

Preparation and Characterization of Bis[(μ -acetato)halo(μ -bis(diphenylphosphino)amine)molybdenum(II)] Complexes

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Molecules of the formula $\text{Mo}_2\text{X}_2(\text{OAc})_2(\mu\text{-dppa})_2$ ($\text{X} = \text{Cl}$ (**2**), Br (**3**), I (**4**); $\text{dppa} = \text{bis}(\text{diphenylphosphino})\text{-amine}$; $\text{OAc} = \text{CH}_3\text{COO}^-$) can be synthesized by the reaction of $\text{Mo}_2(\text{OAc})_4$ (**1**) with dppa and $(\text{CH}_3)_3\text{SiX}$. All three compounds were characterized by IR and UV–visible spectroscopy, mass spectrometry, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Single-crystal diffraction studies yield the following pertinent crystal data: for **2**·2EtOH, orthorhombic $Pbca$ (No. 61), $a = 16.830(2)$ Å, $b = 20.310(4)$ Å, $c = 16.751(2)$ Å, $V = 5726(2)$ Å³, $Z = 4$; for **3**·2(toluene), monoclinic $C2/c$ (No. 15), $a = 22.481(2)$ Å, $b = 19.151(9)$ Å, $c = 14.358(2)$ Å, $\beta = 95.19(2)^\circ$, $V = 6156(3)$ Å³, $Z = 4$; for **4**·EtOH·CH₃CN, monoclinic $P2_1/c$ (No. 14), $a = 20.607(9)$ Å, $b = 16.020(3)$ Å, $c = 17.189(5)$ Å, $\beta = 95.81(2)^\circ$, $V = 5645(3)$ Å³, $Z = 4$. The Mo–Mo distances for compounds **2**–**4** are 2.158(1), 2.176(1), and 2.164(1) Å, respectively. Both crystallographic data and physical measurements indicate that **2** and **3** have nearly identical Mo–X bond distances while those in **3** and **4** differ more significantly; the spectroscopic data bear this out. The Mo–O and Mo–P distances are very similar in all three of the complexes reported.

Introduction

Numerous and varied molecules of the general formula $\text{Mo}_2\text{X}_4(\text{LL})_2$ where LL is a bridging ligand are known,¹ yet examples of those having the formula $[\text{Mo}_2(\text{OAc})_2(\text{LL})_2]\text{X}_2$ where OAc is acetate are quite rare. These compounds have generally been regarded as reactive and unstable.² To our knowledge, only very few cations of this type have been structurally characterized, e.g. $[\text{Mo}_2(\text{OAc})_2(\text{dppm})_2](\text{BF}_4)_2$ ^{3a} and $[\text{Mo}_2(\text{OAc})_2(\text{dmpe})_2](\text{BF}_4)_2$.^{3b}

In our efforts to examine the reaction chemistry of molecules having the formula $\text{Mo}_2\text{X}_4(\mu\text{-dppa})_2$ ($\text{dppa} = \text{bis}(\text{diphenylphosphino})\text{amine}$), which will be reported elsewhere,⁴ we have found that molecules having the formula $\text{Mo}_2\text{X}_2(\text{OAc})_2(\mu\text{-dppa})_2$ may appear as intermediates in their syntheses from $\text{Mo}_2(\text{OAc})_4$ (**1**). In this paper we report efficient syntheses of the new series of $\text{Mo}_2\text{X}_2(\text{OAc})_2(\text{LL})_2$ compounds for $\text{X} = \text{Cl}$, Br , or I and $\text{LL} = \text{dppa}$. Each of these compounds has been characterized by IR, UV–vis, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction.

Experimental Section

All syntheses, manipulations, and spectroscopic studies were carried out under an atmosphere of dry argon or nitrogen unless otherwise specified. Standard Schlenk and vacuum-line techniques were used. Commercial grade solvents were dried and deoxygenated by refluxing for at least 24 h over appropriate drying agents and freshly distilled prior to use.

Bis(diphenylphosphino)amine and dimolybdenum tetraacetate (**1**) were prepared according to modified literature procedures.^{5–7}

Preparation of $\text{Mo}_2\text{Cl}_2(\text{OAc})_2(\mu\text{-dppa})_2$ (2**).** A 0.26 g (0.49 mmol) quantity of **1** and 0.38 g (0.97 mmol) of dppa were combined in a Schlenk tube, which was then evacuated for 20 min. A 20 mL portion of THF was then added under argon atmosphere. To this stirred suspension was added 19.4 mmol of Me_3SiCl . The color of the solution turned red within minutes, and a pink-violet precipitate was formed within about 30 min. The reaction mixture was stirred for an additional 20 h at room temperature. Then the solution was filtered off and the remaining pink residue was washed with 10 mL of diethyl ether and 10 mL of hexanes. The resulting solid was dried under reduced pressure. Yield: 0.46 g, 83% based on **1**. The reaction may also be carried out in acetonitrile (yield 0.44 g, 80% based on **1**).

Preparation of Single Crystals. Suitable crystals of compound **2** were obtained by slow diffusion of diethyl ether through a layer of hexanes into a solution of the compounds in a 1:1 mixture of acetonitrile/ethanol at room temperature. Pink crystals formed within 1 week.

Spectroscopic Data. IR (KBr), ν (cm^{−1}): 3053 m, 1483 m, 1435 vs, 1310 m, 1261 w, 1189 w, 1100 s, 1027 w, 920 m, 741 s, 695 s, 668 m, 528 s, 512 m, 489 m, 420 w. FAB/DIP-MS (nitrobenzyl alcohol (NBA) as FAB matrix): m/z 1151 ($[\text{M}]^+$, relative intensity 3%), 1117 ($[\text{M} - \text{Cl}]^+$, 17%), 765 ($[\text{M} - \text{dppa}]^+$, 17%), 730 ($[\text{M} - \text{Cl} - \text{dppa}]^+$, 43%), 386 ($[\text{dppa}]^+$, 85%), 183 ($[\text{dppa} - (\text{NH}_3\text{P}(\text{C}_6\text{H}_5)_2)]^+$, 100%). UV–vis (acetonitrile): $\lambda = 533$ nm. $^{31}\text{P}\{^1\text{H}\}$ NMR (81 MHz, CH_2Cl_2 , 20 °C): $\delta = 78.7$ ppm.

Preparation of $\text{Mo}_2\text{Br}_2(\text{OAc})_2(\mu\text{-dppa})_2$ (3**).** A Schlenk tube was charged with 0.5 g (1.3 mmol) of dppa and 0.2 g (0.47 mmol) of **1**,

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- (1) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: London, 1993. (b) Cotton, F. A.; Dunbar, K. R.; Hong, B.; James, C. A.; Matonic, J. H.; Thomas, J. L. *C. Inorg. Chem.* **1993**, 32, 5183. (c) Cotton, F. A.; James, C. A. *Inorg. Chem.* **1992**, 31, 5298. (d) Cotton, F. A.; Hong, B. *Inorg. Chem.* **1993**, 32, 2354. (e) Cotton, F. A.; Czuchajowska, J.; Luck, R. L. *J. Chem. Soc., Dalton Trans.* **1991**, 579. (f) Cotton, F. A.; James, C. A.; Luck, R. L. *Inorg. Chem.* **1991**, 30, 4370. (g) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J.; Price, A. C. *Inorg. Chem.* **1991**, 30, 2509. (h) Cotton, F. A.; Daniels, L. M.; Powell, G. L.; Kahaian, A. J.; Smith, T. J.; Vogel, E. F. *Inorg. Chim. Acta* **1988**, 144, 109. (i) Cotton, F. A.; Matusz, M. *Polyhedron* **1988**, 21, 2201. (k) Cotton, F. A.; Dunbar, K. R.; Poli, R. *Inorg. Chem.* **1986**, 25, 3700. (l) Luck, R. L.; Morris, R. H.; Sawyer, J. F. *Inorg. Chem.* **1987**, 26, 2422. (m) Cotton, F. A.; Falvello, L. R.; Harwood, W. S.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1986**, 25, 3949. (n) Campbell, F. L.; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, 23, 4222. (o) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, 17, 3240.
- (2) Bakir, M.; Walton, R. A. *Polyhedron* **1988**, 7, 1279.
- (3) (a) Cotton, F. A.; Eglin, J.; Wiesinger, K. J. *Inorg. Chim. Acta* **1992**, 195, 11. (b) Farrugia, L. J.; McVitie, A.; Peacock, R. D. *Inorg. Chem.* **1988**, 27, 1257.
- (4) Arnold, D. I.; Cotton, F. A.; Kühn, F. E. *Inorg. Chem.*, in press.

- (5) Nöth, N.; Meinel, L. Z. *Anorg. Allg. Chem.* **1967**, 349, 225.
- (6) Wang, F. T.; Najdzionek, J.; Leneker, K. L.; Wasserman, H.; Braitsch, D. M. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, 8 (2), 119.
- (7) (a) Stephenson, T. A.; Bannister, E.; Wilkinson, G. J. *Chem. Soc.* **1964**, 2538. (b) Holste, G. Z. Z. *Anorg. Allg. Chem.* **1975**, 414, 81. (c) McCarley, R. E.; Templeton, J. L.; Colburn, T. J.; Katovic, V.; Hoxmeier, R. J. *Adv. Chem. Ser.* **1976**, 150, 318.

Table 1. Crystal and Structure Refinement Data for **2**·2EtOH, **3**·2(toluene), and **4**·EtOH·CH₃CN

empirical formula	C ₅₆ H ₆₀ Cl ₂ Mo ₂ N ₂ O ₆ P ₄	C ₆₆ H ₆₄ Br ₂ Mo ₂ N ₂ O ₄ P ₄	C ₅₆ H ₅₇ I ₂ Mo ₂ N ₃ O ₅ P ₄
fw	1243.76	1424.80	1421.64
space group	<i>Pbca</i> (No. 61)	<i>C2/c</i> (No. 15)	<i>P2₁/c</i> (No. 14)
crystal system	orthorhombic	monoclinic	monoclinic
<i>a</i> , Å	16.830(2)	22.481(2)	20.607(9)
<i>b</i> , Å	20.310(4)	19.151(9)	16.020(3)
<i>c</i> , Å	16.751(2)	14.358(2)	17.189(5)
β , deg		95.19(2)	95.81(2)
<i>V</i> , Å ³	5726(2)	6156(3)	5645(3)
<i>Z</i>	4	4	4
<i>d</i> (calc), g/cm ³	1.429	1.533	1.662
μ , mm ⁻¹	5.899	1.859	1.700
wavelength, Å	1.541 84	0.710 73	0.710 73
<i>T</i> , K	293(2)	213(2)	173(2)
no. of rflns collected	3265	13068	19012
no. of data, restraints, params	2807, 0, 314	3576, 0, 371	6095, 24, 624
final <i>R</i> ₁ , ^a <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.056, 0.140	0.043, 0.096	0.056, 0.127
final <i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (all data)	0.108, 0.164	0.052, 0.102	0.095, 0.171
GOF ^c	1.052	1.124	1.083

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}. \quad ^c GOF = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{0.5}.$$

evacuated, and filled with N₂; 60 mL of THF was added, dissolving virtually all of the material to yield a yellow solution to which 0.4–0.5 mL (about 3.18 mmol) of Me₃SiBr was added in one portion. The solution underwent immediate color changes from yellow to orange to purplish red and then to dark purple; within about 20 min, a precipitate formed. The reaction mixture was refluxed for 3 h, during which it turned red. A 0.4 g quantity of pink solid (yield 69% based on **1**) was isolated from an olive green filtrate (the green color is due to the formation of Mo₂Br₄(μ -dppa)₂).

Preparation of Single Crystals. A 0.10 g sample of the pink material was dissolved in a mixture of 2 mL of CH₃CN and 7 mL of toluene, and the solution was layered with 10 mL of diethyl ether. Block-shaped pink crystals suitable for X-ray diffraction studies formed at room temperature within 2 days.

Spectroscopic Data. IR (KBr) ν (cm⁻¹): 3132 m, 1482 m, 1435 vs, 1314 m, 1190 w, 1099 s, 1057 w, 927 m, 740 m, 696 s, 668 m, 528 s, 512 m, 488 m, 420 w. FAB/DIP-MS (NBA as FAB matrix): *m/z* 1240 ([M]⁺, relative intensity 1%), 1161 ([M - Br]⁺, 3%), 776 ([M - Br - dppa]⁺, 5%), 386 ([dppa]⁺, 20%), 307 ([dppa - C₆H₆]⁺, 17%), 154 ([C₆H₅]₂⁺, 100%). UV-vis (acetonitrile): λ = 534 nm. ³¹P{¹H} NMR (81 MHz, CH₂Cl₂, 20 °C): δ = 77.8 ppm.

Preparation of Mo₂I₂(OAc)₂(μ -dppa)₂ (4**).** A 0.26 g (0.485 mmol) sample of Mo₂(OAc)₄ and 0.38 g (0.97 mmol) of dppa were combined in a Schlenk tube, which was then evacuated for 20 min. A 20 mL portion of THF was then added under an argon atmosphere. To this stirred suspension was added dropwise by syringe 19.4 mmol of Me₃SiI. The color of the solution immediately turned red, and a dark pink precipitate was formed within about 15 min. The reaction mixture was stirred for 20 h at room temperature. The solution was then filtered off, and the remaining dark pink residue was washed with 10 mL of diethyl ether and 10 mL of hexanes. It was finally dried in oil pump vacuum. Yield: 0.46 g, 72% based on **1**. The reaction can also be done in acetonitrile as solvent (yield 0.50 g, 78% based on **1**).

Preparation of Single Crystals. Suitable crystals of compound **4** were obtained by slow diffusion of diethyl ether through a layer of hexanes into a solution of the compounds in a 1:1 mixture of acetonitrile/ethanol at room temperature. Red-violet crystals formed within 2 days.

Spectroscopic Data. IR (KBr), ν (cm⁻¹): 3053 m, 1483 m, 1435 vs, 1311 m, 1188 w, 1098 s, 1056 w, 1026 w, 918 m, 811 m, 738 m, 699 s, 668 m, 527 s, 512 m, 487 m, 417 w. FAB/DIP-MS (NMA as FAB matrix): *m/z* 1207 ([M - I]⁺, relative intensity 2%), 824 ([M - I - dppa]⁺, 13%), 754 ([Mo₂Ac₂I₂(PPh₂H)]⁺, 14%), 386 ([dppa]⁺, 84%), 136 ([HNP(Ph)(CH₂)]⁺, 100%). UV-vis (acetonitrile): λ = 540 nm. ³¹P{¹H} NMR (81 MHz, CD₂Cl₂, 20 °C): δ (³¹P) 75.2 ppm.

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 783 spectrophotometer using KBr as the IR matrix. UV-vis spectra were recorded in acetonitrile solutions in quartz cells on a Cary 17 UV-vis spectrometer at room temperature. The ³¹P{¹H} NMR data were obtained on a Varian XL-200 broad-band spectrometer at room temperature, and the chemical shifts were referenced externally

and are reported relative to 85% H₃PO₄/D₂O. The FAB/DIP mass spectra (DIP = direct insertion probe) were acquired using a VG Analytical 705 (Manchester, UK) high-resolution, double-focusing, magnetic-sector mass spectrometer. The VG 705 was equipped with a VG 11/250 J data system that allowed computer control of the instrument, data recording, and data processing. Samples for analysis were prepared by mixing ca. 2 mL of the compound that had been dissolved in CH₂Cl₂ with approximately 5 mL of nitrobenzyl alcohol (NBA) matrix on the direct insertion probe tip. The probe was then inserted into the instrument through a vacuum interlock and the sample bombarded with 8 keV xenon primary particles from an Ion Tech FAB gun operating at an emission current of 2 mA. Positive secondary ions were extracted and accelerated to 6 keV and then mass-analyzed.

X-ray Crystallography. Single-crystal diffraction experiments were conducted on a Rigaku AFC5R (**4**) or an Enraf-Nonius FAST (**2**, **3**) automated diffractometer using Cu K α or Mo K α radiation, respectively.

On the Rigaku AFC5R, routine unit cell identification and intensity data collection were performed by utilizing the values specified in Table 1 and general procedures previously described.⁸ Lattice dimensions and Laue symmetry were verified using axial photographs. Three standard reflections were measured during data collection to monitor any intensity and crystal orientation changes. Experimental absorption corrections based on ψ scans were applied to the data using the TEXSAN software package.⁹

For the crystals on the Enraf-Nonius FAST diffractometer, preliminary data collection was carried out first to afford all parameters and an orientation matrix. Fifty reflections were used in indexing and 250 reflections in cell refinement. Axial images were obtained to confirm the Laue group and cell dimensions. No decay correction was applied.

The positions of the heavy atoms were determined by direct methods using SHELXS-86.^{10a} The remaining atoms were found by Fourier analyses using SHELXL-93.^{10b}

Compound 2. A pink crystal with dimensions of approximately 0.10 \times 0.10 \times 0.05 mm was protected with deoxygenated mineral oil in a Lindeman capillary and measured on a Rigaku AFC5R as described above. The space group *Pbca* was determined from systematic absences

- (8) (a) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *Organomet. Chem.* **1973**, *50*, 227. (b) Brüggemann, T.; Debaerdemaeker, B.; Müller, B.; Schmid, G.; Thewalt, U.; *ULM-Programmsystem* (1. Jahrestagung der Deutschen Gesellschaft für Kristallographie, Mainz, 9.–12. Juni 1992, Preprint of Subl.5, Z. Kristallographie, p. 33).
- (9) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.
- (10) (a) Sheldrick, G. M. *SHELXS-86: Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1986. (b) Sheldrick, G. M. *SHELXL-93: FORTRAN-77 Program for the Refinement of Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1993. (c) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

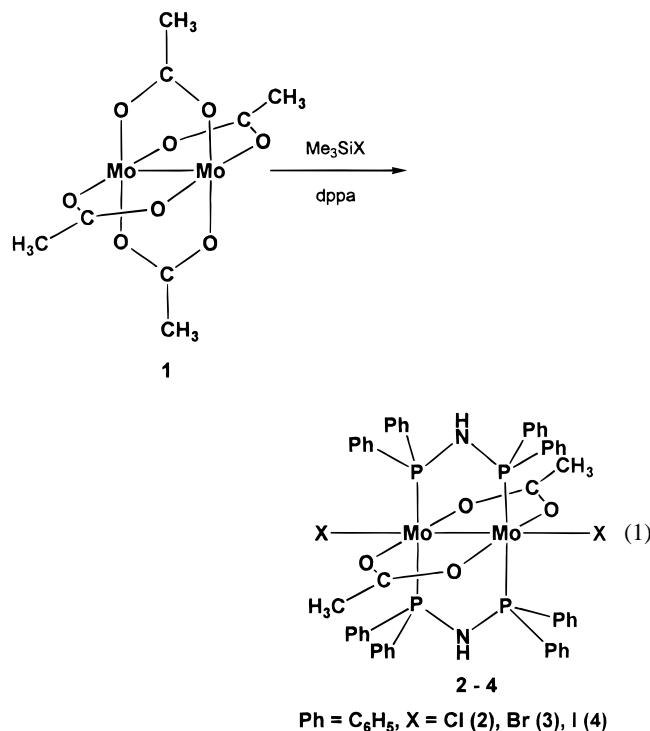
in the data. All non-hydrogen atoms were anisotropically refined; hydrogen atoms were included in the refinement on calculated positions. The crystal contains eight ethanol molecules per unit cell. The ethanol molecules were refined isotropically.

Compound 3. A pink crystal with dimensions of approximately 0.4 × 0.3 × 0.2 mm was mounted on the tip of a glass fiber and fixed with grease. The single-crystal experiment was conducted using an Enraf-Nonius FAST diffractometer at a measurement temperature of −60 °C. The space group *C2/c* was determined from systematic absences in the data. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included in the refinement on calculated positions. The crystal contains eight toluene molecules per unit cell for which no hydrogen atoms have been calculated.

Compound 4. A red-violet crystal with dimensions of approximately 0.4 × 0.3 × 0.1 mm was mounted on the tip of a quartz fiber. The experiment was conducted using an Enraf-Nonius FAST diffractometer and a measurement temperature of −100 °C. The space group *P2₁/c* was determined from systematic absences in the data. All non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included in the refinement on calculated positions. The crystal contains four ethanol and four acetonitrile molecules per unit cell for which no hydrogen atoms have been calculated. The atoms of the solvent molecules were refined isotropically.

Results and Discussion

Synthesis. During our attempts to synthesize compounds of the type Mo₂X₄(dppa)₂ by reacting **1** with dppa and excess Me₃SiX in THF, toluene, or acetonitrile, we observed the formation of purple or pink products which have been identified as Mo₂X₂(OAc)₂(μ-dppa)₂ where X = Cl (**2**), Br (**3**), and I (**4**). These products are obtainable in yields of 70–85%. Higher excess of Me₃SiX accelerates the reaction but apparently has no significant influence on the yield. *In-situ* ³¹P{¹H} NMR studies of the reaction mixtures suggest that no phosphorus-containing byproducts are formed, in agreement with eq 1.



Solubility and Stability. Products **2–4** are soluble in CH₂Cl₂ and also in mixtures of CH₃CN with EtOH, MeOH, or toluene. Their solubilities in CH₂Cl₂ decrease in the order **2**, **3**, **4**; their solubilities in CH₃CN/alcohol follow the opposite trend. The compounds are slightly soluble in acetonitrile and insoluble in hexanes, THF, diethyl ether, and toluene.

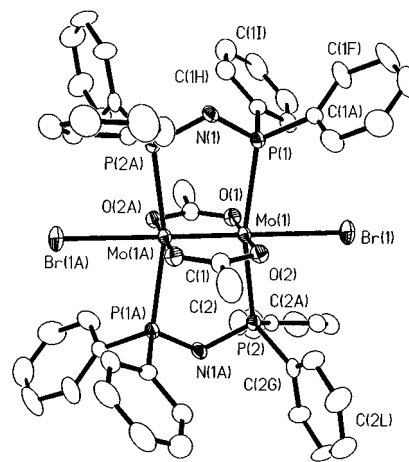


Figure 1. ORTEP drawing of the core atoms in Mo₂Cl₂(dppa)₂(OAc)₂ (**2**) viewed along the Mo–Mo axis. Thermal ellipsoids are shown at 40% probability.

In the solid state, compounds **2–4** may be handled in air for short periods of time; crystals of these complexes decompose only after several days. In solution they decompose yielding brown precipitates within 30 min of exposure to air or moisture. Under an inert-gas atmosphere (N₂, Ar) the compounds are stable in solution for several weeks and show no significant decomposition in the solid state even after several months.

Spectroscopy. The bridging acetato complexes **2–4** are clearly identified by the antisymmetric COO band at 1483 cm^{−1} and the very strong symmetric COO band at 1435 cm^{−1} observed in the IR spectra. The distinctive carbonyl stretch expected at 1750 cm^{−1} for a nonbridging acetate ligand is conspicuously absent. These bands are comparable with the characteristic COO bands for **1** (ν_{as} = 1512, 1494 cm^{−1}; ν_s = 1409 cm^{−1}),^{7a} but they are weaker and no splitting of the antisymmetric band can be observed. The antisymmetric deformation band, observed at 675 cm^{−1} for **1**^{7a} can be found at 695, 696, and 699 cm^{−1} for compounds **2–4**, respectively; this band is more pronounced for **1** than for **2–4**. The C–C and C–H vibrations attributed to the dppa ligand are very similar for the three compounds studied.

The UV spectra of compounds **2–4** exhibit maxima at 533, 535, and 540 nm, respectively; known compounds containing a (Mo₂)⁴⁺ core usually show maxima at ca. 500 nm.^{1a} These results show that the electronic absorption properties of the compounds are insensitive to the identity of the axial halo ligands. For this band, which we assign to the $\delta \rightarrow \delta^*$ transition, the total change from Cl to I is less than 10 nm (ca. 250 cm^{−1}). Similarly, the nature of the halo ligands has little effect on the ³¹P{¹H} NMR spectra of the compounds: while free dppa exhibits a chemical shift of $\delta(^{31}\text{P})$ 42.0 ppm, compounds **2–4** exhibit closely similar chemical shifts of $\delta(^{31}\text{P})$ 78.7, 77.8, and 75.2 ppm, respectively. Nevertheless, the phosphorus nuclei shift upfield (become more shielded) with halo substitution from Cl to Br to I. This upfield shift can be correlated with the increasing covalence of the Mo–X bonds. Because the Mo–X bonds are very long in any case (see X-ray section), their influence is very small, resulting in a $\Delta(\delta(^{31}\text{P}\{^1\text{H}\}))$ of less than 6 ppm from **2** to **4**.

The FAB mass spectra of compounds **2–4** exhibit very small molecular peaks and much more intense peaks attributable to [M – X]⁺; [M – dppa]⁺ and [M – X – dppa]⁺ peaks are also observed as are [M – 2X – dppa]⁺ peaks of much diminished intensities. In the case of **4**, the molecular peak is missing and the highest observed peak is [M – I]⁺. As expected, the decompositions under FAB/DIP conditions are similar for all three compounds.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Mo₂X₂(dppa)₂(OAc)₂: X = Cl (**2**), Br (**3**), I (**4**)

Cl(1)–Mo(1)	2.829(2)	Mo(1)–Br(1)	2.889(1)	I(1)–Mo(1)	3.181(1)
Mo(1)–Mo(1) ^a	2.158(1)	Mo(1)–Mo(1) ^a	2.176(1)	Mo(2)–I(2)	3.171(1)
Mo(1)–O(1)	2.081(6)	Mo(1)–O(1)	2.099(4)	Mo(1)–Mo(2)	2.164(1)
Mo(1)–O(2)	2.097(6)	Mo(1)–O(2)	2.129(4)	Mo(1)–O(1)	2.093(7)
				Mo(1)–O(4)	2.094(7)
				Mo(2)–O(3)	2.095(8)
				Mo(2)–O(2)	2.112(8)
Mo(1)–P(1) ^a	2.588(2)	Mo(1)–P(1)	2.557(2)	Mo(1)–P(3) ^a	2.566(3)
Mo(1)–P(2)	2.564(2)	Mo(1)–P(2)	2.571(2)	Mo(1)–P(1)	2.577(3)
				Mo(2)–P(4)	2.585(3)
				Mo(2)–P(2) ^a	2.588(3)
P(1)–N(1)	1.680(7)	P(1)–N(1)	1.683(4)	P(1)–N(2)	1.678(9)
P(2)–N(1)	1.669(7)	P(2)–N(1) ^a	1.691(5)	P(2)–N(1)	1.686(9)
				P(3)–N(1)	1.673(9)
				P(4)–N(2)	1.680(8)
O(1)–Mo(1)–O(2)	177.9(2)	O(1)–Mo(1)–O(2)	178.7(1)	O(1)–Mo(1)–O(4)	177.5(3)
O(1)–Mo(1)–Mo(1) ^a	91.1(2)	O(1)–Mo(1)–Mo(1) ^a	91.5(1)	O(1)–Mo(1)–Mo(2)	90.7(2)
O(2)–Mo(1)–Mo(1) ^a	91.0(2)	O(2)–Mo(1)–Mo(1) ^a	89.8(1)	O(4)–Mo(1)–Mo(2)	91.5(2)
O(1)–Mo(1)–P(2)	86.7(2)	O(1)–Mo(1)–P(2)	84.3(1)	O(1)–Mo(1)–P(3) ^a	93.5(2)
O(2)–Mo(1)–P(2)	92.6(2)	O(2)–Mo(1)–P(2)	95.7(1)	O(4)–Mo(1)–P(3) ^a	87.5(2)
Mo(1) ^a –Mo(1)–P(2)	98.92(7)	Mo(1) ^a –Mo(1)–P(2)	98.32(4)	Mo(2)–Mo(1)–P(3) ^a	96.45(7)
O(1)–Mo(1)–P(1) ^a	87.4(2)	O(1)–Mo(1)–P(1)	86.8(1)	O(1)–Mo(1)–P(1)	93.2(2)
O(2)–Mo(1)–P(1) ^a	92.7(2)	O(2)–Mo(1)–P(1)	92.8(1)	O(4)–Mo(1)–P(1)	85.2(2)
Mo(1) ^a –Mo(1)–P(1) ^a	97.22(6)	Mo(1) ^a –Mo(1)–P(1)	97.44(4)	Mo(2)–Mo(1)–P(1)	99.68(7)
P(2)–Mo(1)–P(1) ^a	162.93(8)	P(1)–Mo(1)–P(2)	162.08(5)	P(3) ^a –Mo(1)–P(1)	162.43(9)
O(1)–Mo(1)–Cl(1)	89.1(2)	O(1)–Mo(1)–Br(1)	89.1(1)	O(1)–Mo(1)–I(1)	86.7(2)
O(2)–Mo(2)–Cl(1)	88.8(2)	O(2)–Mo(2)–Br(1)	89.7(1)	O(4)–Mo(1)–I(1)	91.1(2)
Mo(1) ^a –Mo(1)–Cl(1)	176.51(7)	Mo(1) ^a –Mo(1)–Br(1)	179.25(4)	Mo(2)–Mo(1)–I(1)	177.25(5)
				Mo(1)–Mo(2)–I(2)	177.23(5)
P(1)–N(1)–P(2)	119.4(4)	P(1)–N(1)–P(2) ^a	118.8(3)	P(1)–N(2)–P(4)	120.3(5)
				P(2)–N(1)–P(3)	119.0(5)

^a Symmetry transformations to generate equivalent atoms are as follows. For **2**: $-x + 1, y, z$. For **3**: $-x + 0.5, -y + 0.5, -z$. For **4**: $x, y + 1, z$.

Molecular Structures. Pertinent crystallographic information for the complexes obtained is given in Table 1. Figure 1 shows an ORTEP representation of molecule **3**.

Compounds **2–4** form purple or pink crystals which can be obtained by layering solutions of the compounds in mixtures of acetonitrile and ethanol, THF, or toluene with hexanes and/or diethyl ether. After a few days at room temperature, crystals of sufficient quality for single-crystal X-ray diffraction studies form.

Compound **2** crystallizes in the space group *Pbca*, compound **3** in *C2/c*, and compound **4** in *P2₁/c*. All examined crystals contain solvent molecules in their unit cells (see Experimental Section).

The dimensions of the three Mo₂X₂(OAc)₂(μ -dppa)₂ molecules are collected and compared in Table 2. In compounds **2–4** the halo ligands occupy axial positions and the two dppa ligands are positioned trans to each other. The latter fact is probably due to the steric bulk of the phenyl groups in dppa. The Mo–Mo bond distances for all three molecules are very similar (see Table 2) and are within the range known for Mo–Mo quadruple bonds. The Mo–O and Mo–P distances do not vary significantly among compounds **2–4**; the ³¹P{¹H} NMR data agree well with the latter observation. The P–N–P angles of the bridging dppa ligands for all these compounds are very similar as well. Free dppa has a P–N–P angle of 118.9(2)°. ¹¹ In mononuclear complexes the P–N–P angle is about 100–102°, ¹² and in dinuclear compounds with bridging dppa the average value for the P–N–P angles is 122.9°. ⁶ In complexes **2–4**, the P–N–P angles range from 118.8 to 120.3°, almost identical to that of free dppa. The P–N distance in the coordinated ligand (in all cases *ca.* 1.68 Å) is also very close

Table 3. Ionic Radii (Å) of Halo and Mo Species

	ionic radii	sum of ionic radii (X–Mo)	bond dist (X–Mo), Å
Cl [–]	1.67	2.55	2.83
Br [–]	1.82	2.70	2.89
I [–]	2.06	2.94	3.18
Mo ²⁺	<i>ca.</i> 0.88		

to that in free dppa (1.692(3) Å).⁵ These facts attest to the stability of dppa as a bridging ligand in the cases of **2–4**, which may result from the apparent lack of ring tension in the dinuclear metal complexes.

The Mo–X distances are comparatively long in all three of the complexes studied, indicating only weak Mo–halo interactions. This explains the small effect of varying the halo ligands on the spectroscopic data (see above). The Mo–X bond, however, is significantly shorter than the expected sum of the van der Waals radii of Mo and X but longer than the combined ionic radii of Mo²⁺–X[–] (see Table 3).¹³ The Mo–X distances also show a strong dependence on the nature of the halo ion. This is particularly evident in **4**, where the Mo–I bond is about 0.292(1) Å longer than the Mo–Br bond distance in **3**. The bond length difference between Mo–Br and Mo–Cl is only 0.060(2) Å. This result is reflected in the UV and ³¹P{¹H} NMR data. While the shifts of **2** and **3** are nearly identical within the experimental errors of the methods, the data for **4** differ more significantly from them (see above).

Conclusions

Molecules of the general type Mo₂X₂(OAc)₂(μ -dppa)₂ are easily formed by reaction of Mo₄(OAc)₄ with dppa and Me₃–SiX. They appear to be intermediates in the preparation of Mo₂X₄(μ -dppa)₂-type compounds. The spectroscopic data for

(11) Nöth, H.; Fluck, E. Z. *Naturforsch.*, B **1984**, 39, 744.

(12) Browning, C. S.; Farrar, D. H.; Frankel, D. C. *Acta Crystallogr.* **1992**, C48, 806.

(13) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

all examined compounds are very similar because the halo ligands are relatively far from the molybdenum atoms and, therefore, have only minor influence. However, single-crystal X-ray measurements show that the Mo–X bond distances vary significantly: the Mo–I bond distance is by far longer than the Mo–Br distance ($\Delta d = 0.29 \text{ \AA}$), which varies only slightly from the Mo–Cl bond distance ($\Delta d = 0.06 \text{ \AA}$). In agreement with this observation the UV–vis bands and the $^{31}\text{P}\{^1\text{H}\}$ NMR signals of compounds **3** (Br) and **4** (I) differ more than those of **2** (Cl) from **3**. The shifts of the latter compounds are nearly identical. It should be possible to replace the I ligand by other ions, e.g. F[–] or CN[–], or by strongly donating solvent molecules. This work is currently underway in our laboratory.

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Supporting Information Available: Full listings of crystallographic data, positional parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and ORTEP representations of compounds **2–4** (21 pages). Ordering information is given on any current masthead page.

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