NMR ($CDCl_3$) δ 244.41, 203.24, 198.82, 140.00, 137.81, 128.90, 128.44, 126.49, 122.99, 53.43, 45.76, 0.86; MS (20.0 eV) *m/e* 571 (M^+, 1%), 543 (1), 515 (8), 487 (6), 459 (2), 431 (14). Anal. Calcd for $C_{19}H_{21}NO_6SiW$: C, 39.95; H, 3.70; N, 2.45. Found: C, 39.89; H, 3.60; N, 2.45. Removal of the solvent from the third yellow band under vacuum afforded 63.0 mg of a yellow oil which turns blue-green upon exposure to air: ^1H NMR ($CDCl_3$) δ 7.54-7.35 (m, 5 H), 5.08 (s, 2 H), 3.96 (s, 3 H), 3.28 (s, 3 H).

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Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, least-squares plane results, and torsion angles (6 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

High-Yield Synthesis of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and Its Dimerization To Form $\{Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2\}_2$, a Complex Characterized by X-ray Crystallography

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The reduction of Mo_2Cl_{10} with Mg in THF in the presence of PMe_2Ph at 70 °C yields the η^6-bonded arylphosphine complex $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ in high yields. This complex does not undergo substitution reactions with CO and $P(OMe)_3$ at ca. 25 °C. A substitution reaction occurs with 1 mol of $P(OMe)_3$ at 45 °C to form the monosubstituted derivative $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_2(P(OMe)_3)$. The reaction of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ with $^1/_2[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) initially results in the bimetallic complex $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}Me_2)(PMe_2Ph)_3$. The dinuclear complex $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ is obtained in the reaction of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and $ReH_7(PPh_3)_2$. The structural assignments are based on ^1H and $^{31}P\{^1H\}$ NMR spectra, elemental analysis, and in the case of the dimer a single-crystal X-ray structural determination. The cyclic voltammograms for $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ and some analogues are also reported. The dimer crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 11.699 (2) Å, b = 12.117 (1) Å, c = 16.352 (2) Å, β = 93.1 (1)°, V = 2314.6 (7) Å^3, and D_{calcd} = 1.465 g/cm^3 for Z = 2. The structure was solved by a three-dimensional Patterson map and refined by least-squares and Fourier methods to final residuals R = 0.031 (R_w = 0.039) for 3299 observed ($F_o^2 > 3\sigma(F_o)^2$) reflections. The geometry about the molybdenum is distorted octahedral. Averaged principal bond lengths are Mo-C(ring) = 2.27 [1] and Mo-P = 2.433 [2] Å, and the Mo-Mo distance is 4.9706 (3) Å.

Introduction

The reductions of high-valent molybdenum halides, such as Mo_2Cl_{10} or $MoCl_4(THF)_2$, with either Mg or Na/Hg in the presence of tertiary phosphines under N_2 are very useful routes to the reactive bis(dinitrogen) complexes of the type $Mo(N_2)_2L_4$, where L = $PMePh_2$ (George;[1a] Morris;[1b] Makhaev[1c]), PMe_2Ph (Chatt[1d]), and PMe_3 (Carmona;[1e] Green[1f]) or L_2 = $PPh_2CH_2CH_2PPh_2$ (dppe) (Hidai;[1g] Chatt[1d]). A dinitrogen ligand is sufficiently activated in some of these complexes that it is converted into ammonia when the complex is treated with acid.[2] An electrocatalytic conversion was accomplished recently by use of the complex $W(N_2)_2(dppe)_2$.[3]

If the reductions mentioned above are carried out in the absence of N_2 and in the presence of arylphosphines (PPhRR′), then complexes of the type $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $Mo(\eta^6\text{-}PhPRR')(PPhRR')(dppe)$ (R = Me or Ph, R′ = Ph) are obtained.[4] These complexes have a rich substitution chemistry including H_2 and N_2,[4c,5] and they can be used as phosphine-like ligands to rhodium(1)[6] and group 6 metal carbonyls.[7] They are

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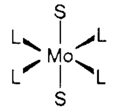
also useful reagents for the regioselective synthesis of quadruply bonded MoW dimers of the type $MoWCl_4(PR_3)_4$.[8]

The formation of these complexes likely involves an intermediate of the type *trans*-$Mo(solvent)_2L_4$[4b] (structure I) since when dinitrogen is present, bis(dinitrogen) complexes are obtained. There is a critical sum of Tolman's cone angles[9] of the four equatorial ligands L in I for which rearrangement to the η^6-arylphosphine complex is favored. The σ to π rearrangement occurs at ambient temperatures only if the sum of these four angles is greater than 510° so that steric interactions weaken the Mo–P bonds (I does not form if the sum exceeds 550°).[4c]


I

S = solvent

The first reported synthesis of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ (**1**) involved the reduction of $MoCl_3(THF)_3$ using sodium amalgam in the presence of PMe_2Ph at ambient temperatures.[10] This method yielded only a few crystals of **1**, but it could not be reproduced. The X-ray diffraction study of one of the crystals confirmed the presence of an η^6-bonded arylphosphine ligand.[11]

Our early attempts at synthesis at room temperature also failed using Mg or Na/Hg as the reducing agents. Then followed the discovery that the photolysis of $MoH_4(PMe_2Ph)_4$ in pentane in the presence of *tert*-butylethylene was also a route to **1**.[12] This was not a high-yield synthetic pathway, and it could only be accomplished on a small scale. We used this method to demonstrate that **1** could reduce $WCl_4(PPh_3)_2$ to produce the unbridged quadruply bonded complex $MoWCl_4(PMe_2Ph)_4$.[8]

Since the sum of cone angles of four PMe_2Ph groups is 488°, the σ to π rearrangement of a PMe_2Ph ligand in intermediate I to give **1** is unfavorable at room temperature and we began to suspect that this is why attempts at its synthesis near 20 °C usually fail. We show here that thermal activation (70 °C) of the Mo–PMe_2Ph bonds does drive this rearrangement to give **1** in good yield. This paper describes this synthesis as well as spectroscopic and electrochemical properties of **1** which have not been reported[10] as well as some interesting bimetallic products from reactions of **1** with other metal complexes.

Experimental Section

General Data. All manipulations were carried out under an atmosphere of pure nitrogen or argon by using vacuum lines or a glovebox. Solvents apart from methanol were dried and distilled from sodium/potassium alloy and were distilled under nitrogen. Tetrahydrofuran (THF) was further distilled over $LiAlH_4$. Methanol was dried over magnesium methoxide. NMR spectra were recorded on a Varian XL-200 (200 MHz for ^1H and 32.3 MHz for ^{31}P NMR) or on a Bruker WP-80 (80 MHz for ^1H and 32.3 MHz for ^{31}P NMR) spectrometer. ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Cyclic voltammetric measurements were performed on a BAS CV 1B instrument and a Houston Instruments 100 recorder using THF solutions which were 0.002 M in the complexes and 0.2 M in $(n\text{-}Bu)_4NBF_4$. Voltammograms were obtained by using a glassy carbon electrode referenced to a Ag/AgCl electrode but are reported relative to the saturated calomel electrode (SCE). The complex $ReH_7(PPh_3)_2$ was prepared as outlined in ref 13 except that the entire preparation was done under hydrogen. $[RhCl(COD)]_2$ was prepared as outlined in ref 14. The microanalysis was performed on the sample handled under an inert atmosphere by the Canadian Microanalytical Service, Vancouver, British Columbia. The phosphine ligands and $MoCl_5$ were used as purchased from Strem and Morton/Thiokol-Alfa Chemicals.

Preparation of $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ (1). Mo_2Cl_{10} (0.50 g, 0.9 mmol) was dissolved in a solution of PMe_2Ph (1.3 g, 9.4 mmol) in THF (45 mL) under Ar. Iodine-activated magnesium (2.0 g, 82 mmol) was added and the mixture stirred for 2 h at 70 °C. The solution was then filtered through Celite, concentrated in vacuo, and treated with methanol (15 mL) to yield orange **1** (0.4 g, 33%). The filtrate was kept at −20 °C overnight and filtered the next day (0.4 g, overall yield 67%): ^1H NMR (acetone-d_6) δ 7.5 (m, 6 H, ortho-*Ph*P–Mo), 7.3–7.2 (m, 9 H, meta, para-*Ph*P–Mo), 4.0 (m, 2 H, ortho-η^6-*Ph*), 3.4 (m, 1 H, para-η^6-*Ph*), 3.2 (m, 2 H, meta-η^6-*Ph*), 1.5 (br, 18 H, *Me*$_2$P–Mo), 1.0 (d, 6 H, $^2J_{HP}$ = 4 Hz, *Me*$_2$P–η^6-Ph); ^{31}P NMR (C_6H_6) δ 15.8 (s, 3 P, *P*–Mo), −46.7 (s, 1 P, η^6-Ph–*P*). Anal. Calcd for $C_{32}H_{44}MoP_4$: C, 59.26; H, 6.84. Found: C, 58.86; H, 6.87.

Preparation of $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}Me_2)(PMe_2Ph)_3$ (2). A solution of the complex $[RhCl(COD)]_2$ (0.03 g, 0.06 mmol) dissolved in 5 mL of C_6H_6 was added dropwise to a stirred solution of complex **1** (80 mg, 0.12 mmol) in 10 mL of C_6H_6. After 15 min of stirring, the solution was filtered and the solvent removed by vacuum distillation leaving dark red complex **2** (0.10 g, 91%): ^1H NMR (C_6D_6) δ 7.3 (m, 6 H, ortho-*Ph*P–Mo), 7.1–7.0 (m, 9 H, meta, para-*Ph*P–Mo), 5.7 (m, 2 H, trans-C_2H_2(COD)–Rh–P), 4.4 (m, 2 H, ortho-η^6-*Ph*), 4.1 (m, 1 H, para-η^6-*Ph*), 3.5 (m, 2 H, trans-C_2H_2(COD)–Rh–Cl), 3.1 (m, 2 H, meta-η^6-*Ph*), 2.1 and 1.7 (m, 8 H, CH_2(COD)), 1.5 (br, 18 H, *Me*$_2$P–Mo), 1.3 (d, 6 H, $^2J_{HP}$ = 8 Hz, *Me*$_2$P–η^6-Ph); ^{31}P NMR (C_6H_6) δ 14.1 (s, 3 P, *P*–Mo), −1.2 (d, J_{PRh} = 147 Hz, 1 P, η^6-Ph–*P*). Satisfactory analytical data for **2** were never obtained even though the spectra showed that no side products were present. Recrystallization at room temperature results in the decomposition of the complex.

Preparation of $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ (3). Complex **1** (0.05 g, 0.07 mmol) was added to a solution of $ReH_7(PPh_3)_2$ (0.06 g, 0.07 mmol) and 20 mL of C_6H_6 and heated at 45 °C for 2 days under Ar. The clear red-green solution was filtered, concentrated to ca. 10 mL, and layered with 15 mL of hexane. After 2 weeks small green crystals of **3** were observed in the Schlenk flask, and these were separated by filtration. The yield of this complex was less than 5 mg: ^1H NMR (C_6D_6) δ 7.6–7.0 (m, 20 H, *Ph*–P–Mo), 3.0–5.0 (small multiplets, 5 H, η^6-*Ph*–P), 1.3 (m, 12 H, *Me*$_3$P–Mo), 1.1 (d, 12 H, *J* = 12 Hz, η^6-PhP*Me*–Mo), 0.9 (m, 12 H, *Me*$_2$P–Mo).

Substitution Reactions. (a) Carbon monoxide was bubbled through a solution of 20 mg of **1** in 2 mL of C_6H_6 for 30 min. A ^{31}P NMR spectrum revealed that CO substitution had not occurred. (b) An equimolar amount of $P(OMe)_3$ was added to 20 mg of **1** in 2 mL of C_6H_6. This solution was stirred for 25 min whereupon the ^{31}P NMR spectrum was obtained. Again no evidence of phosphine substitution was apparent. (c) The above solution in method b was heated at 45 °C for 12 h. The ^{31}P NMR spectrum was then obtained. Besides dissociated PMe_2Ph and complex **1** this spectrum contained peaks attributable to a monosubstituted complex $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_2(P(OMe)_3)$ (**4**). The yield was ca. 50% based on the ^{31}P NMR spectrum: ^{31}P NMR (C_6H_6) δ 180.8 (t, 1 P, $^2J_{PP}$ = 54 Hz, $(MeO)_3P$–Mo), 19.2 (d, 2 P, $^2J_{PP}$ = 54 Hz, Me_2PhP–Mo), −45.8 (s, 1 P, η^6-Ph–*P*).

Crystallographic Analysis of 3. A red-green crystal was selected out of the bunch that crystallized in the preparation of **3**. The crystal was affixed to the top of a thin quartz fiber with 5-min epoxy resin and then mounted under the N_2 cold stream at −80 °C. All relevant crystallographic information is given in Table I. Accurate unit cell parameters were obtained by means of a least-squares analysis of 25 reflections. Intensity data were then collected utilizing the options specified in Table I and the

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Table I. Crystal Data for $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ (3)

formula	$C_{48}H_{66}P_6Mo_2$
formula weight	1020.77
space group	$P2_1/c$
systematic absences	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$
a, Å	11.699 (2)
b, Å	12.117 (1)
c, Å	16.352 (2)
α, deg	90
β, deg	93.1 (1)
γ, deg	90
V, Å^3	2314.6 (7)
Z	2
d_{calcd}, g/cm^3	1.465
cryst size, mm	0.30 × 0.30 × 0.10
μ(Mo Kα), cm^{-1}	7.652
data collectn instrument	Enraf-Nonius CAD4
radiatn (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)
orientatn reflctns, no., range (2θ)	25, $24 < 2\theta < 33$
temp, °C	−80
scan method	2θ–ω
data collectn range, 2θ, deg	$0 \leq 2\theta \leq 50$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4064, 3299
no. of parameters refined	382
trans factors (max, min), %	99.93, 81.23
R^a	0.031
$R_w{}^b$	0.039
quality-of-fit indicator^c	1.215
largest shift/esd, final cycle	0.19
largest peak, e/Å^3	1.132 (0.951 Å from Mo)

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ (3)

atom	x	y	z	B,^{a} Å^2
Mo	0.13428 (2)	0.04044 (2)	0.11917 (1)	1.255 (4)
P(1)	0.15232 (6)	0.08078 (7)	−0.02507 (5)	1.53 (1)
P(2)	0.29700 (7)	0.15823 (7)	0.15695 (5)	1.76 (1)
P(3)	0.26094 (7)	−0.11922 (7)	0.12853 (5)	1.55 (1)
C(11)	0.2815 (3)	0.0553 (3)	−0.0824 (2)	2.72 (7)
C(12)	0.1300 (3)	0.2276 (3)	−0.0483 (2)	2.62 (7)
C(21)	0.2612 (3)	0.2995 (3)	0.1890 (2)	2.91 (7)
C(22)	0.4086 (3)	0.1983 (3)	0.0881 (2)	3.04 (7)
C(31)	0.4092 (3)	−0.1160 (3)	0.0974 (2)	2.76 (7)
C(32)	0.2896 (3)	−0.1676 (3)	0.2336 (2)	2.95 (7)
C(131)	−0.0534 (2)	−0.0140 (3)	0.1000 (2)	1.52 (5)
C(132)	−0.0434 (3)	0.1036 (3)	0.0934 (2)	1.79 (6)
C(133)	0.0041 (3)	0.1685 (3)	0.1571 (2)	2.25 (6)
C(134)	0.0525 (3)	0.1145 (3)	0.2279 (2)	2.31 (6)
C(135)	0.0469 (3)	0.0001 (3)	0.2368 (2)	2.09 (6)
C(136)	−0.0034 (3)	−0.0646 (3)	0.1719 (2)	1.77 (6)
C(231)	0.3890 (3)	0.1183 (3)	0.2478 (2)	1.94 (6)
C(232)	0.5047 (3)	0.0926 (3)	0.2441 (2)	2.39 (6)
C(233)	0.5681 (3)	0.0613 (3)	0.3147 (3)	3.52 (8)
C(234)	0.5199 (4)	0.0584 (3)	0.3890 (2)	3.62 (8)
C(235)	0.4056 (4)	0.0837 (3)	0.3936 (2)	3.20 (8)
C(236)	0.3408 (3)	0.1120 (3)	0.3232 (2)	2.52 (7)
C(331)	0.2170 (3)	−0.2509 (3)	0.0794 (2)	1.67 (6)
C(332)	0.2446 (3)	−0.2741 (3)	−0.0000 (2)	2.12 (6)
C(333)	0.2114 (3)	−0.3730 (3)	−0.0374 (2)	2.70 (7)
C(334)	0.1502 (3)	−0.4496 (3)	0.0038 (3)	2.99 (8)
C(335)	0.1222 (3)	−0.4280 (3)	0.0825 (3)	2.76 (7)
C(336)	0.1540 (3)	−0.3288 (3)	0.1198 (2)	2.20 (6)
H(111)	0.274 (3)	0.085 (3)	−0.132 (2)	1.4 (8)*
H(112)	0.290 (4)	−0.021 (4)	−0.081 (3)	2 (1)*
H(113)	0.345 (4)	0.082 (4)	−0.057 (3)	3 (1)*
H(121)	0.047 (3)	0.247 (3)	−0.039 (2)	0.3 (7)*
H(122)	0.147 (3)	0.242 (3)	−0.099 (2)	1.5 (9)*
H(123)	0.183 (4)	0.269 (4)	−0.020 (3)	3 (1)*
H(211)	0.323 (3)	0.337 (3)	0.208 (2)	0.4 (7)*
H(212)	0.226 (3)	0.335 (3)	0.139 (2)	1.0 (8)*
H(213)	0.207 (3)	0.298 (4)	0.227 (3)	2 (1)*
H(221)	0.447 (3)	0.138 (3)	0.067 (2)	0.4 (7)*
H(222)	0.379 (3)	0.240 (3)	0.045 (2)	1.3 (8)*
H(223)	0.464 (3)	0.248 (3)	0.115 (2)	0.6 (7)*
H(311)	0.448 (3)	−0.064 (3)	0.124 (2)	0.6 (8)*
H(312)	0.440 (3)	−0.186 (3)	0.101 (2)	1.5 (9)*
H(313)	0.407 (3)	−0.088 (3)	0.038 (2)	0.7 (8)*
H(321)	0.216 (3)	−0.190 (3)	0.259 (2)	1.9 (9)*
H(322)	0.336 (3)	−0.242 (3)	0.237 (2)	0.8 (8)*
H(323)	0.324 (3)	−0.116 (3)	0.258 (2)	1.6 (9)*
H(132)^b	−0.067 (3)	0.132 (4)	0.047 (3)	2.0*
H(133)	0.010 (3)	0.240 (3)	0.148 (2)	0.6 (7)*
H(134)	0.085 (3)	0.154 (3)	0.266 (2)	0.2 (7)*
H(135)	0.081 (3)	−0.031 (3)	0.279 (2)	0.9 (8)*
H(136)^b	−0.002 (3)	−0.138 (4)	0.177 (2)	2.0*
H(232)	0.541 (3)	0.101 (3)	0.195 (2)	0.2 (7)*
H(233)	0.648 (3)	0.047 (3)	0.308 (2)	1.0 (8)*
H(234)	0.560 (3)	0.045 (3)	0.431 (3)	1.5 (9)*
H(235)	0.372 (3)	0.083 (3)	0.438 (2)	1.3 (8)*
H(236)	0.264 (3)	0.122 (3)	0.327 (2)	0.0 (7)*
H(332)^b	0.288 (3)	−0.220 (4)	−0.028 (3)	2.0*
H(333)	0.243 (3)	−0.388 (4)	−0.089 (3)	2.0 (9)*
H(334)	0.122 (3)	−0.519 (3)	−0.022 (2)	1.1 (8)*
H(335)	0.084 (4)	−0.471 (4)	0.115 (3)	3 (1)*
H(336)	0.129 (3)	−0.319 (3)	0.174 (2)	0.5 (7)*

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

general procedures for data collection as previously described.[15] No decay was observed. After Lorentz and polarization corrections were applied, the data set was corrected for absorption by using an empirical method based on nine ψ scans (ψ = 0–360° every 10°) for χ values near 90°.[16] Finally equivalent reflections were averaged and systematically absent reflections were excluded. The structure was essentially solved (all non-hydrogen atoms were found) from a three-dimensional Patterson function. These atoms were refined isotropically and then anisotropically to convergence. The hydrogen atoms were found by alternating least-squares full-matrix cycles of refinement and difference Fourier maps for a cutoff ratio $F_o^2/\sigma(F_o^2)$ of 3. For this the Enraf-Nonius SDP software was employed. Three hydrogen atoms (H(132), H(136), and H(332)) had to be refined with fixed thermal parameters because free refinement resulted in negative values. Final positional parameters for the atoms and selected bond lengths and bond angles are given in Tables II and III, respectively.

Results and Discussion

Synthesis. The key to obtaining $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_3$ (1) in high yield is to modify the conventional preparation of η^6-arylphosphine complexes[4] by raising the reaction temperature to 70 °C. This presumably facilitates the rearrangement of the suspected precursor intermediate I with L = PMe_2Ph by weakening the Mo–P σ bonds. Thus, orange crystals of 1 are obtained in 67% yield by reducing Mo_2Cl_{10} with excess magnesium in the presence of PMe_2Ph (8 mol) in rigorously dry THF at 70 °C under Ar. The complex is oxygen sensitive in solution and in the solid state.

The ^{31}P and ^1H NMR spectra of 1 in solution are consistent with the solid-state structure reported earlier.[11] The ^{31}P spectrum consists of a singlet at 15.8 ppm for three Mo-coordinated phosphorus nuclei and a singlet at −46.7 near the chemical shift of free PMe_2Ph (−47.7) for the η^6-$PhPMe_2$ group. Three resonances in the region 3.0–4.0 ppm in the ^1H NMR spectrum correspond to the protons on the η^6-phenyl. The spectra are much simpler than those of the corresponding complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ which has many diastereotopic nuclei due to the presence

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Table III. Selected Bond Lengths and Angles for $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ (3)[a]

Bond Lengths (Å)

Mo-P(1)	2.429 (1)	P(1)-C(11)	1.847 (3)	C(131)-C(132)	1.434 (4)
Mo-P(2)	2.432 (1)	P(1)-C(12)	1.834 (4)	C(131)-C(136)	1.422 (4)
Mo-P(3)	2.437 (1)	P(1)-C(131)[b]	1.828 (1)	C(132)-C(133)	1.396 (4)
Mo-C(131)	2.297 (3)	P(2)-C(21)	1.844 (4)	C(133)-C(134)	1.421 (5)
Mo-C(132)	2.234 (3)	P(2)-C(22)	1.835 (4)	C(134)-C(135)	1.397 (5)
Mo-C(133)	2.283 (3)	P(2)-C(231)	1.851 (3)	C(135)-C(136)	1.421 (4)
Mo-C(134)	2.251 (3)	P(3)-C(31)	1.834 (3)		
Mo-C(135)	2.280 (3)	P(3)-C(32)	1.830 (4)		
Mo-C(136)	2.259 (3)	P(3)-C(331)	1.847 (3)		

Bond Angles (deg)

P(1)-Mo-P(2)	91.20 (3)	P(3)-Mo-C(136)	88.43 (8)	C(11)-P(1)-C(131)[b]	95.3 (1)
P(1)-Mo-P(3)	97.85 (3)	C(131)-Mo-C(132)	36.9 (1)	C(12)-P(1)-C(131)[b]	102.3 (1)
P(1)-Mo-C(131)	93.29 (7)	C(131)-Mo-C(133)	65.5 (1)	Mo-P(2)-C(21)	115.5 (1)
P(1)-Mo-C(132)	82.90 (8)	C(131)-Mo-C(134)	77.2 (1)	Mo-P(2)-C(22)	124.9 (1)
P(1)-Mo-C(133)	102.76 (9)	C(131)-Mo-C(135)	65.5 (1)	Mo-P(2)-C(231)	117.6 (1)
P(1)-Mo-C(134)	138.56 (9)	C(131)-Mo-C(136)	36.4 (1)	C(21)-P(2)-C(22)	96.2 (2)
P(1)-Mo-C(135)	158.26 (8)	C(132)-Mo-C(133)	36.0 (1)	C(21)-P(2)-C(231)	98.4 (2)
P(1)-Mo-C(136)	125.76 (8)	C(132)-Mo-C(134)	65.3 (1)	C(22)-P(2)-C(231)	99.2 (2)
P(2)-Mo-P(3)	89.13 (3)	C(132)-Mo-C(135)	77.2 (1)	Mo-P(3)-C(31)	123.1 (1)
P(2)-Mo-C(131)	158.77 (8)	C(132)-Mo-C(136)	65.8 (1)	Mo-P(3)-C(32)	113.2 (1)
P(2)-Mo-C(132)	123.68 (8)	C(133)-Mo-C(134)	36.5 (1)	Mo-P(3)-C(331)	120.3 (1)
P(2)-Mo-C(133)	93.24 (8)	C(133)-Mo-C(135)	65.2 (1)	C(31)-P(3)-C(32)	98.0 (2)
P(2)-Mo-C(134)	85.72 (9)	C(133)-Mo-C(136)	77.3 (1)	C(31)-P(3)-C(331)	98.2 (2)
P(2)-Mo-C(135)	106.97 (8)	C(134)-Mo-C(135)	35.9 (1)	C(32)-P(3)-C(331)	99.5 (2)
P(2)-Mo-C(136)	142.92 (8)	C(134)-Mo-C(136)	65.2 (1)	C(132)-C(131)-C(136)	117.3 (3)
P(3)-Mo-C(131)	110.73 (8)	C(135)-Mo-C(136)	36.5 (1)	C(131)-C(132)-C(133)	122.3 (3)
P(3)-Mo-C(132)	147.19 (8)	Mo-P(1)-C(11)	125.1 (1)	C(132)-C(133)-C(134)	118.3 (3)
P(3)-Mo-C(133)	159.19 (9)	Mo-P(1)-C(12)	112.2 (1)	C(133)-C(134)-C(135)	121.5 (3)
P(3)-Mo-C(134)	123.36 (9)	Mo-P(1)-C(131)[b]	118.46 (4)	C(134)-C(135)-C(136)	119.3 (3)
P(3)-Mo-C(135)	94.32 (9)	C(11)-P(1)-C(12)	99.7 (2)	C(131)-C(136)-C(135)	121.0 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] This is the symmetry-generated atom by inversion.

of the prochiral η^6-PhPMePh group.[4b]

Substitution reactions of **1** occur at higher temperatures (45 °C) than corresponding reactions for the more crowded complex $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ which readily loses a σ-bonded ligand and reacts at 20 °C with many small ligands, including $P(OMe)_3$, N_2, and H_2.[4b] Complex **1** reacts with $P(OMe)_3$ at 45 °C to give the monosubstituted complex $Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_2(P(OMe)_3)$ but fails to react with N_2. Thus the coordination sphere of **1** is not very crowded, and the Mo–P σ bonds are strong relative to those in the $PMePh_2$ complex.

One consequence of this reduced steric hindrance is that it permits the formation of the heterobimetallic complex $Mo(\eta^6\text{-}PhP\{RhCl(COD)\}Me_2)(PMe_2Ph)_3$ (**2**) by reaction of **1** as a tertiary phosphine-like ligand with $^1/_2$ mol of $[RhCl(COD)]_2$. The analogous heterobimetallic complex cannot be synthesized in the reaction between the more sterically crowded $Mo(\eta^6\text{-}PhPMePh)(PMePh_2)_3$ and $^1/_2$-$[RhCl(COD)]$.[17] In this case a product indicative of extensive ligand exchange, $RhCl(PMePh_2)_3$, is obtained. The molybdenum-containing product from this reaction has not yet been identified. Complex **2** can be obtained in high yield immediately after the synthesis, but, if kept in solution under dinitrogen over a period of 2 days, **2** reacts to form as yet uncharacterized products.

The formation of **2** is easily confirmed by ^1H and ^{31}P NMR spectra. Previously we described how the downfield shift of the resonance for the "dangling" phosphorus atom and coupling to rhodium on the order of 150 Hz signal that complex formation has been accomplished.[6] The ^{31}P NMR of **2** consisted of a singlet due to the three equivalent phosphorus atoms and a doublet due to ^{31}P–^{107}Rh coupling for the phosphorus atom coordinated to rhodium ($^1J_{^{31}P,^{107}Rh} = 147$ Hz). The ^1H spectrum obtained for **2** was assigned on the basis of the integration and by analogy with the spectra obtained for similar heteronuclear complexes.[6]

The formation of the homonuclear dimer $[Mo(\mu\text{-}\eta^1,\eta^6\text{-}PMe_2Ph)(PMe_2Ph)_2]_2$ (**3**) is not easily rationalized. The purpose of the reaction between **1** and $ReH_7(PPh_3)_2$ was to produce the heteronuclear complex $Mo(\eta^6\text{-}PhP\{ReH_5(PPh_3)_2\}Me_2)(PMe_2Ph)_3$. It is known that $ReH_7(PPh_3)_2$ contains a molecular hydrogen ligand and that substitution of this with tertiary phosphine is a facile reaction.[18] The progress of the reaction was monitored by means of ^1H and ^{31}P NMR. There was no evidence for any reaction at room temperature, and thus the reaction mixture was heated. After 15 min of heating there was tentative ^1H NMR evidence for the expected heteronuclear dimer $Mo(\eta^6\text{-}PhP\{ReH_5(PPh_3)_2\}Me_2)(PMe_2Ph)_3$ as well as $ReH_5(PMe_2Ph)(PPh_3)_2$ by the appearance of two quartets at δ −4.7 (J = 19 Hz) and −5.2 (J = 16 Hz) in a 1:10 ratio, respectively. The complex $ReH_5(PMe_2Ph)(PPh_3)_2$ was synthesized independently and did contain a quartet, in the ^1H NMR spectrum, at the δ value given above. The fact that there were many peaks in the arene region (δ 3–5) indicated that a species containing an η^6-$PhPMe_2$ ligand was still present. Thus the reaction was allowed to proceed for 2 days and the isolation of the products attempted by selective precipitation. However, only the slightly soluble crystals of **3**, suitable for X-ray diffraction, were obtained. The $ReH_7(PPh_3)_2$ may have facilitated the formation of **3** by acting like a "phosphine sponge". The action of such an agent would be to trap any dissociated tertiary phosphine that arises in the reaction mixture and form a nonreactive substance, which, in this reaction, would be $ReH_5(PMe_2Ph)(PPh_3)_2$. This would then result in the formation of unsaturated "$Mo(\eta^6\text{-}PhPMe_2)(PMe_2Ph)_2$" fragments which could easily couple to form **3**. Such a technique was used in the reaction between Mo(η^6-

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Table IV. Electrochemical Data on Complexes 1 and 2 and Other Related Complexes

complex	$E_{1/2}$(ox.)[a]
Mo(η^6-PhPMePh)(PMePh$_2$)$_3$	−0.44[b]
Mo(η^6-PhPMePh)(PMePh$_2$)$_2$(PMe$_3$)	−0.47[b]
Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ (1)	−0.51[c]
Mo(η^6-PhP{RhCl(COD)}Me$_2$)(PMe$_2$Ph)$_3$ (2)	−0.48[c]

[a] V vs SCE; 22 °C; solvent, THF; electrolyte, (^{n}Bu)$_4$NBF$_4$; scan rate, 50 mV/s. [b] Reference 19. [c] This work.

PhPMePh)(PMePh$_2$)$_3$ and ca. 2.25 equiv of [9-BBN], 9-bora[1,3,3]bicyclononane, under N$_2$, which resulted in the formation of the complex Mo(η^6-PhP{BH(C$_8$H$_{14}$)}MePh)(N$_2$)(PMePh$_2$)$_2$.[5] Here, [9-BBN] was used as a "phosphine sponge" to trap out dissociated PMePh$_2$ and allow the formation of the dinitrogen complex. Finally, complex 3 has not, thus far, been synthesized in a straightforward manner, such as by simply heating toluene solutions of 1 at reflux temperatures.

The ^{1}H NMR spectrum, done on the crystalline material, contained a doublet at δ 1.1 (J = 12 Hz), which has been assigned to the hydrogen atoms on the methyl groups bonded to the bridging phosphorus atoms. The other hydrogen atoms on the methyl groups appeared in two different positions as broad multiplets, δ 0.9 and 1.4, and this might be related to the axial and equatorial arrangement of the phosphorus atoms to which they are attached, see below. A few other binuclear complexes containing bridging η^1,η^6-arylphosphine groups are known: [Mo(μ-η^1,η^6-PhPPh$_2$)(PPh$_3$)(CNBu)]$_2$,[19] [Cr(μ-η^1,η^6-ArPAr$_2$)(CO)$_2$]$_2$ (Ar = phenyl, *m*-tolyl, *p*-tolyl),[20] and [Rh(μ-η^2,η^6-PhPPhCH$_2$CH$_2$CH$_2$PPh$_2$)]$_2{}^+$.[21]

Electrochemical Results. The results obtained from a cyclic voltammogram study on complexes 1 and 2 together with those obtained for other closely related monomeric molybdenum complexes are listed in Table IV. The $E_{1/2}$ values refer to the reversible reduction couple of Mo(I) $\rightleftharpoons$ Mo(0). First, these data show that 1 is the most easily oxidized complex among this group as its redox potential is 0.04 V less than Mo(η^6-PhPMePh)(PMePh$_2$)$_2$(PMe$_3$) which is the most electron-rich derivative synthesized from Mo(η^6-PhPMePh)(PMePh$_2$)$_3$ so far. A second point is that the attachment of the RhCl(COD) fragment resulted in an increase in the redox potential by 0.03 V. This can be compared to the 0.1–0.15 V increase in redox potential when a more electropositive group VI pentacarbonyl fragment is coordinated to the dangling phosphorus of Mo(η^6-PhPMePh)(PPh$_2$CH$_2$CH$_2$PPh$_2$)(L) (L = P(OMe)$_3$ or CO.[7]

Crystallographic Analysis of 3. An ORTEP drawing with the atomic numbering scheme of 3 and a stereoview that affords a better view of the stereochemistry are presented in Figures 1 and 2, respectively. The molecules crystallize in space group $P2_1/c$ and reside on inversion centers at 0,0,0 and $^1/_2$, $^1/_2$, $^1/_2$ so that $^1/_2$ of the molecule constitutes the asymmetric unit. As can be easily seen in Figure 2, the dimer is held together by the two η^1,η^6-bonded PMe$_2$Ph groups that bridge the two metal centers. Four σ-bonded PMe$_2$Ph ligands, two on each metal, complete the coordination sphere of each molybdenum atom. The geometry around the molybdenum atoms is best described as distorted octahedral with the η^6-Ph moiety occupying one face. It has already been pointed out,[19] and this is also true for 3, that the atoms directly involved in the bridging arrangement, namely, Mo–C(131)–P(1) and the symmetry-generated atoms, Mo′–C(131)′–P(1)′, constitute a cyclohexane-like ring. This exists in 3 in a slight chair configuration, with the Mo atom displaced 0.55 Å above the plane described by P(1) and C(131) and the symmetry-generated atoms P(1)′ and C(131)′ (see Figure 2). The terminal σ-bonded PMe$_2$Ph ligands can then be described as occupying axial and equatorial sites at each metal center.

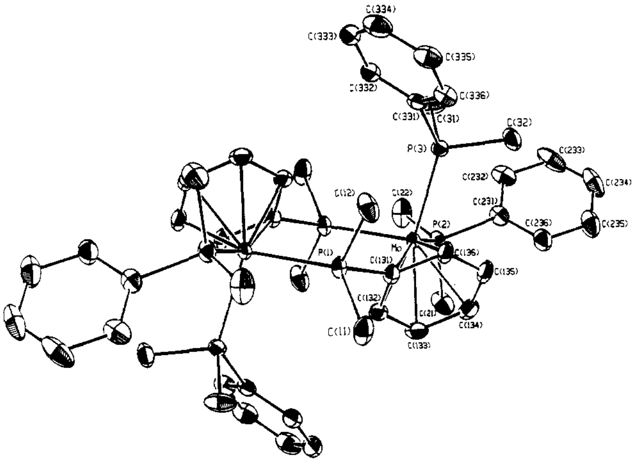

Figure 1. An ORTEP drawing of 3. The ellipsoids represent anisotropic thermal displacements drawn at the 50% probability level.

Tables II and III list selected bond lengths and angles, and Table V lists a comparison of various bond lengths and angles for 3 and other structurally related complexes. Some interesting points are evident in Table V. (1) The average Mo–C$_{\rm ring}$ distances for the complexes listed in Table V are about the same. However, there is some variation in the Mo–C$_{\rm P}$ distance (C$_{\rm P}$ is the ring carbon bonded to phosphorus). In fact this distance is shortest for complex 3. (2) The deviation of the (bridging or "dangling") phosphorus atom from the least-squares plane defined by the six-η^6-carbon atoms is greatest in complex 3. This may be related to the fact that the Mo–P$_{\rm b}$ distance (P$_{\rm b}$ is the bridging phosphorus atom) is smallest for complex 3 (2.429 (1) Å) when compared to those in [Mo(μ-η^1,η^6-PPh$_3$)(PPh$_3$)(CN(CH$_2$)$_3$Me)]$_2$, 2.472 (3) and 2.458 (3) Å. Evidently, the smaller methyl substituents on the bridging phosphorus atom in 3, as opposed to the phenyl groups in [Mo(μ-η^1,η^6-PPh$_3$)(PPh$_3$)(CN(CH$_2$)$_3$Me)]$_2$, permit the bridging phosphorus atom to bond more closely to the molybdenum center. It is notable that the hydrogen atoms on the η^6-bonded phenyl group are all displaced from the least-squares plane mentioned above and are inclined toward the molybdenum atoms by an average of 0.06 Å. This is similar to results from an X-ray and neutron diffraction analysis of Cr(η^6-C$_6$H$_6$)(CO)$_3$ which found the hydrogen atoms similarly displaced toward the chromium atom by 0.03 Å.[22] (3) There is no difference in the Mo–P$_{\rm t}$ distances between 3 and the monuclear complex 1, and, furthermore, the average P–Mo–P angles in these two molecules are also similar. However, a greater range of angles is found in 3 (89.13 (3)–97.85 (3)°) than in complex 1 (89.8 (2)–93.0 (2)°). The large upper value for the P(1)–Mo–P(3) angle in 3 is probably due to the steric interactions between the methyl substituents on P(1) and the phenyl moieties on P(3); see Figure 2. (4) The fact that the Mo–P distances in complex

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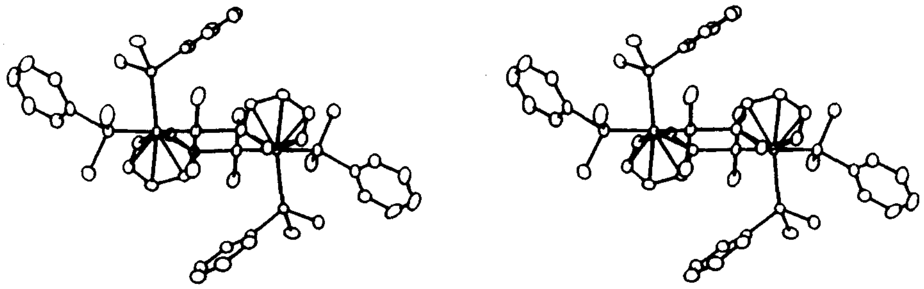

Figure 2. A stereoview of complex 3.

Table V. Selected Bond Lengths and Angles for Compounds 3, [Mo(μ-η^1,η^6-PPh$_3$)(PPh$_3$)(CN(CH$_2$)$_3$Me)]$_2$, Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$, and Mo(η^6-PhPMePh)(PMePh$_2$)$_2$(CNCMe$_3$)

dimensions[a–d]	[Mo(μ-η^1,η^6-PMePh$_2$)(PMe$_2$Ph)$_2$]$_2$	[Mo(μ-η^1,η^6-PPh$_3$)-(PPh$_3$)-(CN(CH$_2$)$_3$Me)]$_2$[f]		Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$[e]	Mo(η^6-PhPMePh)-(PMePh$_2$)$_2$-(CNCMe$_3$)[g]
		Mo(1)	Mo(2)		
av Mo–C$_{ring}$	2.27 [1]	2.28 [1]	2.30 [2]	2.28 [1]	2.28 [1]
Mo–C$_p$	2.297 (3)	2.297 (9)	2.359 (9)	2.30 (1)	2.319 (11)
P$_{d\text{-ring}}$	0.438 (1)	0.362 (3)	0.234 (3)	0.32	0.265 (3)
Mo–P$_b$	2.429 (1)	2.472 (3)	2.458 (3)		
Mo–P$_t$	2.435 [3]	2.472 (3)	2.474 (3)	2.436 [8]	2.418 [2]
av ∠P–Mo–P	93 [3]			92 [1]	
∠P–Mo–P	91.20 (3), 97.85 (3), 89.13 (3)	103.1 (1)	98.0 (1)	91.6 (2), 93.0 (2), 89.8 (2)	94.0 (1)

[a] Numbers within parentheses denote standard deviations and those in brackets signify the variance, viz., $[(\sum\Delta_i^2)/n(n-1)]^{1/2}$. [b] Mo–C$_p$ refers to the distance between the molybdenum and the ring carbon atom bonded to the phosphorus atom. [c] P$_{d\text{-ring}}$ refers to the deviation of the phosphorus atom (bridging or "dangling") away from the least-squares plane defined by the six η^6-bonded carbon atoms. [d] P$_b$ and P$_t$ refer to bridging and terminal phosphorus atoms, respectively. [e] Reference 11. [f] Reference 19. [g] Reference 4b.

3 and Mo(η^6-PhPMePh)(PMePh$_2$)$_2$(CN^{t}Bu) and that the P–Mo–P angles are smaller than those in [Mo(μ-η^1,η^6-PPh$_3$)(PPh$_3$)(CN(CH$_2$)$_3$Me)]$_2$ can be attributed to the smaller tertiary phosphine substituents. However, the Mo–P distances in Mo(η^6-PhPMePh)(PMePh$_2$)$_2$(CN^{t}Bu) are the shortest. This indicates that complexes 1 and 3 still contain a reasonable amount of steric interactions that would be responsible for the lengthening of the Mo–P bond lengths.

Finally, the Mo–Mo distance in 3, 4.9706 (3) Å, is similar to but not identical with that in the related [Mo(μ-η^1,η^6-PPh$_3$)(PPh$_3$)(CN(CH$_2$)$_3$Me)]$_2$, 4.804 (1) Å. The difference arises because the six-membered rings have slightly different conformations, due to the presence of substituents that make different steric demands.

Conclusions

The formation of Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ occurs at 70 °C where thermal activation facilitates a σ–π rearrangement of an intermediate species that contains four σ-bonded PMe$_2$Ph ligands. This represents a significant advance in the synthesis of these complexes and may be useful in the synthesis of other η^6-bonded arylphosphine complexes, with either molybdenum or some other transition metal at the center. The complex Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ is more thermally stable than the congener Mo(η^6-PhPMePh)(PMePh$_2$)$_3$, and this permited the formation of the dinuclear molybdenum–rhodium complex Mo(η^6-PhP{RhCl(COD)}Me$_2$)(PMe$_2$Ph)$_3$.

The dimer [Mo(μ-η^1,η^6-PMe$_2$Ph)(PMe$_2$Ph)$_2$]$_2$ resulted from a reaction between Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ and ReH$_7$(PPh$_3$)$_2$. We propose that ReH$_7$(PPh$_3$)$_2$ may be serving as a phosphine sponge, assisting in the generation of unsaturated molybdenum fragments which then couple to form the dimer. This, unfortunately, might be a disadvantage if Mo(η^6-PhPMe$_2$)(PMe$_2$Ph)$_3$ is used in reactions to form heterononuclear multiply bonded species.[8a]

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Registry No. 1, 56054-39-8; 2, 119820-43-8; 3, 119820-44-9; 4, 119820-45-0; Mo$_2$Cl$_{10}$, 26814-39-1; [RhCl(COD)]$_2$, 12092-47-6; ReH$_7$(PPh$_3$)$_2$, 12103-40-1.

Supplementary Material Available: A stereoview of the unit cell and tables containing full listings of bond lengths and bond angles and thermal parameters for 3 (10 pages); a listing of final structure amplitudes for 3 (18 pages). Ordering information is given on any current masthead page.