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Molybdenum Complexes of 1,2-Bis(diphenylphosphino)benzene. Mononuclear Molybdenum(II) Species Formed by Facile Metal–Metal Bond Cleavage of the $(\mathrm{Mo}\overset{4}{-}\mathrm{Mo})^{4+}$ Core

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The quadruply bonded dimolybdenum(II) complexes $K_4Mo_2Cl_8$, $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$, and $(NH_4)_4Mo_2Br_8$ react with 1,2-$C_6H_4(PPh_2)_2$ (dppbe) in methanol at room temperature to afford α-$Mo_2X_4(dppbe)_2$ complexes (X = Cl, Br), which do not isomerize to the β isomers. Under more forcing reaction conditions (refluxing 1-propanol), these same reactions give mononuclear *trans*-$MoX_2(dppbe)_2$ in good yield (ca. 50%) together with some $[MoOX(dppbe)_2]X{\cdot}nH_2O$. An alternative synthetic strategy for the preparation of α-$Mo_2X_4(dppbe)_2$ involves the reaction of $Mo_2(O_2CCH_3)_4$ with dppbe and Me_3SiX in THF. The compound $MoCl_2(dppbe)_2$ forms crystals in space group $P2_1/n$, with the following unit cell parameters: $a = 10.884$ (2) Å, $b = 12.753$ (2) Å, $c = 18.141$ (4) Å, $\beta = 91.43$ (2)°, $V = 2517$ (2) Å^3, and $Z = 2$. The centrosymmetric trans molecule has Mo–Cl = 2.410 (1) Å, Mo–P = 2.481 (1), 2.511 (1) Å, and P–Mo–P(intra-ring) = 78.68 (4)°.

Introduction

Bidentate phosphine ligands have been most useful in studying the reactivities of complexes that contain triple and quadruple metal–metal bonds because of the variety of structural types that result from binding these molecules.[2,3] In particular, investigations involving tetrahalodimolybdenum(II) complexes and the $Ph_2P(CH_2)_nPPh_2$ ligands have shown that the occurrence of chelating and bridging phosphine (L-L) isomers of $Mo_2X_4(L\text{-}L)_2$ is quite common and that they can be selectively prepared under appropriate conditions.[4-6] Moreover, we and others have observed that generally the chelating (α) form will isomerize into the thermodynamically more favorable bridging (β) complex but the reverse reaction is uncommon.[6,7] Although rhenium–rhenium bond cleavage or lowering of the bond order is frequently encountered with use of these ligands, such outcomes are rare for molybdenum unless strong π-acid ligands are employed in addition.[8] We now report the results of a study of the reactions between 1,2-bis(diphenylphosphino)benzene (dppbe) and the octahalodimolybdate(II) ions in alcohol solvents in which the formation of mononuclear complexes becomes the preferred reaction course under certain conditions. Strategies for preparing α-$Mo_2X_4(dppbe)_2$ (X = Cl, Br) have also been devised.

Experimental Section

Starting Materials. The following compounds were prepared by standard procedures: $Mo_2(O_2CCH_3)_4$,[9] $K_4Mo_2Cl_8$,[10a] $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$,[10b] and $(NH_4)_4Mo_2Br_8$.[11] The ligand 1,2-bis(diphenylphosphino)benzene was purchased from Strem Chemical Co. and used as received. Solvents used in the preparation of the complexes were of commercial grade and were thoroughly deoxygenated prior to use.

Reaction Procedures. All reactions were performed under a nitrogen atmosphere with use of standard vacuum line techniques. Chromatographic separations were performed on a silica gel column (60–200 mesh, Davidson Grade 62).

A. Reactions of $K_4Mo_2Cl_8$ with dppbe. (i) In Methanol. A mixture of $K_4Mo_2Cl_8$ (0.05 g, 0.08 mmol), dppbe (0.08 g, 0.18 mmol), and methanol (10 mL) was stirred at room temperature for 22 h. A green solid was filtered off, washed with water, hexanes, and diethyl ether, and dried; yield 0.045 g (50%). This product was identified as α-$Mo_2Cl_4(dppbe)_2$ (see part D(i)) from its electrochemical properties. When the reaction was carried out in refluxing methanol for 3 days, a mixture of α-$Mo_2Cl_4(dppbe)_2$ and *trans*-$MoCl_2(dppbe)_2$ was isolated.

(ii) In 1-Propanol. A mixture of $K_4Mo_2Cl_8$ (0.10 g, 0.16 mmol), dppbe (0.16 g, 0.36 mmol), and 1-propanol (30 mL) was refluxed for 3 days. The resulting reaction mixture was cooled to room temperature, and the orange solid was filtered off, washed with 1-propanol, methanol, hexanes, and diethyl ether, and dried; yield 0.08 g (48%). Anal. Calcd for $C_{60}H_{50}Cl_2MoOP_4$ (i.e. $MoCl_2(dppbe)_2{\cdot}H_2O$): C, 66.86; H, 4.68. Found: C, 66.05; H, 5.16.

The purple filtrate was evaporated to dryness and the residue recrystallized from CH_2Cl_2/diethyl ether. The product was filtered off, washed with water, hexanes, and diethyl ether, and dried. The product was tentatively identified as $[MoOCl(dppbe)_2]Cl{\cdot}3H_2O$ from its electrochemical properties and IR spectrum (Nujol mull, ν(Mo=O) at 943 cm^{-1}).

B. Reactions of $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ with dppbe. (i) In Methanol. A suspension of $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ (0.06 g, 0.10 mmol) in methanol (10 mL) was treated with an excess of dppbe (0.11 g, 0.25 mmol) and the mixture brought to reflux. Within 5 min the blue-green suspension had turned dark green. After a reflux of 3 h, the reaction mixture was cooled to room temperature and filtered. The resulting green solid α-$Mo_2Cl_4(dppbe)_2$ (see section D(i)) was washed with methanol, water, ethanol, toluene, and diethyl ether and finally dried under vacuum; yield 59%.

(ii) In 1-Propanol. A reaction similar to that in part B(i) was carried out in 1-propanol (15 mL) with reflux for 24 h. The resulting reaction mixture was cooled to room temperature, and the orange-brown solid was filtered off, washed with 1-propanol, methanol, water, methanol, hexanes, and diethyl ether, and dried; yield 31%. Anal. Calcd for $C_{60}H_{50}Cl_2MoOP_4$ (i.e. $MoCl_2(dppbe)_2{\cdot}H_2O$): C, 66.86; H, 4.68; Cl, 6.59. Found: C, 66.52; H, 4.86; Cl, 7.02. The presence of H_2O was confirmed by IR spectroscopy (Nujol mull, ν(OH) at 3300 cm^{-1}).

The purple filtrate was worked up the same as in part A(ii) and purified by chromatography (silica gel column with methanol as eluent) and the purple product recrystallized from CH_2Cl_2/diethyl ether; yield 0.04 g (22%). Anal. Calcd for $C_{60}H_{54}Cl_2MoO_4P_4$ (i.e. $[MoOCl(dppbe)_2]Cl{\cdot}3H_2O$): C, 63.78; H, 4.82. Found: C, 63.30; H, 4.27. The presence of water was confirmed by IR spectroscopy (Nujol mull), which showed ν(OH) at ~3350 (br) cm^{-1}.

This salt undergoes anion exchange with KPF_6 in methanol to form $[MoOCl(dppbe)_2]PF_6$ as described in the following procedure. A mixture of $[MoOCl(dppbe)_2]Cl{\cdot}3H_2O$ (0.05 g, 0.04 mmol), KPF_6 (0.05 g, 0.27 mmol), and methanol (10 mL) was stirred at room temperature for 2 h. A light purple solid was filtered off, washed with methanol, hexanes, and diethyl ether, and dried; yield 0.04 g (76%). The presence of PF_6^- was confirmed by IR spectroscopy (Nujol mull, ν(PF) at 841 cm^{-1}).

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C. Reaction of $(NH_4)_4Mo_2Br_8$ with dppbe. (i) In Methanol. With the use of a procedure similar to that described in part A(i), green α-$Mo_2Br_4(dppbe)_2$ was isolated in 51% yield. Anal. Calcd for $C_{60}H_{48}Br_4Mo_2P_4$: C, 51.31; H, 3.44. Found: C, 50.16; H, 3.70.

(ii) In 1-Propanol. With the use of a procedure similar to that described in part A(ii), yellow-orange *trans*-$MoBr_2(dppbe)_2$ was isolated in 43% yield. Anal. Calcd for $C_{60}H_{48}Br_2MoP_4$: C, 62.72; H, 4.21; Br, 13.91. Found: C, 61.10; H, 3.96; Br, 13.21.

From the filtrate of this reaction purple $[MoOBr(dppbe)_2]Br \cdot 2H_2O$ was isolated. Anal. Calcd for $C_{60}H_{52}Br_2MoO_3P_4$: C, 60.02; H, 4.37. Found: C, 60.20; H, 4.36. The presence of water was confirmed by IR spectroscopy (Nujol mull, $\nu(OH)$ at 3650 and 3380 cm^{-1}).

D. Reaction of $Mo_2(O_2CCH_3)_4$ with dppbe in the Presence of Me_3SiX. (i) Preparation of α-$Mo_2Cl_4(dppbe)_2$. A mixture of $Mo_2(O_2CCH_3)_4$ (0.10 g, 0.23 mmol), dppbe (0.22 g, 0.49 mmol), THF (10 mL), and Me_3SiCl (0.40 mL) was stirred at room temperature for 20 h. A green solid was filtered off, washed with THF, methanol, CH_2Cl_2, hexanes, and diethyl ether and dried; yield 0.18 g (63%). Anal. Calcd for $C_{60}H_{48}Cl_4Mo_2P_4$: C, 58.75; H, 3.94. Found: C, 58.48; H, 4.32.

(ii) Preparation of α-$Mo_2Br_4(dppbe)_2$. A mixture of $Mo_2(O_2CCH_3)_4$ (0.10 g, 0.23 mmol), dppbe (0.23 g, 0.52 mmol), THF (10 mL), and Me_3SiBr (0.5 mL) was stirred at room temperature for 1 h. A green solid was filtered off, washed with THF, CH_2Cl_2, hexanes, and diethyl ether, and dried; yield 0.23 g (70%). This product was further purified by refluxing a quantity of it in CH_2Cl_2 for 12 h. The suspension was cooled to room temperature and filtered, and the insoluble material was washed and diethyl ether and dried. Anal. Calcd for $C_{60}H_{48}Br_4Mo_2P_4$: C, 51.31; H, 3.44. Found: C, 49.32; H, 3.62. The slightly low carbon microanalysis reflects the difficulty of purifying such an insoluble compound.

(iii) Preparation of *trans*-$MoCl_2(dppbe)_2$. A mixture of $Mo_2(O_2CCH_3)_4$ (0.20 g, 0.47 mmol) and dppbe (0.417 g, 0.935 mmol) was placed in a 100-mL round-bottom flask, which was evacuated and filled with argon. Freshly distilled THF (50 mL) was added and the resulting mixture brought to reflux and then cooled. Trimethylsilyl chloride (0.237 mL, 1.87 mmol) was then added and the mixture again brought to reflux and maintained at reflux for 4 h. The mixture was allowed to cool slowly to room temperature, and the solvent was removed under vacuum to leave a crude product, which was washed with two 30-mL portions of diethyl ether; yield 0.45 g (90%). From this crude product single crystals suitable for X-ray crystallography were obtained.

E. Oxidation of $MoX_2(dppbe)_2$ with $NOPF_6$. (i) Preparation of $[MoCl_2(dppbe)_2]PF_6$. A mixture of *trans*-$MoCl_2(dppbe)_2 \cdot H_2O$ (0.06 g, 0.06 mmol), $NOPF_6$ (0.01 g, 0.07 mmol), and CH_3CN (10 mL) was stirred at room temperature for 1 h. The solvent was then evaporated to dryness. The product was extracted into CH_2Cl_2 and filtered into a flask that contained diethyl ether. The insoluble blue product that formed was filtered off, washed with hexanes and diethyl ether, and dried; yield 0.06 g (80%). Anal. Calcd for $C_{60}H_{48}Cl_2F_6MoP_5$: C, 59.82; H, 4.02. Found: C, 59.45; H, 4.34. The presence of PF_6^- was confirmed by IR spectroscopy (Nujol mull, $\nu(PF)$ at 841 cm^{-1}).

(ii) Preparation of $[MoBr_2(dppbe)_2]PF_6$. With the use of a procedure similar to that described in part E(i), the blue complex $[MoBr_2(dppbe)_2]PF_6$ was isolated in 63% yield. Anal. Calcd for $C_{60}H_{52}Br_2F_6MoO_2P_5$ (i.e. $[MoBr_2(dppbe)_2]PF_6 \cdot 2H_2O$): C, 54.38; H, 3.95. Found: C, 54.41; H, 3.58. The presence of water was confirmed by IR spectroscopy.

F. Reaction of α-$Mo_2Cl_4(dppbe)_2$ with dppbe. A mixture of α-$Mo_2Cl_4(dppbe)_2$ (0.03 g, 0.03 mmol), dppbe (0.04 g, 0.09 mmol), and THF (10 mL) was refluxed for 4 days. The reaction mixture was allowed to cool to room temperature, and the orange solid was filtered off, washed with THF, hexanes, and diethyl ether, and dried; yield 0.02 g (35%). The product was identifed as *trans*-$MoCl_2(dppbe)_2$ on the basis of its electrochemical properties.

When the complexes α-$Mo_2Cl_4(dppbe)_2$ and α-$Mo_2Br_4(dppbe)_2$ were heated in refluxing 1-propanol for periods of 3 and 4 days, respectively, orange $MoCl_2(dppbe)_2$ and $MoBr_2(dppbe)_2$ were isolated in low yields (ca. 20%). These products were identified by IR and electronic absorption spectroscopy. The identities of the dppbe-deficient molybdenum species that are formed in these thermolysis reactions are unknown.

Physical Measurements. IR spectra were recorded as Nujol mulls supported by KBr disks (4000–400 cm^{-1}) and polyethylene disks (400–200 cm^{-1}) with the use of Perkin-Elmer 1800 FTIR and Pye-Unicam SP3-300 spectrophotometers. Electronic absorption spectra were recorded as CH_2Cl_2 solutions or Nujol mulls on Perkin-Elmer 330 and HP 8451A spectrophotometers. Electrochemical measurements were made on CH_2Cl_2 solutions of the complexes that contained tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. The $E_{p,a}$, $E_{p,c}$, and $E_{1/2}$ $(=(E_{p,a} + E_{p,c})/2)$ values were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the Cp_2Fe^+/Cp_2Fe couple. Voltammetric experiments were performed with the use of a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 x-y recorder. $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 spectrometer. An internal deuterium lock and an external reference, 85% H_3PO_4, were used. Magnetic measurements were carried out with the use of a Cahn/Ventron Faraday magnetic susceptibility balance and $HgCo(NCS)_4$ as the calibrant. Diamagnetic corrections were made by using Pascal's constants.

Table I. Crystal Data for $MoCl_2(dppbe)_2$

formula	$MoCl_2P_4C_{60}H_{48}$
fw	1059.79
space group	$P2_1/n$
systematic absences	$(0k0)$, $k \neq 2n$; $(h0l)$, $h + l \neq 2n$
a, Å	10.884 (2)
b, Å	12.753 (2)
c, Å	18.141 (4)
β, deg	91.43 (2)
V, Å^3	2517 (2)
Z	2
d_{calcd}, g/cm^3	1.398
cryst size, nm	0.3 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	5.30
data collecn instrument	Enraf-Nonius CAD-4S
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientation reflns: no.; range (2θ), deg	22; 13–35
temp, °C	23 ± 1
scan method	ω scans
data collecn range, 2θ, deg	4–47
no. of unique data, total	3275
with $F_o^2 > 3\sigma(F_o^2)$	2714
no. of params refined	304
transmission factors	no abs cor made
R^a	0.0443
R_w^b	0.0624
quality-of-fit indicator^c	1.778
largest shift/esd, final cycle	0.03
largest peak, e/Å^3	0.58

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

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Crystallographic Study. A suitable crystal of *trans*-$MoCl_2(dppbe)_2$ was mounted with epoxy cement in a glass capillary and placed on the diffractometer. Table I records the usual crystallographic and procedural data. The structure was solved from a Patterson function followed by an alternating series of Fourier maps and least-squares refinements. It converged smoothly with all atoms anisotropic. All crystallographic procedures were routine for this laboratory and have been previously described.[12]

Results and Discussion

In the ensuing discussion the following ligand abbreviations will be used: dppbe = 1,2-$C_6H_4(PPh_2)_2$; dppe = $Ph_2PCH_2CH_2PPh_2$; dppee = *cis*-$Ph_2PCH{=}CHPPh_2$; dmpe = $Me_2PCH_2CH_2PMe_2$; diars = 1,2-$C_6H_4(AsMe_2)_2$.

A. Preparation and Characterization of α-$Mo_2X_4(dppbe)_2$ (X = Cl, Br). The green complexes α-$Mo_2X_4(dppbe)_2$ were prepared for the first time here from the reactions of dppbe either with the octahalodimolybdate(II) anions $[Mo_2X_8]^{4-}$ (as present in $K_4Mo_2Cl_8$, $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, and $(NH_4)_4Mo_2Br_8$) in methanol or with $Mo_2(O_2CCH_3)_4$ in the presence of Me_3SiX in THF under mild reaction conditions. The identification of these species as α-$Mo_2X_4(dppbe)_2$ was based upon a comparison of their electronic absorption spectra (Table I) with those reported for other complexes of the type α-$Mo_2X_4(L\text{-}L)_2$ (L-L = dppe, dppee).[4-6,13] Most importantly, both exhibit a broad, moderately intense band,

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Table II. Positional Parameters and Their Estimated Standard Deviations for $MoCl_2(dppbe)_2$[a]

atom	x	y	z	B, Å^2
Mo(1)	0.000	0.000	0.000	2.19 (1)
Cl(1)	0.1993 (1)	0.0153 (1)	0.05997 (8)	3.62 (3)
P(1)	0.1136 (1)	0.0665 (1)	−0.10930 (7)	2.49 (3)
P(2)	−0.0142 (1)	0.1924 (1)	0.01810 (7)	2.64 (3)
C(1)	0.1152 (5)	0.2542 (4)	−0.0290 (3)	2.7 (1)
C(2)	0.1648 (5)	0.2022 (4)	−0.0893 (3)	2.5 (1)
C(3)	0.2521 (5)	0.2514 (5)	−0.1322 (3)	3.5 (1)
C(4)	0.2948 (5)	0.3517 (5)	−0.1139 (3)	3.7 (1)
C(5)	0.2513 (6)	0.4023 (5)	−0.0516 (4)	4.1 (1)
C(6)	0.1603 (6)	0.3538 (5)	−0.0093 (3)	3.8 (1)
C(7)	0.2599 (5)	0.0018 (4)	−0.1276 (3)	2.7 (1)
C(8)	0.2623 (5)	−0.0845 (4)	−0.1752 (3)	3.4 (1)
C(9)	0.3755 (6)	−0.1357 (5)	−0.1862 (4)	4.5 (1)
C(10)	0.4827 (6)	−0.1045 (5)	−0.1485 (4)	4.6 (1)
C(11)	0.4777 (5)	−0.0214 (5)	−0.0996 (3)	4.1 (1)
C(12)	0.3666 (5)	0.0319 (5)	−0.0884 (3)	3.4 (1)
C(13)	0.0430 (5)	0.0844 (4)	−0.2020 (3)	2.7 (1)
C(14)	0.1133 (6)	0.0828 (4)	−0.2658 (3)	3.5 (1)
C(15)	0.0571 (6)	0.1021 (5)	−0.3343 (3)	4.2 (1)
C(16)	−0.0669 (7)	0.1235 (5)	−0.3406 (4)	4.8 (2)
C(17)	−0.1366 (6)	0.1269 (6)	−0.2770 (4)	5.2 (2)
C(18)	−0.0811 (5)	0.1078 (5)	−0.2076 (3)	4.0 (1)
C(19)	−0.0068 (5)	0.2529 (4)	0.1097 (3)	3.3 (1)
C(20)	0.0495 (6)	0.1968 (5)	0.1668 (3)	4.4 (1)
C(21)	0.0592 (7)	0.2405 (7)	0.2375 (4)	6.2 (2)
C(22)	0.0165 (7)	0.3389 (8)	0.2515 (4)	7.3 (2)
C(23)	−0.0413 (7)	0.3979 (6)	0.1947 (4)	7.0 (2)
C(24)	−0.0540 (6)	0.3544 (5)	0.1226 (4)	5.1 (2)
C(25)	−0.1462 (5)	0.2605 (4)	−0.0239 (3)	3.0 (1)
C(26)	−0.1340 (6)	0.3389 (5)	−0.0781 (4)	4.5 (1)
C(27)	−0.2387 (7)	0.3906 (6)	−0.1056 (4)	5.3 (2)
C(28)	−0.3517 (6)	0.3650 (5)	−0.0792 (4)	5.3 (2)
C(29)	−0.3681 (6)	0.2852 (6)	−0.0274 (4)	4.9 (2)
C(30)	−0.2622 (5)	0.2339 (5)	0.0002 (3)	4.1 (1)

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

at 680 nm for the chloride and at 694 nm for the bromide in the solid state. The positions, shapes, and relative intensities of these absorptions are entirely consistent with their arising from metal-centered $\delta \rightarrow \delta^*$ transitions. The shift to lower energy when chloride is replaced by bromide is also characteristic of this transition. Thus, the occurrence of this band reveals that the quadruple bond has been retained in these molecules.

The low-frequency IR spectrum of α-$Mo_2Cl_4(dppbe)_2$ shows bands at 312 s, 293 s, and 279 sh cm^{-1} that can be assigned to ν(Mo–Cl); for α-$Mo_2Cl_4(dppe)_2$ and α-$Mo_2Cl_4(dppee)_2$ comparable modes are at 307 s and ~290 s cm^{-1}, whereas β-$Mo_2Cl_4(dppe)_2$ and β-$Mo_2Cl_4(dppee)_2$ have ν(Mo–Cl) at 350–340 s and 295–290 s cm^{-1}.[4,13]

As solution of α-$Mo_2Cl_4(dppbe)_2$ in 0.1 M TBAH/CH_2Cl_2 exhibits electrochemical properties, as measured by the cyclic voltammetric (CV) technique, in which there is an irreversible oxidation at $E_{p,a}$ = +0.45 V and an irreversible reduction at $E_{p,c}$ = −1.23 V vs Ag/AgCl. These processes did not show coupled waves with the use of sweep rates up to 700 mV/s. The oxidation at +0.45 V is typical of the behavior of mixed halide–phosphine complexes of $(Mo\overset{4}{-}Mo)^{4+}$.[14] The related bromide complex was not very soluble in CH_2Cl_2, and these solutions gave a poor electrochemical response.

Attempts to isomerize α-$Mo_2X_4(dppbe)_2$ to β-$Mo_2X_4(dppbe)_2$ in solution were unsuccessful. The green α isomers were recovered unchanged when refluxed in THF or CH_2Cl_2 for extended periods of time. The mononuclear *trans*-$MoCl_2(dppbe)_2$ was isolated when α-$Mo_2Cl_4(dppbe)_2$ was refluxed in THF in the presence of excess dppbe or when $Mo_2(O_2CCH_3)_4$ was refluxed with dppbe and Me_3SiCl in THF for 4 h.

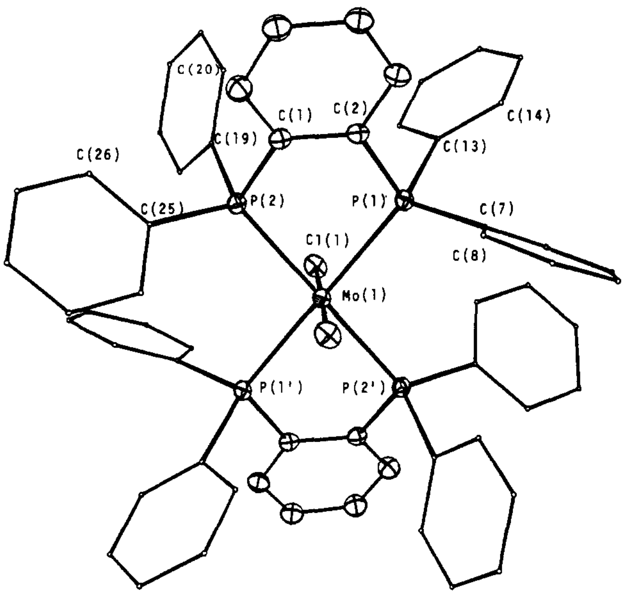
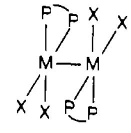


Figure 1. Molecular structure of *trans*-$MoCl_2(dppbe)_2$, with the atom-labeling scheme defined. The carbon atoms of the phenyl rings are represented by arbitrarily small circles for clarity, while the other atoms are represented by their thermal displacement ellipsoids at the 30% probability level.

Table III. Principal Bond Distances and Angles in $MoCl_2(dppbe)_2$

Distances (Å)			
Mo–Cl	2.410 (1)	P(1)–C(2)	1.850 (5)
Mo–P(1)	2.511 (1)	P(2)–C(1)	1.842 (5)
Mo–P(2)	2.481 (1)		
Angles (deg)			
Cl(1)–Mo–P(1)	82.74 (4)	Cl(1)–Mo–P(2)′	94.67 (5)
Cl(1)–Mo–P(1)′	97.26 (4)	P(1)–Mo–P(2)	78.68 (4)
Cl(1)–Mo–P(2)	85.33 (5)	P(1)–Mo–P(2)′	101.32 (4)

For the $Mo_2X_4(dppbe)_2$ compounds, therefore, we conclude that they possess the molecular structure **1** with chelating phosphines and an eclipsed rotational geometry. This particular orientation of the organic ligands, i.e., related approximately by a symmetry inversion operation, presumably minimizes steric repulsions and has been observed through structure determinations of several α-$M_2Cl_4(LL)_2$ complexes.



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B. Preparation and Characterization of *trans*-$MoX_2(dppbe)_2$ and $[MoX_2(dppbe)_2]PF_6$. The reactions of the ligand dppbe with $K_4Mo_2Cl_8$ or with $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ in refluxing 1-propanol produce the orange complex *trans*-$MoCl_2(dppbe)_2{\cdot}H_2O$ in isolated yields of up to ~50%. The bromo analogue *trans*-$MoBr_2(dppbe)_2$ was obtained in a similar fashion from the reaction of $(NH_4)_4Mo_2Br_8$ with dppbe in refluxing 1-propanol (43% yield). These reactions resemble that reported previously whereby *trans*-$MoBr_2(dppe)_2$ was formed in low yield (~7%) by the reaction of $(NH_4)_4Mo_2Br_8$ with $Ph_2PCH_2CH_2PPh_2$ for extended periods in ethanol.[6] We have also found that *trans*-$MoCl_2(dppbe)_2$ can be obtained in high yield by reacting $Mo_2(O_2CCH_3)_4$ with dppbe and Me_3SiCl for long periods (ca. 4 h) in refluxing tetrahydrofuran.

These complexes can be assigned a trans geometry, largely on the basis of a comparison of their properties with those of the previously characterized *trans*-$MoX_2(dppe)_2$ (X = Cl, Br)[6,15-17]

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Table IV. Spectroscopic and Electrochemical Properties of Molybdenum(II) and Molybdenum(III) Complexes of 1,2-Bis(diphenylphosphino)benzene

complex	voltammetric half-wave potentials,[a] V	electronic abs spectra, nm[b]
α-Mo_2Cl_4(dppbe)$_2$	$E_{p,a}$ + 0.45, $E_{p,c}$ −1.23	680 s, ~500 sh, 420 m, ~350 sh (A) 680 (2340), 513 sh, 480 sh, 415 (940), 337 (6700) (B)
α-Mo_2Br_4(dppbe)$_2$	*c*	695 s, ~550 sh, ~500 br, sh, ~400 sh, ~385 sh (A) 680 s, 520 sh, 490 sh, 410 sh, 339 vs[i] (B)
trans-$MoCl_2$(dppbe)$_2$·H_2O	$E_{p,a}$ +1.45,[d] $E_{1/2}$(ox) −0.10,[e] $E_{p,c}$ ~−1.8[f]	~480 br, sh, ~380 br, sh, 348 s[i] (B)
trans-$MoBr_2$(dppbe)$_2$	$E_{p,a}$ +1.48,[d] $E_{1/2}$(ox) −0.09,[e] $E_{p,c}$ ~−1.9[f]	346 s[i,j] (B)
trans-[$MoCl_2$(dppbe)$_2$]PF_6	$E_{p,a}$ +1.45,[d] $E_{1/2}$(red) −0.10,[e] $E_{p,c}$ ~−1.8[f]	583 (3800), 480 (600), 376 (4300) (B)
trans-[$MoBr_2$(dppbe)$_2$]PF_6·$2H_2O$	$E_{p,a}$ +1.45,[d] $E_{1/2}$(red) −0.09,[e] $E_{p,c}$ ~−1.9[f]	602 (5200), 384 (2020) (B)
[MoOCl(dppbe)$_2$]Cl·$3H_2O$	$E_{p,a}$ ~+1.8, $E_{p,a}$ +1.15,[g] $E_{1/2}$(red) −1.17	546 (120), 315 (~4400) (B)
[MoOBr(dppbe)$_2$]Br·$2H_2O$	$E_{p,a}$ ~+1.9, $E_{p,a}$ +1.05,[h] $E_{p,a}$ +0.80,[h] $E_{1/2}$(red) −1.10	562 (90), 322 (4500) (B)

[a] Vs. Ag/AgCl; recorded on solutions in 0.1 M TBAH/CH_2Cl_2 using a Pt-bead electrode. Data were obtained at $v = 200$ mV/s. For the reversible couples the ΔE_p values ($=E_{p,a} - E_{p,c}$) are in the range 90–130 mV. [b] λ_{max} values with molar extinction coefficients in parentheses. Spectra were recorded as Nujol mulls (A) or solutions in CH_2Cl_2 (B). [c] Low solubility in CH_2Cl_2 precluded the recording of a satisfactory CV. [d] Mo(III) → Mo(IV) oxidation. [e] Mo(III)/Mo(II) couple. [f] Mo(II) → Mo(I) reduction. [g] Electrochemical process due to outer-sphere Cl^-; absent in the CV of [MoOCl(dppbe)$_2$]PF_6. [h] Electrochemical process due to outer-sphere Br^-. [i] Very low solubility in CH_2Cl_2 precluded the measurement of accurate molar extinction coefficients. [j] Pronounced low-energy tail that did not reveal any resolvable structure.

and *trans*-$MoCl_2$(dmpe)$_2$.[18] For $MoCl_2$(dppbe)$_2$ the trans geometry has been conclusively demonstrated by X-ray crystallography. The molecular structure is shown in Figure 1, and the positional parameters and principal molecular dimensions are collected in Tables II and III. The molecule has a rigorous center of inversion.

Although centrosymmetric, the structure shows a number of significant deviations from the highest symmetry (D_{4h}) that might be envisioned for a *trans*-MX_2L_4 type of molecule. Some of these have to do with the requirements of the chelating ligands. Thus, the P–Mo–P angles are of two distinct types: intraring angles are 78.68 (1)° while those between phosphorus atoms in different rings are 101.32 (4)°. The MoP_4 set of atoms is, as a whole, completely planar, however. On the other hand, the five-membered $\overline{\text{MoPCCP}}$ rings are far from planar. There is a torsion angle of 9.0 (6)° around the C(1)–C(2) bond; thus, the relative rigidity of the benzene ring is still not sufficient to enforce complete planarity of the P–C–C–P portion of the ring, although the deviations are not large. The C atoms lie ±0.05 Å above and below the mean plane, while the P atoms lie ±0.02 Å out of the mean plane. The major deviation from planarity within the chelate rings is the dihedral angle of 24.8 (2)° between the plane of the MoP_2 group and the mean plane of the P(1)–C(2)–C(1)–P(2) group.

The nonplanarity of the chelate rings causes steric forces to act upon the chlorine atoms in such a way that the linear Cl–Mo–Cl unit is considerably tilted from the perpendicular to the MoP_4 plane. Thus, the atom Cl(1) leans toward P(1) and P(2), making angles of 82.7 and 85.3° to these Mo–P bonds, and away from P(1)′ and P(2)′, making angles of 97.3 and 94.7° to these Mo–P bonds.

The low-frequency IR spectrum (Nujol mull) of *trans*-$MoCl_2$(dppbe)$_2$·H_2O shows a single ν(MoCl) mode at 314 cm^{-1} while for the bromide the ν(MoBr) mode is probably at 247 cm^{-1}. The ratio of these frequencies is 0.78, which is an acceptable figure.[19] Similar results have been reported for *trans*-$MoCl_2$(dppee)$_2$,[13] *trans*-$MoCl_2$(diars)$_2$,[20] and isoelectronic *trans*-[$ReCl_2$(dppee)$_2$]$^+$.[21] The magnetic properties of the *trans*-MoX_2(dppbe)$_2$ compounds are consistent with their mononuclear structures,[16,18] with the assumption that the d-orbital splitting pattern gives an energy order of $d_{xz} \approx d_{yz} > d_{xy}$, leading to a $d_{xy}^2 d_{xz} d_{yz}$ electron configuration. The value of μ_{eff} for $MoCl_2$(dppbe)$_2$·H_2O is 2.9 ± 0.1 μ_B and for $MoBr_2$(dppbe)$_2$ is 3.0 ± 0.1 μ_B, which are in accord with two unpaired electrons. We have previously reported a value of 2.8 μ_B for *trans*-$MoBr_2$(dppe)$_2$.[6]

The electronic absorption spectra of these complexes (Table IV) exhibit intense LMCT bands (probably X(π) → Mo) at ~350 nm (X = Cl) and ~370 nm (X = Br), as seen previously in the spectrum of *trans*-$MoBr_2$(dppe)$_2$ (λ_{max} 360 nm in CH_2Cl_2). Note that a similar shift has been reported by Deutsch and co-workers[22] in the spectra of [$TcCl_2$(dppe)$_2$]$^+$ (480 nm, $\epsilon = 2500$) and [$TcBr_2$(dppe$_2$]$^+$ (504 nm, $\epsilon = 4200$), where halogen-to-metal charge transfer was proposed. Related features are seen in the spectra of *trans*-[ReX_2(dppee)$_2$]$^+$ (X = Cl, Br).[21]

Like other complexes of the type MoX_2(bidentate phosphine)$_2$, the related dppbe species display well-defined redox chemistry. The CV's of solutions of these complexes in 0.1 M TBAH/CH_2Cl_2 display processes associated with the Mo(IV)/Mo(III), Mo(III)/Mo(II), and Mo(II)/Mo(I) couples (Table IV). These electrochemical properties are similar to those described for *trans*-MoX_2(dppe)$_2$[17] and *trans*-Mo(SR)$_2$(dppe)$_2$.[23] In the case of *trans*-$MoCl_2$(dppe)$_2$, the Mo(III)/Mo(II) and Mo(II)/Mo(I) couples are at $E_{1/2} = -0.05$ V and $E_{1/2} = -1.68$ V vs SCE, respectively, for solutions in 0.2 M (n-Bu_4N)BF_4/THF. Interestingly, for *trans*-$MoCl_2$(dmpe)$_2$ this potential is much lower ($E_{1/2} = -0.51$ V vs SCE in CH_3CN),[18] reflecting the ease of oxidation to *trans*-[$MoCl_2$(dmpe)$_2$]$^+$.

The accessibility of the Mo(III)/Mo(II) couple in these complexes has been demonstrated by chemical oxidation to the blue salts *trans*-[MoX_2(dppbe)$_2$]PF_6 with $NOPF_6$ as the oxidizing agent in CH_3CN. These ionic species display cyclic voltammetric behavior (in 0.1 M TBAH/CH_2Cl_2 solutions) similar to that of their neutral cogeners *trans*-MoX_2(dppbe)$_2$, with the exception that the process at ~0.1 V now corresponds to a reduction. These complexes behave as 1:1 electrolytes in acetonitrile solutions (Λ_M = 120 Ω^{-1} cm^2 mol^{-1} for X = Cl and 142 Ω^{-1} cm^2 mol^{-1} for X = Br). The electronic absorption spectra of these complexes in CH_2Cl_2 (Table IV) show λ_{max} at 588 nm (X = Cl) and 602 nm (X = Br), features that are characteristic of such mononuclear Mo(III) species. These complexes are also ESR-active. A sharp signal in the X-band spectrum at $g = 1.93$ was observed for a frozen CH_2Cl_2 solution of [$MoCl_2$(dppbe)$_2$]PF_6. This behavior is similar to that observed for [$MoCl_2$(dppee)$_2$]PF_6[13] and the ESR-active thiolato derivatives *trans*-[Mo(SR)$_2$(dppe)$_2$]$^+$.[23]

C. Preparation and Characterization of [MoOX(dppbe)$_2$]X. Workup of the purple filtrates from the reactions of dppbe with the octahalodimolybdate(II) anions [Mo_2X_8]$^{4-}$ (X = Cl, Br) in refluxing 1-propanol affords the purple species [MoOX(dppbe)$_2$]X·$n$$H_2O$. These oxo complexes are air-stable and behave as 1:1 electrolytes in CH_3CN solutions (Λ_M = 123 Ω^{-1} cm^2 mol^{-1} for X = Br). The IR spectra (Nujol mull) show a strong band at 943 cm^{-1} (X = Cl) and 942 cm^{-1} (X = Br) assigned to the ν(Mo=O) mode. This assignment was based upon a comparison of the IR spectra of these complexes with the spectrum reported

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for the structurally characterized complex *trans*-[MoOCl(dppe)$_2$]Cl (ν(Mo=O) at 942 cm^{-1}).[24]

CV's of solutions of these complexes in 0.1 M TBAH/CH$_2$Cl$_2$ revealed the presence of a reversible one-electron reduction at $E_{1/2} = -1.17$ V (X = Cl) and $E_{1/2} = -1.10$ V (X = Br) and an irreversible oxidation at $E_{p,a} = +1.8$ V (X = Cl) and +1.9 V (X = Br) vs Ag/AgCl. Irreversible processes associated with the oxidation of the outer-sphere halide ion are also seen (Table IV).

The $^{31}P\{^1H\}$ NMR spectra of these complexes recorded in CD$_2$Cl$_2$ exhibit a singlet at δ +48.8 (X = Cl) and δ +47.6 (X = Br). These chemical shifts are characteristic of five-membered rings formed by chelating phosphines.[25] The ^{1}H NMR spectra of [MoOX(dppbe)$_2$]X·nH$_2$O (X = Cl, Br) recorded in CD$_2$Cl$_2$ showed the expected phenyl ring resonances between δ +8.8 and +6.5. These spectra are almost identical with one another.

The low-frequency IR spectrum (Nujol mull) for [MoOCl(dppbe)$_2$]Cl·3H$_2$O exhibits a strong absorption at 293 cm^{-1}, which is probably due to the ν(MoCl) mode. A similar band (at ~290 cm^{-1}) is seen the spectrum of the analogous PF$_6^-$ salt.

D. Consideration of Reactivities. In view of previous observations concerning the occurrence of chelating (α) and bridging (β) isomers for Mo$_2$X$_4$(LL)$_2$ compounds, the lack of evidence for the bridging form when LL = dppbe was unexpected. The recovery of the α-Mo$_2$X$_4$(dppbe)$_2$ species from methanol after brief reactions suggests that these isomers result from a kinetically favored pathway, behavior typical of other α-Mo$_2$X$_4$(LL)$_2$ complexes formed in this solvent.[4,5] In addition, the conversion of these products to the mononuclear compounds *trans*-MoX$_2$(dppbe)$_2$ further substantiates kinetic reaction control for dinuclear complex formation. Isolation of *trans*-MoX$_2$(dppbe)$_2$ as the major products from both [Mo$_2$X$_8$]$^{4-}$ and α-Mo$_2$X$_4$(dppbe)$_2$ reactants in the higher boiling 1-propanol solvent indicates greater thermodynamic stability for these mononuclear complexes. Thus, the principal question regarding the observed reactivities involves the ready breakage of the metal-metal quadruple bond in preference to $\alpha \rightarrow \beta$ isomerization. Interestingly, while the formation of *trans*-MoBr$_2$(dppe)$_2$ does accompany the rearrangement reaction of α-Mo$_2$Br$_4$(dppe)$_2$ to its β isomer, this mononuclear species is formed as a *minor* side product only.[6]

We are unable to say at present whether the bridging (β) dppbe isomer cannot be generated because of the inability of this ligand to bridge two metal centers in this type of complex or whether this form is accessible through an alternative synthetic route. However, we note that in the case of the analogous dirhenium(II) systems only the α isomers have been isolated, the β forms having defied our attempts to prepare them.[13]

The isolation and characterization of the mononuclear oxo species [MoOX(dppbe)$_2$]X·nH$_2$O from the reactions of octahalodimolybdate(II) anions with dppbe in refluxing 1-propanol marks the first time that oxo-molybdenum(IV) species have been isolated from reactions of this type. Whether the oxygen is derived from 1-propanol or from adventitious water has not been established.

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Supplementary Material Available: Tables of bond distances, bond angles, and thermal displacement parameters (4 pages); a list of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Bonding Mode Variations in Palladium(II) and Platinum(II) Azaphosphole Complexes: Identification by ^{1}H, ^{31}P, and ^{195}Pt NMR of N- and P-Coordination, Pt-Cl Addition to P, and Dimerization

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The 1,2,3-diazaphosphole $\overline{\mathrm{P{=}C(H)C(Me){=}NN}}\mathrm{Me}$ (L$_A$) and the 1,2,4,3-triazaphospholes $\overline{\mathrm{P{=}NC(Ph){=}NN}}\mathrm{Me}$ (L$_B$) and $\overline{\mathrm{P{=}NN(Me)C(Me){=}N}}$ (L$_C$) react with the halo-bridged dimers [MX$_2$(PEt$_3$)]$_2$ (M = Pt^{II}, Pd^{II}) to afford a variety of products with MX$_2$(PEt$_3$)L (L = di- or triazaphosphole) stoichiometry. With [PdCl$_2$(PEt$_3$)]$_2$ these azaphospholes produce *trans*-[PdCl$_2$(PEt$_3$)L] with σ-N-bonded L. From [PtBr$_2$(PEt$_3$)]$_2$ is obtained [PtBr$_2$(PEt$_3$)L] as a mixture of the cis σ-P coordination isomer with lesser amounts of the trans σ-N isomer. These azaphospholes all afford different products with [PtCl$_2$(PEt$_3$)]$_2$; the diazaphosphole L$_A$ produces mononuclear *cis*-[PtCl$_2$(PEt$_3$)L$_A$] (σ-P bound) whereas the triazaphospholes L$_B$ and L$_C$ produce dinuclear species that have symmetric and asymmetric structures, respectively. The new air-sensitive complexes have been principally characterized by a combination of ^{1}H, ^{31}P, and ^{195}Pt NMR solution spectroscopy.

Introduction

The azaphospholes[2] are heteratomic aromatic ring systems which contain a two-coordinate trivalent phosphorus atom that is doubly bonded to carbon or nitrogen. Normally, i.e. in the acyclic nonconjugated case, such bonds readily undergo addition reactions, but in azaphospholes these bonds are stabilized by the cyclic delocalization. Complex formation can modify the tendency of an azaphosphole to give additions[2-4] to the various bonds depending on the coordination mode present.

The 1,2,3-diazaphosphole L$_A$ and the 1,2,4,3-triazaphospholes L$_B$ and L$_C$ (see Figure 1) have a variety of potential ligating sites available, of which the lone pair of phosphorus is common to all

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