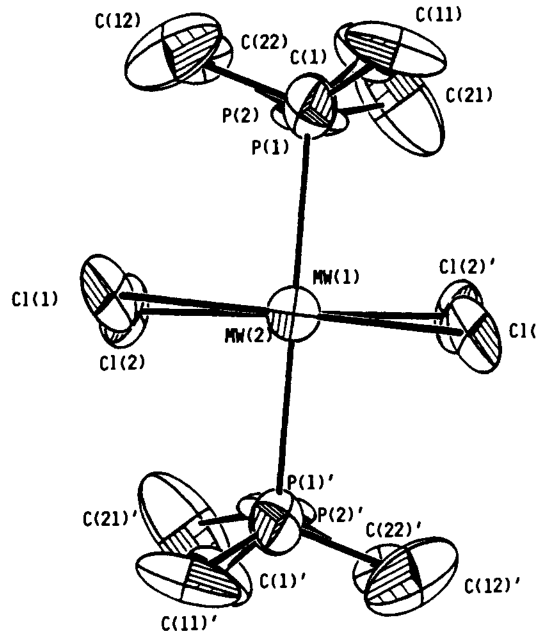

Figure 1. ORTEP drawing of complex $MoWCl_4(dmpm)_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

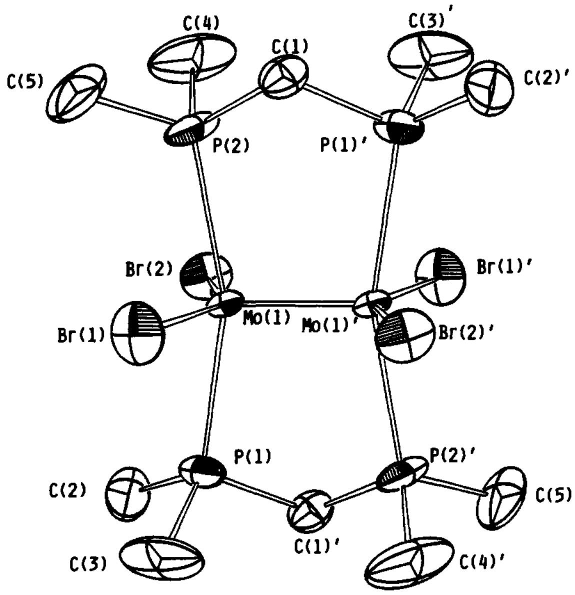

Figure 2. ORTEP drawing of complex $Mo_2Br_4(dmpm)_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level.

entirety. Selected bond distances and angles are listed in Table V. The structure of **2** clearly resembles that of the monoclinic structure of $Mo_2Cl_4(dmpm)_2$. The Mo–Mo bond distance of the former, 2.1271(8) Å, was virtually the same as observed in the latter, 2.1253(4) Å. The molecules of **2** also had almost perfect C_{2h} symmetry with an average torsion angle of 0°.

Compound **3** crystallizes in the space group $P2_1/c$ with four molecules per unit cell. Figure 3 presents one molecule of **3** with the atom-labeling scheme; selected metric parameters are also listed in Table V. The Mo–Mo distance of 2.132(2) Å is slightly longer than that observed in the compounds $Mo_2X_4(dmpm)_2$ (X = Cl, Br). In agreement with this lengthening is the fact that this compound exhibits the greatest twist, with the torsion angle P(1)–Mo(1)–Mo(2)–P(2) = –11.1°. The other three torsional angles, I(1)–Mo(1)–Mo(2)–I(3), I(2)–Mo(1)–Mo(2)–I(4), and P(3)–Mo(1)–Mo(2)–P(4) are –14.8, –8.8, and –11.0°, respectively. The average torsional angle in **3**, then, is 11.4°. Most likely the steric bulk of the I^- ligands accounts for the greater degree of twisting in this molecule.

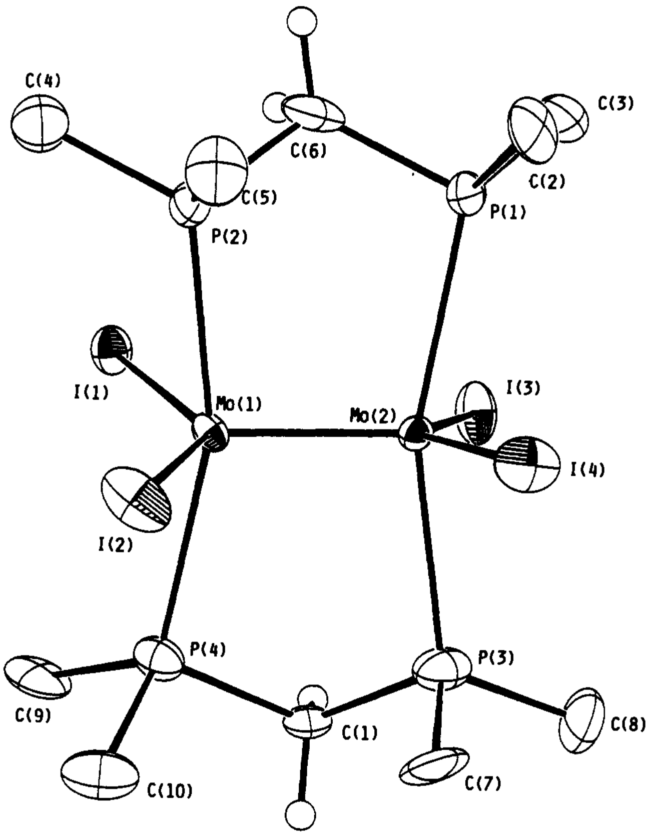

Figure 3. ORTEP drawing of complex $Mo_2I_4(dmpm)_2$ (**3**). Thermal ellipsoids are drawn at the 50% probability level.

Electronic Absorption Spectra. The solution electronic spectrum of the complex $MoWCl_4(dmpm)_2$ (**1**) in THF exhibited a prominent absorption band at λ_{max} = 628 nm (15 6900 cm^{-1}), that is assigned to the corresponding $\delta_{xy} \rightarrow \delta_{xy}^{*}$ transition. This band is shifted to higher energy relative to $MoWCl_4(dppm)_2$ (665 nm, 15 000 cm^{-1}).[4] This shift may be attributed to the increased basicity of the phosphine ligands. For the spectra of compounds $Mo_2X_4(dmpm)_2$ (X = Br (**2**), I (**3**)) recorded in CH_2Cl_2, the corresponding $\delta_{xy} \rightarrow \delta_{xy}^{*}$ transitions were at 630 nm (15 900 cm^{-1}) and 700 nm (14 300 cm^{-1}) for **2** and **3**, respectively. An absorption band at 604 nm (16 600 cm^{-1}) for the $\delta_{xy} \rightarrow \delta_{xy}^{*}$ transition had been previously reported for the complex $Mo_2Cl_4(dmpm)_2$. This band clearly displays a sensitivity to the nature of the halogen ligands. The energy of this band is red-shifted as the halogen ligands are changed from Cl to Br to I. This red-shift is ~680 cm^{-1} when changing from Cl to Br, and ~1590 cm^{-1} in going from Br to I. The large red shift from Br to I may be partly due to the presence of a torsion angle of 11° compared to 0° in the Cl and Br compounds. These shifts are somewhat larger than those previously reported[18] for $Mo_2X_4(dpcp)_2$ (X = Cl, Br, I), for which the torsion angles are 22°; in this case the red shifts are 170 cm^{-1} for Cl to Br and 1180 cm^{-1} for Br to I.

NMR Analysis and Magnetic Anisotropy of the Mo–Mo Quadruple Bond. A detailed NMR analysis of complex **1** has been previously discussed along with a comparison to other heteronuclear complexes.[4] The identities of the homonuclear complexes **2** and **3** were readily established by their distinctive $^{31}P\{^1H\}$ NMR spectra. Since all four phosphorus nuclei are equivalent, singlets were observed for both compounds; these were centered at δ –3.35 ppm for **2** and δ –7.04 ppm for **3**. The previously reported $^{31}P\{^1H\}$ NMR spectrum of $Mo_2Cl_4(dmpm)_2$ displayed a singlet at δ –0.77 ppm. The chemical shifts of the phosphorus nuclei seem to shift upfield (become more shielded) with halogen substitution from Cl to Br to I. This upfield shift correlates with the increasing covalence of the M–X bonds.

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(18) Chen, J.-D.; Cotton, F. A.; DeCanio, E. C. *Inorg. Chim. Acta* **1990**, 215.

Table VI. Magnetic Anisotropy of Mo–W or Mo–Mo for Complexes **1**–**3**

complex	G_{av}[a]	$\Delta\delta$, ppm	$\Delta\chi$[b]
1[c]	5.11	2.0	–4915
2	5.70	1.72	–3810
3	4.52	1.83	–5090

[a] Units in 10^{-27}; $G = (1 - 3\cos^2\theta)/3r^3$. [b] Unit in 10^{-36} m^3 molecule^{-1}. [c] See ref 4.

This series of complexes provides a good opportunity to study the magnetic anisotropy of the Mo–Mo quadruple bond. All of the previous studies were carried out on similar dimolybdenum systems containing phosphines with phenyl rings, which may have affected the chemical shift of the test protons.[6–8] The ^{1}H NMR spectra of **2** and **3** are quite similar: both exhibit a multiplet for the terminal methyl groups located upfield and a pentet for the central methylene group resonating at a downfield position. With the use of the ^{1}H NMR data and the positions of the hydrogen atoms calculated from the X-ray crystal structure data for complexes **2** and **3**,[19] the magnetic anisotropy was estimated based on the chemical shift values. Those of the methylene protons should be most affected, as they are situated over the center of Mo–Mo quadruple bond. The values for the terminal methyl protons should be affected the least since their positions are fluxional in solution due to free rotation about the P–C bond. The change of chemical shift values is related to the magnetic anisotropy ($\Delta\chi$) by the following equation:[8]

$$\Delta\delta = \frac{\Delta\chi}{4\pi}\left[\frac{1 - 3\cos^2\theta}{3r^3}\right] = \frac{\Delta\chi}{4\pi}G$$

Here $\Delta\delta$ is the change in the chemical shift value of the proton relative to the free ligand, and r is the distance from the nucleus under consideration to the center of the Mo–Mo bond. Table VI lists the observed $\Delta\delta$ values, G factors, and the calculated $\Delta\chi$ values for complexes **1**-**3**. The calculated values of $\Delta\chi$ are –3810 × 10^{-36} m^3 molecule^{-1} for complex **2** and –5090 × 10^{-36} m^3 molecule^{-1} for complex **3**, with an average value of –4450 × 10^{-36} m^3 molecule^{-1} for the Mo–Mo quadruple bond in these two homonuclear compounds. This number is much smaller than the value previously reported for the average magnetic anisotropy of the Mo–Mo quadruple bond, –6500 × 10^{-36} m^3 molecule^{-1}.[6,8] This difference may be caused by the ring current effect of the phenyl groups in the previously investigated systems. For complex **1**, the calculated value of $\Delta\chi$ is –4915 × 10^{-36} m^3 molecule^{-1}.[4]

Acknowledgment. We are grateful to the National Science Foundation for support.

Supplementary Material Available: Full list of crystallographic data, bond distances, bond angles, torsional angles, and anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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(19) C–H distances of 1.08 Å, and P–C–H angles of 109° were employed to determine the positions of the H atoms, which had not been included in the structure refinement.