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

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Complexes having the formula $Mo_2X_4(\mu\text{-dppa})_2$ (X = Cl (**2**) Br (**3**); dppa = bis(diphenylphosphino)amine) can be synthesized by the reaction of $Mo_2(OAc)_4$ (OAc = μ-CH_3COO) with dppa and an excess of $(CH_3)_3SiX$ under reflux conditions. Both compounds were characterized by IR and UV/vis spectroscopy and by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Single-crystal diffraction studies afford the following pertinent crystal data for **2** and **3**, respectively: monoclinic $P2_1/c$, $a = 15.522(4)$ Å, $b = 17.881(5)$ Å, $c = 16.898(3)$ Å, $\beta = 91.15(2)°$, $Z = 4$; orthorhombic $P2_12_12_1$, $a = 19.654(2)$, $b = 19.865(2)$ $c = 14.792(1)$, $Z = 4$. Both compounds exhibit significant torsion angles but, nevertheless, have comparatively short Mo−Mo bond distances (**2**, d(Mo−Mo) = 2.134(1) Å; **3**, d(Mo−Mo) = 2.137(2) Å).

Introduction

A broad variety of compounds of the general type $Mo_2(LL)_2X_4$ (X = Cl, Br, I) is known.[1] However, few data are available upon which to base comparisons between compounds having the same diphosphine ligand LL and varying halo substituents. It is also notable that until now only compounds with carbon-bridged diphosphine ligands have been examined. Most of the $Mo_2(LL)_2X_4$ compounds found in the literature are prepared by starting from $Mo_2(OAc)_4$ (**1**), where Ac = μ-CH_3COO, or from $Mo_2(CF_3COO)_4$ (**1a**),[1] but little attention has been focused upon possible intermediates in this reaction. We now report the first $Mo_2(LL)_2X_4$-type compounds with NH-bridged diphosphines. Some noteworthy differences from the already known compounds, both in their preparation and in their spectroscopic and crystallographic properties, are described.

Experimental Section

All syntheses, manipulations, and spectroscopic studies were carried out under an atmosphere of dry argon or nitrogen at room temperature 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 drying agents under a dry N_2 atmosphere and freshly distilled prior to use.

Bis(diphenylphosphino)amine (dppa), tetrakis(acetato)dimolybdenum (**1**), tetrakis(trifluoroacetato)dimolybdenum (**1a**), and bis[(μ-acetato)-halo(μ-bis(diphenylphosphino)amine)molybdenum(II)] complexes (halo = chloro, bromo, iodo) were prepared according to literature procedures or modified literature procedures.[2] Trimethylsilyl halides $(CH_3)_3SiX$ (X = Cl, Br, I) were purchased from Aldrich Chemical Co. and used as received.

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 16 PC FTIR spectrophotometer using KBr as the matrix. UV/vis spectra were recorded in acetonitrile solutions in quartz cells on a Cary 17 UV/vis spectrometer. The $^{31}P\{^1H\}$ NMR data were obtained on a Varian XL-200 broad-band spectrometer with the chemical shifts referenced externally and are reported relative to 85% H_3PO_4/D_2O. The ^1H NMR spectra were recorded on a Varian XL-200E spectrometer, and the data are reported relative to TMS.

Preparation of $Mo_2(dppa)_2Cl_4$. Method 1. A 200 mg (0.47 mmol) sample of $Mo_2(CH_3COO)_4$ (**1**) and 370 mg (0.96 mmol) of dppa were combined in a flask with 30 mL of tetrahydrofuran (thf) to yield a yellow solution with some fine white suspended solid. To this mixture

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was added in one portion about 0.7 mL (5.5 mmol) of chlorotrimethylsilane; the solution immediately turned red. The mixture was refluxed for about 70 min, during which it turned first purple, then brown, and then emerald green and deposited a fine, bright green solid. A 400 mg (0.36 mmol) quantity of this air-stable solid was isolated (yield 77% based on **1**).

A 100 mg sample of the green solid was dissolved in 10 mL of CH_2Cl_2, and the resulting solution was layered with 10 mL of hexanes. After 5 days at room temperature, 5 mL of hexanes were mixed with the solution and an additional 15 mL of hexanes were layered on top; crystalline material began to deposit within 1 h. Emerald green hexagonal-shaped plates formed within 1 week.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3048 m, 1588 w, 1482 w, 1435 m, 1401 m, 1311 w, 1261 m, 1092 m, 930 m, 802 m, 741 s, 719 m, 612 vs, 525 m; UV/vis (acetonitrile) λ (nm) 699 st, 453 sh; $^{31}P\{^1H\}$ NMR (81 MHz, acetonitrile, 22 °C) δ (ppm) 73.6; ^1H NMR (200.1 MHz, acetonitrile, 22 °C) δ (ppm) = 7.6−7.2 (m, 40H), 5.32 (t, 2H).

Method 2. A 250 mg (0.47 mmol) sample of **1** was combined with 15 mL of acetonitrile in a Schlenk tube. A 240 μL (1.90 mmol) portion of Me_3SiCl was added to the stirred suspension, which immediately turned red. A 360 mg portion of dppa was added to the reaction mixture, and the resultant mixture was stirred at room temperature for 5 h, during which a pink precipitate formed. A 10 mL portion of EtOH were then added, and the pink residue dissolved. Within 3 h, the reaction solution turned green and a green precipitate formed. The solution was filtered off, and the green residue was rinsed with 10 mL of hexanes and 10 mL of diethyl ether and dried under vacuum for several hours. The spectroscopic data of the resulting green powder are identical with those of **2** (method 1). Yield: 75% based on **1**.

Method 3. A 250 mg (0.47 mmol) sample of **1** and 360 mg of dppa were combined in a Schlenk tube and dissolved in 15 mL of MeOH; the solution turned orange within a few minutes. To the solution was added dropwise 470 μL (3.7 mmol) of Me_3SiCl, and the reaction mixture turned dark red. It was then refluxed for 20 min, during which it turned green and deposited green precipitate. The precipitate was isolated as described in method 2 and was identical with **2** on the basis of spectroscopic results (yield 72% based on **1**).

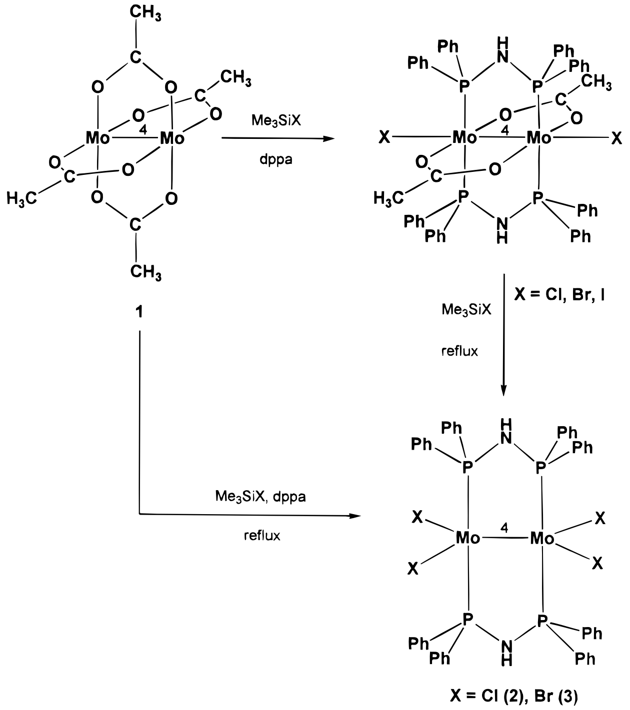
Preparation of $Mo_2(dppa)_2Br_4$. Method 1. A 250 mg (0.39 mmol) sample of **1a** and 450 mg (1.2 mmol) of dppa were combined in a flask with 20 mL of thf to yield an orange solution. To this solution was added in one portion 0.40 mL (3.0 mmol) of $(CH_3)_3SiBr$; the solution immediately turned red and then violet-red and quickly deposited a red solid. The reaction mixture was heated for 2 days, during which it became olive-colored and then brown. A red solid was filtered out of the reaction mixture, and about 10 mL of the green solution was layered with 10 mL of hexanes; within 24 h at room temperature, small green crystals began to form.

Spectroscopic data: IR (KBr) ν (cm^{-1}) 3049 m, 1571 w, 1484 w, 1434 s, 1314 m, 1261 w, 1095 st, 916 st, 816 m, 742 s, 691 s, 525 s; UV/vis (acetonitrile) λ (nm) 725 st, 620 sh, 475 sh; $^{31}P\{^1H\}$ NMR (81 MHz, acetonitrile, 22 °C) δ (ppm) 70.2; ^1H NMR (200.1 MHz, acetonitrile, 22 °C) δ (ppm) 7.20−7.40 (m, 40H), 5.71 (t, 2H).

Method 2. A 200 mg (0.47 mmol) sample of **1** and 500 mg (1.3 mmol) of dppa were combined in a flask with 20 mL of thf. To this mixture was added in one portion 0.45 mL (3.4 mmol) of $(CH_3)_3SiBr$; over a period of 5 min the mixture turned red and then purple. The reaction mixture was refluxed overnight, after which 400 mg of pink solid was separated from the green solution and ca. 15 mL of this solution was layered with 15 mL of hexanes. After 2 days at room temperature, a pink solid was deposited and green crystals began to form. The cell constants were measured using an Enraf-Nonius FAST area detector diffractometer and found to be identical with those obtained for $Mo_2(dppa)_2Br_4$ as prepared by method 1.

X-ray Crystallography. Single-crystal diffraction experiments were conducted using an Enraf-Nonius CAD4 automated diffractometer (Mo Kα radiation) for compound **2** and a Rigaku AFC5R automated diffractometer (Cu Kα radiation) for compound **3.** Data were corrected for Lorentz and polarization effects. Structure refinement was carried out using SHELXL-93.[3]

Scheme 1



A green crystal of compound **2** was mounted on the tip of a quartz fiber on the Enraf-Nonius CAD4. Routine unit cell identification and intensity data collection procedures were followed by utilizing the values specified in Table 4 and well-established procedures fully described elsewhere.[4] Intensity measurements were carried out at ambient temperature. The intensities of three representative reflections were measured at regular intervals and revealed that no significant decay occurred during data collection. An empirical absorption correction based on ψ scans was applied to the data. Space group selection was based on examination of systematic absences. The positions of the metal atoms were determined through the use of direct methods[5] and the remaining non-hydrogen atoms found by successive least-squares refinement followed by difference Fourier synthesis. The hydrogen atoms were placed at calculated positions and allowed to ride on the associated carbon atoms. All non-hydrogen atoms were refined using anisotropic displacement parameters.

A greenish brown needlelike crystal of compound **3** was mounted on the tip of a quartz fiber on the Rigaku AFC5R. Routine unit cell identification and intensity data collection procedures were followed by utilizing the values specified in Table 4 and general procedures previously described.[6] Lattice dimensions and Laue symmetry were verified using axial photography. Three standard reflections were measured during data collection to monitor intensity and crystal orientation stability. Experimental absorption corrections based on ψ scans were applied to the data using the TEXSAN software package.[7] The positions of the metal atoms were determined by direct methods, and all of the non-hydrogen atoms except those of the included solvent molecules (eight thf molecules per unit cell) were refined using anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions riding on the associated carbon atoms. The Flack x parameter[8] of compound **3** is −0.03(3).

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Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Mo_2(dppa)_2Cl_4$

	x	*y*	*z*	*U*(eq)
Mo(2)	2080(1)	9537(1)	2308(1)	30(1)
Mo(1)	3236(1)	9918(1)	2882(1)	30(1)
P(3)	4178(1)	10007(1)	1636(1)	40(1)
P(1)	2694(1)	9987(1)	4301(1)	31(1)
P(2)	1046(1)	9837(1)	3448(1)	30(1)
Cl(4)	1491(1)	10583(1)	1595(1)	47(1)
Cl(2	3150(1)	11251(1)	2901(1)	54(1)
P(4)	2725(1)	9189(1)	974(1)	39(1)
Cl(3)	1940(1)	8237(1)	2566(1)	53(1)
Cl(1)	4025(1)	8862(1)	3323(1)	50(1)
N(1)	1620(3)	10084(2)	4264(2)	34(1)
N(2)	3597(3)	9730(3)	841(3)	49(1)
C(3A)	4565(4)	10929(4)	1379(4)	52(2)
C(3B)	5414(5)	11139(4)	1439(4)	70(2)
C(3C)	5652(6)	11871(5)	1300(6)	100(3)
C(3D)	5062(7)	12380(5)	1100(6)	102(3)
C(3E)	4224(7)	12198(5)	1026(6)	105(3)
C(3F)	3968(5)	11470(4)	1168(4)	77(2)
C(3G)	5169(4)	9464(4)	1648(4)	50(2)
C(3H)	5413(5)	9024(5)	1024(5)	78(2)
C(3I)	6176(6)	8640(6)	1051(7)	112(4)
C(3K)	6695(7)	8699(7)	1699(8)	119(4)
C(3L)	6482(5)	9140(6)	2313(6)	101(4)
C(3M)	5710(5)	9516(5)	2294(4)	73(2)
C(1A)	2896(4)	9216(3)	5000(3)	33(1)
C(1B)	2454(4)	8559(3)	4908(3)	41(2)
C(1C)	2564(4)	7979(3)	5448(4)	50(2)
C(1D)	3144(4)	8056(4)	6060(4)	54(2)
C(1E)	3612(5)	8693(4)	6138(4)	63(2)
C(1F)	3491(4)	9279(4)	5621(4)	52(2)
C(1G)	3097(3)	10770(3)	4861(3)	32(1)
C(1H)	2644(4)	11110(3)	5453(3)	37(1)
C(1I)	3015(4)	11660(3)	5922(3)	44(2)
C(1K)	3859(4)	11854(3)	5825(4)	52(2)
C(1L)	4325(4)	11514(4)	5252(4)	54(2)
C(1M)	3953(4)	10976(3)	4765(3)	48(2)
C(4A)	3082(4)	8239(4)	804(4)	49(2)
C(4B)	2805(4)	7805(4)	173(4)	61(2)
C(4C)	3122(5)	7100(5)	59(5)	78(2)
C(4D)	3704(6)	6808(4)	564(5)	80(3)
C(4E)	4012(6)	7221(5)	1200(5)	87(3)
C(4F)	3676(5)	7928(4)	1319(4)	66(2)
C(4G)	2031(4)	9367(3)	119(3)	40(2)
C(4H)	1177(4)	9192(4)	162(4)	58(2)
C(4I)	621(4)	9294(4)	−479(4)	58(2)
C(4K)	914(5)	9571(4)	−1161(4)	67(2)
C(4L)	1756(6)	9754(5)	−1212(4)	93(3)
C(4M)	2325(5)	9662(5)	−575(4)	75(2)
C(2A)	344(3)	9076(3)	3743(3)	32(1)
C(2B)	99(4)	8687(3)	3154(3)	44(2)
C(2C)	−667(4)	8128(3)	3353(4)	44(2)
C(2D)	−789(4)	7948(3)	4132(4)	46(2)
C(2E)	−356(4)	8328(3)	4715(4)	48(2)
C(2F)	216(4)	8894(3)	4529(3)	41(2)
C(2G)	285(4)	10601(3)	3315(3)	34(1)
C(2H)	−603(4)	10501(3)	3361(3)	46(2)
C(2I)	−1156(4)	11098(4)	3259(4)	61(2)
C(2K)	−820(5)	11787(4)	3110(4)	65(2)
C(2L)	51(5)	11900(4)	3053(4)	62(2)
C(2M)	609(4)	11311(3)	3149(4)	51(2)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Mo_2(dppa)_2Br_4$

	x	*y*	*z*	*U*(eq)
Mo(1)	1991(1)	7980(1)	8582(1)	37(1)
Mo(2)	1981(1)	7119(1)	7715(1)	38(1)
Br(1)	772(1)	8335(1)	8864(1)	57(1)
Br(2)	3201(1)	8303(1)	8887(1)	58(1)
Br(3)	792(1)	6647(1)	7755(1)	60(1)
Br(4)	3156(1)	6921(1)	7052(1)	58(1)
P(3)	1981(2)	8888(2)	7343(2)	42(1)
P(1)	1933(2)	7339(2)	10117(2)	41(1)
P(2)	2243(2)	6228(2)	8937(3)	41(1)
P(4)	1589(2)	7737(2)	6263(3)	42(1)
C(4G)	744(7)	7606(8)	5795(10)	49(4)
C(1A)	1185(7)	7424(7)	10834(10)	42(4)
C(1G)	2661(7)	7534(8)	10852(11)	47(4)
C(4A)	2110(7)	7557(8)	5252(10)	48(4)
C(2A)	3086(8)	5891(7)	9263(9)	47(4)
C(3A)	1495(7)	9593(7)	7692(11)	46(4)
C(2G)	1771(7)	5462(8)	8684(11)	51(4)
C(3G)	2757(8)	9261(8)	6889(10)	52(4)
N(1)	1946(6)	6500(5)	9929(7)	41(3)
N(2)	1595(6)	8575(6)	6431(8)	48(3)
C(1H)	2774(7)	8195(8)	11095(11)	58(4)
C(2H)	1953(9)	5133(8)	7873(13)	72(5)
C(2F)	3668(7)	6307(9)	9170(11)	53(4)
C(1K)	3845(8)	7905(11)	11728(11)	70(5)
C(4M)	191(7)	7837(8)	6281(11)	60(5)
C(2B)	3155(9)	5300(8)	9714(11)	63(5)
C(1I)	3361(9)	8365(9)	11536(12)	68(5)
C(1F)	573(7)	7144(8)	10494(11)	53(4)
C(3B)	852(8)	9764(8)	7316(12)	66(5)
C(1B)	1162(9)	7740(9)	11662(12)	70(5)
C(2L)	875(9)	4672(10)	8851(15)	83(6)
C(3H)	3313(8)	8862(8)	6697(11)	61(5)
C(2I)	1563(12)	4575(9)	7598(14)	88(7)
C(4H)	618(9)	7325(11)	4962(15)	85(6)
C(1E)	−5(8)	7184(10)	11008(16)	83(6)
C(3F)	1703(9)	9966(8)	8428(12)	65(5)
C(1M)	3136(7)	7045(10)	11055(10)	64(4)
C(2M)	1223(9)	5246(9)	9147(11)	73(6)
C(3C)	497(9)	10306(8)	7678(14)	70(5)
C(4F)	2249(8)	6896(9)	5055(11)	69(5)
C(3D)	725(12)	10670(9)	8393(14)	82(6)
C(2E)	4274(8)	6095(11)	9578(12)	75(6)
C(4L)	−471(8)	7767(9)	5951(15)	77(6)
C(3E)	1356(11)	10501(9)	8746(13)	75(5)
C(2C)	3737(10)	5104(10)	10086(14)	80(6)
C(4B)	2293(8)	8053(10)	4665(11)	70(5)
C(4I)	−34(10)	7274(12)	4613(15)	102(8)
C(4E)	2560(10)	6743(12)	4246(15)	93(7)
C(1L)	3726(8)	7249(10)	11474(11)	62(5)
C(2D)	4318(9)	5471(10)	10034(11)	68(5)
C(4K)	−571(9)	7484(13)	5103(15)	89(7)
C(1C)	569(9)	7767(10)	12156(14)	83(6)
C(1D)	−10(11)	7499(11)	11807(16)	95(8)
C(3M)	2818(9)	9954(9)	6674(15)	87(7)
C(3I)	3883(9)	9142(10)	6343(15)	82(6)
C(4D)	2742(10)	7236(16)	3657(15)	103(9)
C(4C)	2606(11)	7885(14)	3876(14)	100(8)
C(2K)	1016(10)	4381(9)	8069(15)	73(5)
C(3K)	3957(10)	9802(12)	6161(15)	89(6)
C(3M)	3404(10)	10206(10)	6326(16)	93(7)
O(1)	8304(8)	623(8)	3440(11)	110(5)
C(100)	8384(15)	1040(14)	2661(21)	139(10)
C(101)	9120(18)	227(18)	2476(24)	166(13)
C(102)	8972(19)	906(19)	2207(27)	187(14)
C(103)	8760(17)	2(17)	3377(23)	165(13)
O(2)	3950(10)	600(11)	−12(14)	157(7)
C(105)	3755(15)	−62(16)	−233(21)	136(10)
C(106)	4167(23)	−145(22)	−1095(32)	221(18)
C(107)	4157(21)	565(22)	−1464(28)	203(16)
C(108)	4397(17)	931(17)	−718(25)	167(13)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

Synthesis, Stability, and Solubility. Complexes of the type $Mo_2(LL)_2X_4$ are usually synthesized by reacting $Mo_2(OAc)_4$ (**1**) with the diphosphine ligand LL and an excess of Me_3SiX in thf, toluene, or acetonitrile[1j,9] and are generally green or bluishgreen.[1] We observed the formation of pink or reddish violet compounds when we carried out the reaction with LL = dppa and Me_3SiX (X = Cl, Br, I); these reddish materials were identified as $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ (X = Cl, Br, I) and have been reported previously.[2h] The formation of intermediate red

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Mo_2(dppa)_2X_4$ (X = Cl, Br)[a]

Mo(1)−Mo(2)	2.1336(8)	2.137(2)	P(3)−C(3G)	1.818(6)	1.82(2)
Mo(1)−X(2)	2.387(2)	2.505(2)	P(1)−N(1)	1.677(4)	1.69(1)
Mo(1)−X(1)	2.365(2)	2.531(2)	P(1)−C(1A)	1.838(5)	1.82(1)
Mo(1)−P(3)	2.591(2)	2.571(4)	P(1)−C(1G)	1.797(5)	1.84(2)
Mo(1)−P(1)	2.560(2)	2.605(4)	P(2)−N(1)	1.685(4)	1.67(1)
Mo(2)−X(3)	2.375(2)	2.519(2)	P(2)−C(2G)	1.817(6)	1.82(2)
Mo(2)−X(4)	2.397(2)	2.539(2)	P(2)−C(2A)	1.819(5)	1.85(2)
Mo(2)−P(2)	2.588(2)	2.582(4)	P(4)−N(2)	1.683(5)	1.68(1)
Mo(2)−P(4)	2.561(2)	2.592(4)	P(4)−C(4G)	1.814(6)	1.82(2)
P(3)−N(2)	1.678(5)	1.67(1)	P(4)−C(4A)	1.811(7)	1.85(1)
Mo(2)−Mo(1)−X(2)	106.17(5)	108.74(7)	Mo(1)−Mo(2)−X(4)	106.71(5)	110.35(7)
Mo(2)−Mo(1)−X(1)	108.28(5)	108.28(7)	Mo(3)−Mo(2)−X(4)	145.15(6)	142.65(7)
Mo(2)−Mo(1)−X(1)	145.30(6)	142.89(7)	Mo(1)−Mo(2)−P(2)	97.11(4)	97.3(1)
Mo(2)−Mo(1)−P(3)	97.69(4)	97.7(1)	Mo(1)−Mo(2)−P(4)	97.90(4)	96.9(1)
Mo(2)−Mo(1)−P(1)	98.73(4)	97.56(9)	P(2)−N(1)−P(1)	120.8(3)	117.9(6)
Mo(1)−Mo(2)−X(3)	107.98(5)	106.98(7)	P(3)−N(2)−P(4)	118.9(3)	119.4(7)

[a] First values given is for X = Cl; second is for X = Br.

solutions during the preparations of $Mo_2(LL)_2X_4$-type compounds was noted in the literature in some cases,[1b,10] but no attempts to isolate the red intermediates were reported.

When an excess of Me_3SiCl is combined with **1** and dppa and the reaction mixture is refluxed or stirred at ambienttemperature for several hours, one may observe color changes from red to purple to green and the formation of an emerald green product in good yield. The green product has been identified as $Mo_2(\mu\text{-dppa})_2Cl_4$ (**2**). It appears that the sequence in which dppa and Me_3SiCl are added to **1** is of no importance.

It is also possible to prepare **2** from the reaction of $Mo_2(\mu\text{-dppa})_2(OAc)_2Cl_2$ and an excess of Me_3SiCl either at room temperature for several hours or under reflux conditions for less than 1 h. The addition of EtOH to the reaction solution (thf or acetonitrile) accelerates the reaction, presumably because $Mo_2(\mu\text{-dppa})_2(OAc)_2Cl_2$ is much more soluble in EtOH than in acetonitrile or thf whereas **2** is less soluble in EtOH than in thf and acetonitrile. $Mo_2(dppa)_2Cl_4$ is an air-stable substance.

Reaction of **1** with dppa and Me_3SiBr in thf produces a green solution and a pink solid. The use of an excess of Me_3SiBr and reflux conditions does not appear to help to transform **1** into **3** quantitatively; $Mo_2(\mu\text{-dppa})_2(OAc)_2Br_2$ remains a significant product. $Mo_2(dppa)_2Br_4$ is somewhat air-sensitive, and therefore, it can be handled without decomposition only under an inert-gas atmosphere. When solutions of **3** in acetonitrile or thf are exposed to air, they decompose within ca. 15 min to form brownish or pinkish brown insoluble residues. The use of $Mo_2(CF_3COO)_4$, which is known to be more reactive than $Mo_2(CH_3COO)_4$, as a starting material does not show any advantages over the use of **1**.

Reaction of **1** with dppa and Me_3SiI leads only to the formation of $Mo_2(\mu\text{-dppa})_2(OAc)_2I_2$, regardless of the solvent (MeOH, thf, acetonitrile, toluene, CH_2Cl_2) and reaction conditions used. Refluxing for 1 week does not appear to lead to the formation of $Mo_2(\mu\text{-dppa})_2I_4$. In some cases (where MeOH or toluene is used as the reaction solvent), the reaction solution seems to turn greenish for a brief period of time under reflux conditions, but the suspended solid remains violet-red and attempts to grow crystals from the slightly greenish solution led only to the isolation of pink $Mo_2(\mu\text{-dppa})_2(OAc)_2I_2$.

These observations and results are notable when one considers the ease with which other compounds of the type $Mo_2(LL)_2X_4$,[1,9,10] such as $Mo_2(\mu\text{-dppm})_2X_4$ (dppm = bis(diphenylphosphino)methane) which is available in high yields (>90%), are synthesized.[1k,9] The only apparent source of these differences is the electronic nature of the dppa ligand.[11] The low solubilities of the $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ compounds, which appear to act as intermediates in the formation of $Mo_2(\mu\text{-dppa})_2X_4$, and their high stabilities may also play a significant role.

Scheme 1 shows the reaction pathway we assume leads to compounds **2** and **3**, starting from **1**.

Spectroscopy. The nature of the halo ligands exerts a more significant influence on the $^{31}P\{^1H\}$ NMR shifts of compounds **2** and **3** than on those of the previously examined compounds of the type $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ (X = Cl, Br, I).[2h] The spectra of both **2** and **3** exhibit singlets since all four phosphorus nuclei are equivalent. The chemical shift of **2** is $\delta(^{31}P) = 73.5$ ppm while that of **3** is $\delta(^{31}P) = 70.2$ ppm; the difference between these shifts is 3.3 ppm. The difference between the shifts of $Mo_2(\mu\text{-dppa})_2(OAc)_2Cl_2$ and $Mo_2(\mu\text{-dppa})_2(OAc)_2Br_2$ is only 0.9 ppm.[2h] A shift difference of the same order of magnitude as that between **2** and **3** can be observed between $Mo_2(\mu\text{-dmpm})_2Cl_4$ (dmpm = bis(dimethylphosphino)methane) and its Br derivative ($\Delta\delta = 2.6$ ppm).[1b,11] In all mentioned cases, the phosphorus nuclei become more shielded (signals shift upfield) when Br is substituted for Cl. This upfield shift correlates with the increasing covalence of the M−X bond.

As expected, the halo substitution between **2** and **3** has little effect on the ^1H NMR spectra (see data listed in the Experimental Section). In the IR spectra, the C−C and C−H vibrations attributed to the dppa ligand are also very similar for compounds **2** and **3**.

The solution electronic spectra recorded in acetonitrile show the $d_{xy} \rightarrow d_{xy}{}^*$ transitions at 699 nm (14 300 cm^{-1}) for compound **2** and at 725 nm (13 800 cm^{-1}) for compound **3**. This band is red-shifted ca. 500 cm^{-1} as the halo ligands are changed from Cl to Br. This shift difference is in the range of those for known compounds of similar type: e.g., a shift difference of 170 cm^{-1} has been reported for $Mo_2(\mu\text{-dpcp})_2X_4$ (X = Cl, Br; dpcp = (±)-*trans*-1,2-bis(diphenylphosphino)cyclopentane),[12] and for $Mo_2(\mu\text{-dmpm})_2X_4$ (X = Cl, Br) the shift difference reported is ca. 680 cm^{-1}.[1b] For the $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$-type compounds, the shift difference between the Cl and Br derivatives is only about 60 cm^{-1}.[2h]

Molecular Structures. Tables 1 and 2 list the positional and thermal parameters for complexes **2** and **3**, respectively,

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Table 4. Crystal and Structure Refinement Data for **2** and **3**·2thf

	2	**3**·2thf
empirical formula	$C_{48}H_{42}Cl_4Mo_2N_2P_4$	$C_{56}H_{58}Br_4Mo_2N_2O_2P_4$
fw	1104.40	1426.34
space group	$P2_1/c$	$P2_12_12_1$
crystal system	monoclinic	orthorhombic
a, Å	15.522(4)	19.654(2)
b, Å	17.881(5)	19.865(2)
c, Å	16.898(3)	14.7920(10)
β, deg	91.15(2)	
V, Å^3	4689(2)	5775.2(9)
Z	4	4
d(calc), g/cm^3	1.564	1.640
μ, mm^{-1}	0.936	8.119
wavelength, Å	0.709 30	1.541 84
temp, K	293(2)	293(2)
no. of reflns collected	6932	4757
data, restraints, params	6127/0/543	4755/0/583
final R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.037, 0.085	0.045, 0.093
final R_1, wR_2 (all data)[b]	0.081, 0.100	0.104, 0.112
goodness of fit on F^2	1.022	1.069

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp$, $p = [\max(F_c^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.0425$ and $b = 1.9215$ for **2**; $a = 0.0233$ and $b = 17.3596$ for **3**.

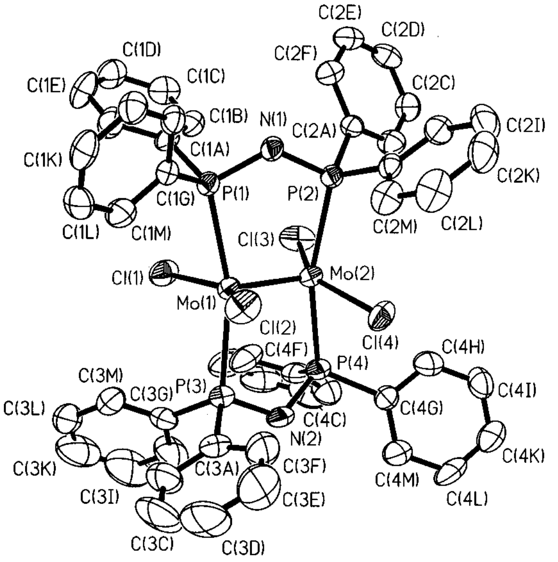

Figure 1. Drawing of $Mo_2(\mu\text{-dppa})_2Cl_4$ (**2**). Thermal ellipsoids are shown at 50% probability.

and Table 3 lists selected bond distances and angles for both compounds. Pertinent crystallographic information is given in Table 4.

Compounds **2** and **3** form green crystals which can be obtained by layering solutions of the compounds in thf or in a mixture of thf and hexanes with hexanes. After a few days at room temperature, crystals of sufficient quality for single-crystal X-ray diffraction studies form.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) and compound **3** in the orthorhombic space group $P2_12_12_1$ (No. 19). The latter contains eight thf molecules per unit cell. ORTEP drawings of compounds **2** and **3** are shown in Figures 1 and 2. In both cases, the Mo−Mo bond distances (2.134(1) and 2.137(2) Å, respectively) are slightly shorter than those in the analogous dppm complexes $Mo_2(dppm)_2X_4$ (X = Cl, Br)[1m,9]

A more significant difference is seen in the torsion angles of **2** and **3**. Side views of compounds **2** and **3** are given in Figures 3 and 4. In the dppm compounds, the average torsion angle is in both cases 0°, the rotational conformations being strictly eclipsed.[1m] Both dppm compounds are centrosymmetric.[1m] In the cases of **2** and **3**, the average torsion angles are 14.4 and 15.2°, respectively. This result is notable with regard to the comparatively short Mo−Mo bond distances in the dppa compounds. The apparent inconsistencies may be rationalized by first noting that the presence of a δ bond strength at a twist

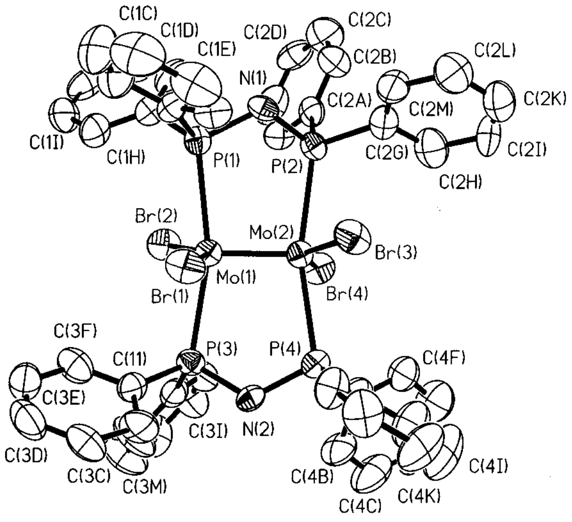

Figure 2. Drawing of $Mo_2(\mu\text{-dppa})_2Br_4$ (**3**). Thermal ellipsoids are shown at 50% probability.

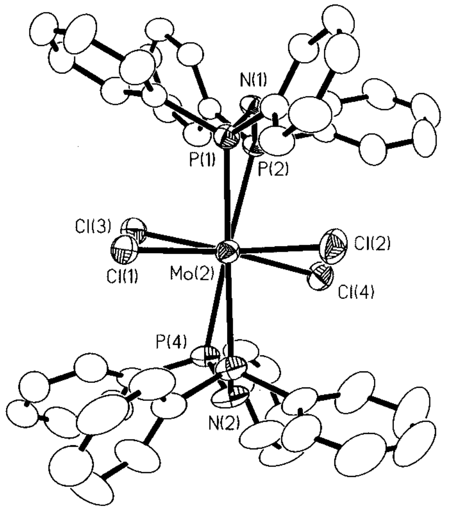

Figure 3. Representation of $Mo_2(\mu\text{-dppa})_2Cl_4$ (**2**) viewed along the Mo−Mo axis. Thermal ellipsoids are shown at 50% probability.

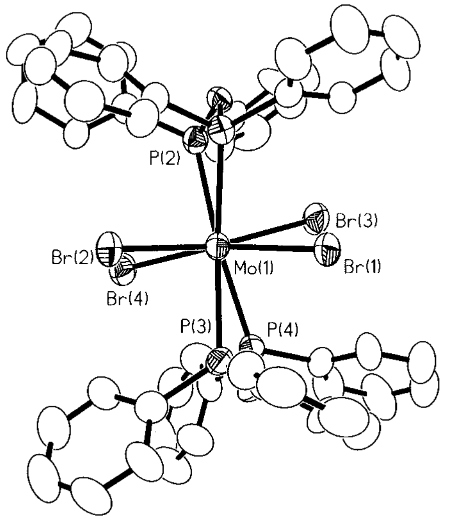

Figure 4. Representation of $Mo_2(\mu\text{-dppa})_2Br_4$ (**3**) viewed along the Mo−Mo axis. Thermal ellipsoids are shown at 50% probability.

angle of *ca*. 15° is reduced from the maximum (at 0°) by $1 - \cos(2 \times 15°) = 1 - 0.866$, that is less than 13%; this puts the significance of the twists found in **2** and **3** in energetic perspective. Energetically these twists are almost negligible. To attempt to say exactly which nonbonded repulsions are responsible in these compounds but not in the dppm analogs would be futile.

Another noteworthy observation is that the Mo−Mo bond distances in $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$-type compounds (X = Cl, 2.158(1) Å; X = Br, 2.176 Å) are longer than those in **2** and **3**. The acetato ligands and the diphosphines adopt nearly eclipsed arangements in $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$-type complexes.

The Mo−X bond distances are significantly shorter in **2** (average value 2.38(1) Å) and in **3** (average value 2.52(1) Å) than in the $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ complexes (X = Cl, 2.829(2) Å; X = Br, 2.889(1) Å).[2h] The difference between the Mo−X bond distances in **2** and **3** is $\Delta d(\text{Mo}-\text{X}) = 0.14$ Å; in the case of the $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ complexes, this difference is considerably less ($\Delta d(\text{Mo}-\text{X}) = 0.06$ Å).[2h] Because of the longer Mo−X bond distances in the latter case, the relative sizes of the halo atoms are of minor importance. The Mo−X bond distance difference between $Mo_2(\mu\text{-dppa})_2(OAc)_2Br_2$ and $Mo_2(\mu\text{-dppa})_2Ac_2I_2$ is more significant ($\Delta d = 0.29$ Å).[2h] For the hypothetical $Mo_2(dppa)_2I_4$ molecule, a Mo−I bond distance of about 2.75 Å would be expected on the basis of the trends observed in the analogous dppm complexes and in the $Mo_2(\mu\text{-dppa})_2X_4$ complexes.

The Mo−X bond distances of **2** and **3** are only slightly shorter than those in the dppm derivatives (X = Br, 2.54(1) Å; X = Cl, 2.39(1) Å).[1m,n,9] The Mo−P distances for both the dppa and dppm derivatives are the same within the range of error (**2**, 2.58(2) Å; **3**, 2.59(1) Å; $Mo_2(dppm)_2Cl_4$, 2.58(4) Å; $Mo_2(dppm)_2Br_4$, 2.61(5) Å).[1m,n]

The P−N(H) distances and the P−N−P angles for **2** and **3** are similar to those in the free ligand (1.692(3) Å, 118.9(2)°);[11c] therefore, no ring strain should occur.

Conclusions

Molecules of the general type $Mo_2(\mu\text{-dppa})X_4$ are produced by the reaction of $Mo_2(OAc)_4$ with dppa and an excess of Me_3SiX. The yield decreases when Br is substitued for Cl, and the I derivative apparently cannot be prepared using this method. $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ compounds appear to be intermediates in this preparation. In contrast to the case of the latter compounds, variation of the halo ligands in $Mo_2(\mu\text{-dppa})_2X_4$ complexes exerts notable effects on the spectroscopic properties of the complexes. This is because the equatorial Mo−X bond distances in $Mo_2(\mu\text{-dppa})X_4$ complexes are significantly shorter than the axial ones in $Mo_2(\mu\text{-dppa})_2(OAc)_2X_2$ compounds, resulting in more covalent character and hence greater influence on the Mo_2^{4+} core. Single-crystal X-ray measurements show considerable torsion angles in the $Mo_2(\mu\text{-dppa})_2X_4$ molecules in contrast to the structures of the analogous dppm complexes. However, the Mo−Mo bond distances in the dppa derivatives are not longer than those in the dppm compounds, because of presumably greater basicity of the dppa ligand.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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