double LF excitations symmetry factored for each of the irreducible representations belonging to the point group D_{2h}, by making use of the hole formalism.[32] By solving then the corresponding four CI matrices we obtained the energies of the ligand field states, which have been used for the calculation of the electronic transition energies.

As can be seen from Tables VII–IX the agreement between the calculated and experimentally observed transitions is remarkably good. For all five complexes there are many allowed transitions in the entire region of observed spectral transitions including intraligand L → L* and charge-transfer (CT) L → M* and M → L* transitions. In addition, there are forbidden LF transitions (d → d*), most of them being hidden under the more intense CT transitions. The only observable LF transition is that appearing in the region $(12.9–13.7) \times 10^3$ cm^{-1} of the spectra, which is assigned to the $^1B^+_{1g} \leftarrow {}^1A_g$ electronic transition.

It is interesting to compare for the five complexes the calculated energy difference $E(xy) - E(z^2)$, this quantity representing the ligand field splitting Δ_1 of the metal d orbitals. The values of Δ_1 are 18.7×10^3, 19.07×10^3, 19.39×10^3, 19.48×10^3, and 19.67×10^3 cm^{-1} for the parent complex and its 3-, 4-, 2–hydroxy- and 2,4-dihydroxy-substituted derivatives, respectively. According to these values the following spectrochemical series for the ligands under investigation can be proposed:

$(2,4\text{-}(OH)_2)dtb^- > (2\text{-}OH)dtb^- > (4\text{-}OH)dtb^- >$
$$(3\text{-}OH)dtb^- > dtb^-$$
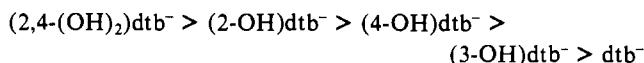
This series is in agreement with the spectrochemical series of the ligands under investigation established previously[33] from the $10Dq$ values of their octahedral complexes.

Concluding our discussion on the electronic spectra, it is important to note that despite the simplistic approach adopted in the calculations, for example the neglect of spin–orbit coupling, multiplet structure, and many electron effects, they have provided a reasonable basis for the interpretation of the spectra.

(32) Sugano, S.; Tanabe, Y.; Kamimura, H. *Multiplets of Transition Metal Ions in Crystals*; Academic: New York, 1970.

(33) Tsipis, C. A.; Sigalas, M. P.; Hadjikostas, C. C. *Z. Anorg. Allg. Chem.* **1983**, *505*, 53.

Contribution from the Chemical Laboratories of Harvard University, Cambridge, Massachusetts 02138, and Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

Octahedral d³ and d⁴ Complexes of Molybdenum with 1,2-Bis(dimethylphosphino)ethane

Lawrence K. Fong,[†] James R. Fox,[†] Bruce M. Foxman,[‡] and N. John Cooper*[†§]

Reaction of amorphous molybdenum dichloride with 1,2-bis(dimethylphosphino)ethane (dmpe) affords a convenient route to *trans*-[Mo(dmpe)$_2$Cl$_2$], while reaction of [Mo(CO)$_4$Cl$_2$] with dmpe leads to the formation of the seven-coordinate cation [Mo(dmpe)$_2$(CO)$_2$Cl]$^+$, isolated as the PF$_6^-$ salt and shown by a single-crystal X-ray diffraction study to have a capped-trigonal-prismatic geometry (orthorhombic space group *Pnma*, with $a = 13.483$ (3) Å, $b = 11.065$ (2) Å, $c = 17.796$ (3) Å, $\rho_{calcd} = 1.54$ g cm^{-3}, $\rho_{obsd} = 1.54$ g cm^{-3}, $Z = 4$, and $R_w = 3.83\%$). Cyclic voltammetry has established that the neutral dichloride is reversibly oxidized to *trans*-[Mo(dmpe)$_2$Cl$_2$]$^+$ with $(E_a + E_c)/2 = -0.510$ V vs. SCE. The cation can be obtained as the PF$_6^-$ salt if AgPF$_6$ is the oxidant, or as the SnCl$_3^-$ salt if SnCl$_2$ is the oxidant. The d^4 and d^3 dichlorides have both been characterized by single-crystal X-ray diffraction studies: [Mo(dmpe)$_2$Cl$_2$] crystallizes in the monoclinic space group *P*2$_1$/*c* with $a = 13.218$ (3) Å, $b = 12.640$ (2) Å, $c = 13.327$ (3) Å, $\beta = 93.18$ (2)°, $\rho_{calcd} = 1.40$ g cm^{-3}, $\rho_{obsd} = 1.42$ g cm^{-3}, $Z = 4$, and $R_w = 3.22\%$, while [Mo(dmpe)$_2$Cl$_2$]SnCl$_3$ crystallizes in the monoclinic space group *P*2$_1$/*n* with $a = 14.756$ (4) Å, $b = 10.808$ (2) Å, $c = 18.572$ (5) Å, $\beta = 109.80$ (2)°, $\rho_{calcd} = 1.65$ g cm^{-3}, $\rho_{obsd} = 1.65$ g cm^{-3}, $Z = 4$, and $R_w = 4.01\%$. Both have octahedral geometries with trans dichlorides. [Mo(dmpe)$_2$Cl$_2$] can be reduced by 40% sodium amalgam in the presence of N$_2$ or CO to give [Mo(dmpe)$_2$(N$_2$)$_2$] and [Mo(dmpe)$_2$(CO)$_2$], respectively, both of which are formed as a mixture of the cis and trans isomers.

Introduction

We have recently been examining the chemistry of some of the electron-rich complexes formed by the strongly σ-donating bis-chelate phosphane (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$ (dmpe), and a brief report[1] on the existence and paramagnetism of the 16-electron complex [Mo(dmpe)$_2$Cl$_2$], together with our recent observation of unusual hydrogen abstraction reactions from some paramagnetic transition-metal alkyls,[2–4] have led us to attempt to prepare the 16-electron alkyl complex [Mo(dmpe)$_2$(CH$_3$)$_2$]. A recent publication on the preparation of the isologous complex [Cr(dmpe)$_2$(CH$_3$)$_2$][5] has prompted us to report some of our results in this area, including the development of a synthetically convenient route to *trans*-[Mo(dmpe)$_2$Cl$_2$] from "monomeric" MoCl$_2$,[6] one-electron oxidation of this complex to the 15-electron cationic

complex [Mo(dmpe)$_2$Cl$_2$]$^+$, and reduction of [Mo(dmpe)$_2$Cl$_2$] under N$_2$ to give the dinitrogen complexes *cis*- and *trans*-[Mo(dmpe)$_2$(N$_2$)$_2$]. The closely related d^4 and d^3 dihalides [Mo(dmpe)$_2$Cl$_2$] and [Mo(dmpe)$_2$Cl$_2$]$^+$ have been structurally characterized, as has the seven-coordinate cation [Mo(dmpe)$_2$(CO)$_2$Cl]$^+$.

Experimental Section

General Data. All manipulations were carried out under a dry, oxygen-free atmosphere of nitrogen. Most solvents were freshly distilled

[†] Harvard University.
[‡] Brandeis University.
[§] Fellow of the Alfred P. Sloan Foundation, 1982–1985.

(1) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639.

(2) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

(3) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570.

(4) Hayes, J. C.; Cooper, N. J. In *Organometallic Compounds*; Shapiro, B. L., Ed.; Texas A&M: College Station, TX, 1983; p 353.

(5) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954.

(6) Holste, G.; Schafer, H. *J. Less-Common Met.* **1970**, *20*, 164.

under nitrogen by using suitable drying agents as follows: sodium benzophenone ketyl for diethyl ether and tetrahydrofuran (THF); LiAlH₄ for pentane; CaH₂ for toluene and CH₂Cl₂. Acetonitrile was purified by a literature procedure.[7] A 40% sodium amalgam was prepared by the literature method.[8] Molybdenum hexacarbonyl was used as purchased from Pressure Chemical Co. Tetracarbonylmolybdenum dichloride was prepared by a modification of the literature method[9] in which [Mo(CO)₆] was stirred for 12 h in Cl₂ at −78 °C. Susceptibilities of paramagnetic substances were measured in solution by the NMR method[10] and converted to effective magnetic moments after a diamagnetic correction was applied.[11] Bis(dimethylphosphino)ethane (dmpe) was prepared according to the literature procedure.[12] Silver hexafluorophosphate was used as received from Alfa. Stannous chloride (Alfa) was dried by stirring with anhydrous acetic anhydride, washed with diethyl ether, and dried in vacuo at 120 °C for 24 h.

Preparation of Amorphous MoCl₂. Amorphous MoCl₂ was prepared by a modification of the literature method[6] in which [Mo(CO)₄Cl₂] (prepared from 10 g ▣ 38 mmol of [Mo(CO)₆]) was heated at 150 °C at a pressure of 10⁻³ torr until CO evolution ceased (ca. 75 min). Traces of [Mo(CO)₆] were sublimed off the resulting black powder at 35 °C by using a −196 °C cold finger at 10⁻³ torr to yield 5.75 g (34 mmol ≡ 89%) of MoCl₂, which was used without further purification.

Preparation of [Mo(dmpe)₂Cl₂]. A sample of amorphous MoCl₂ prepared from 5 g (19 mmol) of [Mo(CO)₆] was suspended in 30 mL of THF to yield a deep red solution. Addition of a solution of dmpe (5.63 g, 37.5 mmol) in 10 mL of THF to this stirred suspension produced a gray precipitate. The stirred mixture was heated to 80 °C for 24 h to give a tan-orange solution and a tan powder. The solution was filtered and the filtrate concentrated under vacuum to give a muddy orange solid. Extraction with toluene (3 × 30 mL) gave an orange solution, which precipitated orange cubes when cooled slowly (24 h) to −78 °C. The crystals were collected by filtration and dried under vacuum to give 2.58 g (5.51 mmol ≡ 29%) of [Mo(dmpe)₂Cl₂]: ¹H NMR (C₆D₆, 80 MHz) δ 5.98 (br, 8 H, CH₂), −17.94 (br, 24 H, CH₃); μ_eff (toluene, 2% Me₄Si) 2.65 μ_B; mass spectrum, *m/z* (parent ion) 468. Anal. Calcd for C₁₂H₃₂Cl₂MoP₄: C, 30.86; H, 6.90. Found (Dornis und Kolbe, Mülheim a.d. Ruhr, W. Germany): C, 30.89; H, 6.94.

Reaction of [Mo(CO)₄Cl₂] with dmpe. A sample of freshly prepared [Mo(CO)₄Cl₂] (3.75 mmol, prepared from 0.99 g of [Mo(CO)₆]), was dissolved in 15 mL of THF and cooled to 0 °C to yield a deep red solution (IR (THF) ν_CO 2100 (w), 2010 (s), 1980 (m), 1925 (s) cm⁻¹). Addition of dmpe (1.42 g, 9.40 mmol) in 5 mL of THF at 0 °C resulted in immediate gas evolution and formation of a yellow brown solution (IR (THF) ν_CO 1840 (s), 1935 (s), 1985 (m) cm⁻¹). The reaction was allowed to warm to room temperature and then heated for 3 h at 80 °C to give a light yellow powder and a green solution. The solid was collected by filtration and washed with THF. IR spectra of a Nujol mull showed the presence of CO stretching modes at 1835 (w), 1875 (s), 1885 (s), 1935 (s), and 1945 (s) cm⁻¹. Comparison with literature data[13] shows that these absorptions are consistent with the crude solid being [Mo(dmpe)₂(CO)₂Cl]Cl. The solid was dissolved in degassed H₂O (30 mL) and NH₄PF₆ added until precipitation of the resulting yellow solid was complete. The solid was collected by filtration, washed with three 30-mL aliquots of H₂O, dried under vacuum, and recrystallized from the minimum amount of acetone by slow (2 weeks) diffusive mixing with a layer of twice this volume of diethyl ether. The light orange rectangular rods formed were collected by filtration and dried under vacuum for 4 h to yield 1.55 g (2.44 mmol ≡ 65%) of [Mo(dmpe)₂(CO)₂Cl]PF₆: IR (Nujol mull, ν_CO only) 1880 (s), 1945 (s) cm⁻¹; ¹H NMR (CD₂Cl₂, 80 MHz) δ 2.01 (br m, 8 H, CH₂), 1.67 (m, 24 H, CH₃); conductivity (CH₃CN) 185 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₁₄H₃₂ClF₆MoO₂P₅: C, 26.58; H, 5.10. Found (Schwarzkopf, Woodside, NY): C, 26.58; H, 5.20.

Reduction of [Mo(dmpe)₂(CO)₂Cl]PF₆. A slurry of [Mo(dmpe)₂(CO)₂Cl]PF₆ (0.735 g, 1.16 mmol) in THF (35 mL) was added to ca. 12 g of 40% sodium amalgam covered by 20 mL THF. The mixture was vigorously stirred magnetically for 24 h and allowed to settle for 12 h. The solution was decanted off and the solvent removed under vacuum. The resulting solid was stirred with pentane (50 mL) for 12 h and the yellow-green solution filtered. The solution was concentrated under

vacuum until saturated and cooled over 24 h to −78 °C to precipitate 0.213 g (0.47 mmol ≡ 41%) of *cis*-[Mo(dmpe)₂(CO)₂] (solution IR).

Preparation of [Mo(dmpe)₂Cl₂]PF₆. A solution of AgPF₆ (0.420 g, 1.66 mmol) in toluene (50 mL) was added dropwise to a stirred solution of [Mo(dmpe)₂Cl₂] (0.655 g, 1.40 mmol) in toluene (50 mL) to give an immediate black precipitate. After 1 h the solution was filtered off and the solid dried under vacuum. Extraction with CH₂Cl₂ (60 mL) gave a red-orange solution, which was concentrated to ca. 20 mL and then slowly (24 h) cooled to −78 °C to precipitate opaque red octahedra, which were collected by filtration and shown to be 0.44 g (0.72 mmol ≡ 52%) of [Mo(dmpe)₂Cl₂]PF₆: conductivity (CH₃CN) 172 Ω⁻¹ cm² mol⁻¹; μ_eff (CH₃CN) 3.61 μ_B. Anal. Calcd for C₁₂H₃₂Cl₂F₆MoP₅: C, 23.55, H, 5.27. Found (Galbraith, Knoxville, TN): C, 23.35; H, 5.29.

Preparation of [Mo(dmpe)₂Cl₂][SnCl₃]. A 0.29 M solution of SnCl₂ in THF (10 mL, 2.5 equiv) was syringed into a solution of [Mo(dmpe)₂Cl₂] (0.214 g, 0.46 mmol) in THF (20 mL). The stirred mixture slowly turned red and deposited a white flocculent solid. After 12 h the solvent was removed under vacuum. The product was extracted into three 15-mL aliquots of CH₂Cl₂ and the solvent removed under vacuum to give a red amorphous solid. The compound was recrystallized from the minimum volume of acetone by slow diffusive mixing with a layer of twice this volume of diethyl ether to yield 0.240 g (0.35 mmol ≡ 75%) of [Mo(dmpe)₂Cl₂]SnCl₃ as red needles: conductivity (CH₃CN) 161 Ω⁻¹ cm² mol⁻¹; μ_eff (CH₃CN) 2.90 μ_B. Anal. Calcd for C₁₂H₃₂Cl₅MoP₄Sn: C, 20.82; H, 4.66. Found (Dornis und Kolbe, Mülheim a.d. Ruhr, W. Germany): C, 20.55; H, 4.70.

Preparation of [MoO(dmpe)₂Cl]Cl. A sample of [Mo(dmpe)₂Cl₂]SnCl₃ prepared from 0.28 g (0.59 mmol) of [Mo(dmpe)₂Cl₂] was stirred with 50 mL of H₂O for 24 h to give a purple solution over some tan solid. The solution was filtered and the solvent removed under vacuum. The product was extracted into acetone (2 × 10 mL) to give a purple solution, which was cooled slowly (24 h) to −78 °C to precipitate translucent purple plates of [MoO(dmpe)₂Cl]Cl (0.14 g, 0.29 mmol ≡ 50%), which were collected by filtration. IR (Nujol mull, ν_Mo=O only): 955 (s), 932 (s) cm⁻¹; ¹H NMR (CDCl₃, 80 MHz) δ 2.17 (m, 8 H, CH₂), 1.74 (d, *J*_P−H = 10 Hz, 24 H, PCH₃); conductivity (CH₃CN) 186 Ω⁻¹ cm² mol⁻¹. Anal. Calcd for C₁₂H₃₂Cl₂MoOP₄: C, 29.83; H, 6.68. Found: (Galbraith, Knoxville, TN): C, 30.03; H, 6.39.

Reduction of [Mo(dmpe)₂Cl₂] under CO. A solution of [Mo(dmpe)₂Cl₂] (0.21 g, 0.45 mmol) in THF (20 mL) was added to ca. 12 g of 40% sodium amalgam covered with 20 mL of THF. The mixture was placed under 1.5 atm of CO and vigorously stirred magnetically for 20 h. The finely dispersed amalgam was allowed to settle for 24 h and the solution decanted off. The solvent was removed under vacuum and the reduced product extracted with pentane (3 × 30 mL). Absorption-mode IR spectra (see below for extinction coefficients) indicated that this solution contained a 1.6:1 mixture of *cis:trans*-[Mo(dmpe)₂(CO)₂]. The filtered solution was concentrated until almost saturated and recrystallized from pentane at −78 °C to give 0.056 g (0.11 mmol ≡ 25%) of pale yellow *cis*-[Mo(dmpe)₂(CO)₂]: IR (pentane, ν_CO only) 1871 (s, ε = 0.45), 1813 (s, ε = 0.39) cm⁻¹. The mother liquor was further concentrated under vacuum at room temperature and recooled to −78 °C over 24 h to give a yellow solid, which was collected by filtration and shown by solution IR to be principally *trans*-[Mo(dmpe)₂(CO)₂] (0.043 g, 0.087 mmol ≡ 19%): IR (pentane, ν_CO only) 1813 (s, ε = 0.87) cm⁻¹ (ε measured on a pure sample from the reaction of [Mo(dmpe)₂(N₂)₂] with CO).

Preparation of [Mo(dmpe)₂(N₂)₂]. A solution of [Mo(dmpe)₂Cl₂] (1.42 g, 3.04 mmol) in THF (70 mL) was vigorously stirred magnetically with ca. 12 g of 40% amalgam under 1.5 atm of N₂ for 24 h to yield an orange-brown solution. The solution was decanted off the excess amalgam and evaporated to dryness under a stream of N₂. The resulting solid was extracted with pentane and slowly concentrated at 0 °C under a stream of N₂ to yield 0.58 g (1.28 mmol ≡ 42%) of [Mo(dmpe)₂(N₂)₂]: ³¹P{¹H} NMR (THF, 121.5 MHz) δ 47.5 (s, trans isomer), 44.3 (t, *J*_P−P = 9.7 Hz, cis isomer), 41.8 (t, *J*_P−P = 9.7 Hz, cis isomer); IR (cyclohexane, ν_NN only): 2037 (m) and 1982 (s) (cis isomer), 1960 (s) (trans isomer) cm⁻¹. Anal. Calcd for C₁₂H₃₂MoN₄P₄: C, 31.87; H, 7.13. Found (Galbraith, Knoxville, TN): C, 31.33; H, 6.83.

Reaction of [Mo(dmpe)₂(N₂)₂] with CO. A solution of [Mo(dmpe)₂(N₂)₂] (0.036 g, 0.08 mmol) in 30 mL of pentane was placed under 1.5 atm of CO. The mixture was stirred for 24 h to give a bright yellow solution, which was shown by IR to contain *trans*-[Mo(dmpe)₂(CO)₂] but none of the cis isomer. The solution was concentrated under vacuum until saturated and cooled slowly (24 h) to −78 °C to precipitate 0.013 g (0.026 mmol ≡ 33%) of *trans*-[Mo(dmpe)₂(CO)₂]. This was collected by filtration, dried under vacuum, and identified by solution IR spectroscopy.

X-ray Crystallography. General Data. Crystals were grown as described above and were handled under nitrogen and sealed in glass cap-

(7) Walter, M.; Ramaley, L. *Anal. Chem.* **1973**, *45*, 165.
(8) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; p 1033.
(9) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1966**, *19*, 1143.
(10) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Bartle, K. D.; Jones, D. W.; Maricic, S. *Croat. Chem. Acta* **1968**, *40*, 227.
(11) Mulay, L. N. *Magnetic Susceptibility*; Wiley: New York, 1963; p 1782.
(12) Burt, R. J.; Chatt, J.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *182*, 203.
(13) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1979**, *174*, 173.

Table I. Summary of Crystallographic Data

	[Mo(dmpe)$_2$(CO)$_2$Cl][PF$_6$]	[Mo(dmpe)$_2$Cl$_2$]	[Mo(dmpe)$_2$Cl$_2$][SnCl$_3$]
space group	*Pnma*	*P2$_1$/c*	*P2$_1$/n*
a, Å	13.483 (3)	13.218 (3)	14.756 (4)
b, Å	11.065 (2)	12.640 (2)	10.808 (2)
c, Å	17.796 (3)	13.327 (3)	18.572 (5)
β, deg		93.18 (2)	109.80 (2)
V, Å^3	2655.0 (9)	2223.4 (8)	2787 (1)
Z	4	4	4
ρ_{calcd}	1.54	1.40	1.65
ρ_{obsd}	1.54	1.42	1.65
μ(Mo Kα), cm^{-1}	9.31	10.93	20.49
		Data Collection	
radiation	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.71069	0.71069	0.71069
collcn mode	θ:2θ	θ:2θ	θ:2θ
2θ range, deg	4–52	3–52.5	3–47
scan range, deg	1.8	2.1	1.6
scan speed, deg/min	2.93–19.53	2.55–14.65	2.93–14.65
bkgd/scan	0.50	1.00	1.00
exposure, h	79.58	128.18	78.50
no. of reflcns	3842	5176	4723
decrease in check intens, %	2	1	2
		Agreement Factors	
R^a	0.0328	0.0299	0.0369
$R_w{}^b$	0.0383	0.0322	0.0401
g	0.0012	0.0003	0.0005
max peak in final difference map, e Å^{-3} ^{c}	0.57 (0.33)	0.49	1.01 (0.34)

$^a R = \sum(|F_o - F_c|)/\sum(F_o)$. $^b R_w = \sum(w^{1/2}|F_o - F_c|)/\sum(w^{1/2}F_o)$, $w = (\sigma^2(F) + gF^2)^{-1}$. ^{c} Large peaks are associated with the anions. The largest peak of the cation is presented in parentheses.

illaries for diffraction studies. The data were collected on a Nicolet R3 diffractometer using graphite-monochromated Mo Kα radiation. Lorentz and polarization corrections were applied by using the SHELXTL programs.[14] The final unit cell parameters for each structure were determined by a least-squares treatment of the setting angles of 12 sets of precisely centered Friedel pairs. A semiempirical absorption correction was applied to each data set with SHELXTL procedures. Atomic scattering factors were based on literature values for Mo[15] and on those in the SHELXTL and SHELX[16] programs for other atoms. Weights were taken as $w = (\sigma^2(F) + gF^2)^{-1}$. In all three structure determinations the hydrogen atom parameters (tabulated in the supplementary material) were calculated from those of the adjacent carbon atoms with r(C–H) = 0.96 Å and $U_{iso} = 1.2U_{equiv}$.

Structure Solution and Refinement. [Mo(dmpe)$_2$Cl$_2$]. The crystal studied measured 0.2 × 0.4 × 0.4 mm. The unit cell was found to have two angles near 90°; the monoclinic cell was confirmed by the presence of mirror symmetry uniquely along the *b* axis. A trial data collection suggested that the space group was *P2$_1$/c*, and a single quadrant of data was therefore collected [(*hkl*): +*h*,+*k*,±*l*]. The intensities of three reflections were monitored during the data collection; no significant decrease in *I* was observed for these reflections. Further details of the data collection are summarized in Table I, which also includes the cell parameters. Some intense reflections had to be recollected at a lower tube current and scaled to the rest of the data during the data reduction by the least-squares method of the SHELXTL program.[14] The structure was solved by noting the *F*-centered pattern of intensities; two independent Mo atoms were placed at (0, 0, 0) and ($^1/_2$, 0, $^1/_2$). Difference electron density maps revealed the non-hydrogen atoms. The structure was refined by using the blocked-cascade least-squares procedure of SHELXTL. The refinement was continued to convergence (($\Delta/\sigma)_{max}$ < 0.1). Final atomic positional parameters are presented in Table II, and anisotropic thermal parameters are given in Table SI of the supplementary material.

[Mo(dmpe)$_2$(CO)$_2$Cl]PF$_6$. The light orange crystal studied measured 0.3 × 0.35 × 0.55 mm. The unit cell was found to be orthorhombic. A trial data collection indicated the presence of an *n* glide on the *a* axis, a 2$_1$ screw axis along the *b* axis, and an *a* glide on the *c* axis. One octant of data [(*hkl*): +*h*,+*k*,+*l*] was collected for the centrosymmetric space

(14) Sheldrick, G. M. *SHELXTL User's Manual, Issue 4.0*; Nicolet: Madison, WI, 1981.
(15) *International Tables for X-Ray Crystallography*; Ibers, J., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98.
(16) Sheldrick, G. M. *SHELX-76 Instructions*; Cambridge University: Cambridge, England, 1976.

Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters for [Mo(dmpe)$_2$Cl$_2$]

atom	*x*	*y*	*z*	*U*^{a}
Mo(1)	0	0	0	36 (1)
P(1)	68 (1)	1137 (1)	−1496 (1)	54 (1)
P(2)	1762 (1)	−636 (1)	114 (1)	56 (1)
Cl(1)	572 (1)	1500 (1)	1029 (1)	68 (1)
Mo(2)	5000	0	5000	35 (1)
Cl(2)	5613 (1)	1412 (1)	6128 (1)	60 (1)
P(3)	5004 (1)	−1238 (1)	6428 (1)	51 (1)
P(4)	6743 (1)	−276 (1)	4491 (1)	55 (1)
C(11)	−1130 (3)	1872 (3)	−1675 (3)	95 (2)
C(12)	168 (3)	526 (3)	−2720 (2)	79 (2)
C(13)	1013 (4)	2178 (3)	−1538 (3)	118 (2)
C(21)	2012 (3)	−1172 (3)	1389 (2)	85 (1)
C(22)	2082 (3)	−1734 (3)	−696 (3)	80 (2)
C(23)	2849 (3)	226 (4)	−3 (4)	99 (2)
C(31)	3780 (4)	−1169 (4)	6983 (4)	139 (2)
C(32)	5843 (4)	−1024 (4)	7526 (3)	126 (2)
C(33)	5138 (4)	−2637 (3)	6219 (3)	95 (2)
C(41)	6969 (3)	632 (4)	3467 (4)	164 (3)
C(42)	7105 (3)	−1540 (3)	3993 (3)	100 (2)
C(43)	7813 (3)	7 (4)	5356 (4)	108 (2)

^{a} Isotropic *U* is defined as one-third of the trace of the orthogonalized **U**$_{ij}$ tensor (Å^2 × 10^3).

group *Pnma*. No significant decrease was observed in the intensities of three check reflections monitored during data collection. Further details of the data collection are summarized in Table I together with the unit cell parameters. The structure was solved by comparing the Patterson map to the results of the SHELXTL[14] direct-methods procedure EEES to locate the Mo atom. Electron density and difference maps revealed the remaining non-hydrogen atoms. Structure refinement was carried out by using the SHELXTL program. Final atomic positional parameters are presented in Table III, and anisotropic thermal parameters are given in Table SIII of the supplementary material.

[Mo(dmpe)$_2$Cl$_2$][SnCl$_3$]. The red-orange crystal studied measured 0.2 × 0.25 × 0.5 mm. The unit cell was found to be monoclinic; the 2/*m* Laue symmetry was confirmed by the mirror symmetry uniquely observed along the *b* axis in the axial photographs. A preliminary data collection demonstrated the space group to be *P2$_1$/n* and an appropriate quadrant of data [(*hkl*): +*h*, +*k*, ±*l*] was then collected. The intensities of three reflections monitored during the data collection underwent no significant decrease. Further details of the data collection are summa-

Table III. Fractional Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters for [Mo(dmpe)₂(CO)₂Cl][PF₆]

atom	x	y	z	U^a
Mo	7014 (1)	2500	3930 (1)	37 (1)
Cl	5370 (1)	2500	4623 (1)	47 (1)
P(1)	6200 (1)	667 (1)	3346 (1)	51 (1)
P(2)	7457 (1)	756 (1)	4824 (1)	52 (1)
C(11)	5989 (3)	−484 (3)	4057 (2)	72 (1)
C(12)	4971 (3)	889 (4)	2954 (2)	81 (1)
C(13)	6858 (3)	−145 (4)	2612 (2)	89 (2)
C(21)	6941 (3)	−679 (3)	4495 (3)	79 (1)
C(22)	6974 (3)	899 (5)	5775 (2)	83 (1)
C(23)	8739 (3)	359 (4)	4987 (3)	82 (1)
C(1)	7410 (4)	2500	2880 (3)	66 (2)
O(1)	7661 (4)	2500	2260 (2)	98 (2)
C(2)	8463 (3)	2500	3872 (3)	61 (2)
O(2)	9312 (2)	2500	3831 (3)	93 (2)
P(A)	462 (1)	2500	6674 (1)	68 (1)
F(1)	729 (4)	2500	5805 (2)	121 (2)
F(2)	173 (4)	2500	7525 (2)	128 (2)
F(3)	470 (3)	1089 (2)	6661 (2)	141 (2)
F(4)	−663 (4)	2500	6472 (3)	156 (3)
F(5)	1601 (4)	2500	6837 (4)	163 (3)

^{a} The equivalent isotropic U (Å² × 10³) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Fractional Atomic Coordinates (×10⁴) and Thermal Parameters for [Mo(dmpe)₂Cl₂][SnCl₃]

atom	x	y	z	U^a
Sn	4445 (1)	481 (1)	1886 (1)	82 (1)
Cl(10)	5948 (1)	1619 (2)	2272 (1)	105 (1)
Cl(11)	5278 (2)	−1515 (2)	2280 (1)	107 (1)
Cl(12)	4105 (2)	698 (2)	3094 (1)	116 (1)
Mo(1)	0	0	0	47 (1)
Cl(1)	−1516 (1)	365 (2)	178 (1)	79 (1)
P(11)	525 (1)	2203 (1)	394 (1)	65 (1)
P(12)	792 (2)	−253 (2)	1427 (1)	82 (1)
Cₐ(1)	−386 (6)	3323 (6)	333 (5)	105 (4)
Cₐ(2)	1294 (7)	2991 (8)	−31 (7)	134 (6)
Cₐ(3)	1242 (8)	2152 (9)	1398 (5)	164 (6)
C♭(1)	1883 (5)	−1155 (7)	1759 (4)	103 (4)
C♭(2)	26 (9)	−896 (12)	1928 (6)	190 (8)
C♭(3)	1125 (11)	1262 (8)	1825 (5)	215 (9)
Mo(2)	5000	5000	0	53 (1)
Cl(2)	4307 (1)	3880 (2)	806 (1)	73 (1)
P(21)	6466 (1)	5681 (1)	1114 (1)	54 (1)
P(22)	3868 (1)	6806 (1)	−56 (1)	56 (1)
C(11)	6870 (5)	7267 (6)	1123 (4)	76 (3)
C(12)	6442 (5)	5411 (7)	2069 (3)	78 (3)
C(13)	7465 (4)	4728 (5)	1067 (3)	61 (2)
C(21)	4271 (5)	8376 (5)	−101 (4)	79 (3)
C(22)	3334 (5)	6851 (7)	692 (4)	82 (3)
C(23)	2847 (4)	6627 (5)	−946 (3)	62 (2)

^{a} The equivalent isotropic U (Å² × 10³) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

rized in Table I, which also includes the cell parameters. The positions of the Sn and of the two crystallographically independent Mo atoms, which are both on centers of inversion, were revealed by comparison of the Patterson map with the results of the EEES direct-methods procedure of SHELX.[16] Iterative refinement of the atomic parameters and difference maps revealed the positions of all chlorine, phosphorous, and carbon atoms. Least-squares refinement was carried out by using the SHELX program. Refinement was continued to convergence (($\Delta/\sigma)_{max} < 0.1$). Despite the large thermal parameters on some of the tin-bound chlorine and dmpe-backbone carbon atoms, no alternative orientation could be found for either of these fragments; attempts to model these high-amplitude vibrations as disorder were unsuccessful. Final atomic positional parameters are given in Table IV, and anisotropic thermal parameters are presented in Table SV of the supplementary material.

Results and Discussion

Preparation and Structural Characterization of [Mo(dmpe)₂Cl₂]. We initially wished to approach the synthesis of paramagnetic alkyl complexes of the type [Mo(dmpe)₂R₂] by examining the alkylation of [Mo(dmpe)₂Cl₂]. Although this chloride has been
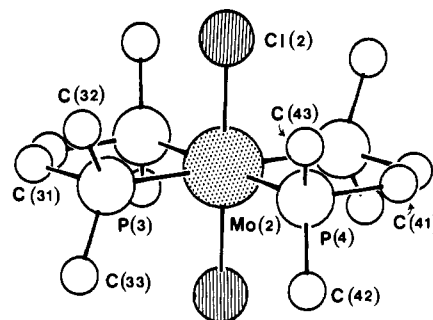
Figure 1. SNOOPI drawing of the independent molecule of [Mo(dmpe)₂Cl₂] containing Mo(2). Atoms are drawn at 50% of their covalent radii, and hydrogen atoms have been omitted for clarity.

Table V. Selected Bond Lengths (Å) and Angles (deg) within [Mo(dmpe)₂Cl₂]^a

Mo(1)–Cl(1)	2.435 (1)	Mo(1)–P(1)	2.464 (1)
Mo(1)–P(2)	2.460 (1)	P(1)–C(11)	1.839 (4)
P(1)–C(12)	1.816 (3)	P(1)–C(13)	1.817 (5)
P(2)–C(21)	1.841 (3)	P(2)–C(22)	1.823 (4)
P(2)–C(23)	1.817 (4)	C(11)–C(21')	1.528 (6)
Mo(2)–Cl(2)	2.443 (1)	Mo(2)–P(3)	2.464 (1)
Mo(2)–P(4)	2.463 (1)	P(3)–C(31)	1.818 (5)
P(3)–C(32)	1.807 (4)	P(3)–C(33)	1.800 (3)
P(4)–C(41)	1.820 (6)	P(4)–C(42)	1.805 (4)
P(4)–C(43)	1.809 (5)	C(31)–C(41')	1.317 (7)
P(1)–Mo(1)–Cl(1)	88.7 (1)	Cl(2)–Mo(2)–P(3)	90.1 (1)
P(2)–Mo(1)–Cl(1)	87.5 (1)	Cl(2)–Mo(2)–P(4)	89.4 (1)
P(1)–Mo(1)–P(2)	99.4 (1)	P(3)–Mo(2)–P(4)	99.2 (1)

^{a} Primed atoms are symmetry generated by a center of inversion.

reported previously,[1] the compound is only available in very poor yield from reduction of MoCl₃(THF)ₓ in the presence of dmpe and a convenient synthesis of the dichloride was required if the compound was to be an accessible starting material.

Halides of molybdenum in oxidation states <III typically contain clusters of metal atoms with extensive metal–metal bonding or dimeric units with quadruple metal–metal bonds[17] and can therefore rarely be used for the preparation of mononuclear molybdenum complexes. It has been reported,[6] however, that a material of composition "MoCl₂" can be obtained from the mononuclear complex [Mo(CO)₄Cl₂] by removing the CO under vacuum and that X-ray powder diffraction shows that this amorphous MoCl₂ does not contain the [Mo₆Cl₈]⁴⁺ clusters characteristic of MoCl₂ prepared by the usual routes. It was further suggested[6] that amorphous MoCl₂ might contain monomeric MoCl₂, and we have now observed that this material can indeed be used as a source of monomeric MoCl₂ in the direct preparation of [Mo(dmpe)₂Cl₂]. The reaction is carried out by adding 2 equiv of dmpe to a freshly prepared suspension of MoCl₂ in THF, and the product was isolated in 30% yield after the mixture was stirred at 80 °C for 24 h. The reaction does not proceed in high yield, presumably as a consequence of oligomerization of the MoCl₂, but does provide a reliable and convenient route to [Mo(dmpe)₂Cl₂] on a 5-g scale.

Since the only data previously reported for the complex are elemental analyses, we have characterized [Mo(dmpe)₂Cl₂] both structurally and spectroscpically. A single-crystal X-ray diffraction study established the presence of two similar independent molecules of the 16-electron *trans*-dichloride; the molecular structure of one of these is shown in Figure 1. Important bond lengths and angles are listed in Table V, and details of the structure determination are given in the Experimental Section and in the supplementary material. The only closely related Mo(II) molecules that have been structurally characterized are the PMe₃ and dppe (=Ph₂PCH₂CH₂PPh₂) analogues *trans*-[Mo(PMe₃)₄Cl₂][18]

(17) Cotton, F. A.; Wilkinson, G. W. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; Chapter 22-C.
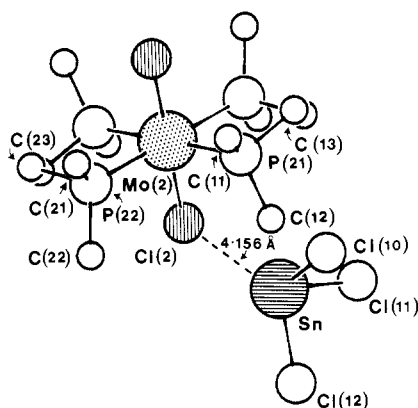
Figure 2. SNOOPI drawing of the independent cation in [Mo-(dmpe)$_2$Cl$_2$]SnCl$_3$ containing Mo(2) and of the nearest neighbor [Sn-Cl$_3$]$^-$. Atoms are drawn at 50% of their covalent radii, and hydrogen atoms have been omitted for clarity.

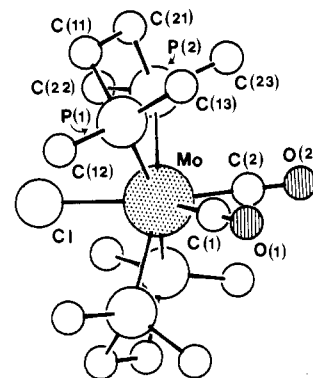**Figure 3.** SNOOPI drawing of the cation in [Mo(dmpe)$_2$(CO)$_2$Cl$_2$]PF$_6$. Atoms are drawn at 50% of their covalent radii, and hydrogen atoms have been omitted for clarity.

and *trans*-[Mo(dppe)$_2$Cl$_2$],[19] and as in those cases, the structure approximates octahedral coordination.

The magnetic susceptibility of the complex in solution has been measured by the NMR method,[10] and corresponds to an effective magnetic moment of 2.65 μ_B. This is within experimental error of the spin-only value which would be predicted for an approximately octahedral d^4 complex with two unpaired electrons, and is consistent with the solid-state molecular structure.

Despite the paramagnetism of the molecule, it is possible to observe the ^{1}H NMR resonances of the dmpe methylene and methyl groups. These are at positions (δ 5.98 and −17.94, respectively) quite close to the normal diamagnetic range, although they exhibit marked paramagnetic broadening ($w_{1/2}$ ca. 340 and 600 Hz, respectively, at 80 MHz). A number of other octahedral d^4 complexes have been reported to have slightly shifted, sharp absorptions in their ^{1}H NMR spectra,[20] and it has been established that this arises because the complexes exhibit temperature-independent paramagnetism.[21] A similar mechanism may well operate in the case of [Mo(dmpe)$_2$Cl$_2$], although this has not been confirmed by detailed magnetic studies and the effective magnetic moment of the complex is somewhat higher than in the previous examples.

In an attempt to circumvent the reduction in yield associated with oligomerization of "monomeric" MoCl$_2$, we tried to prepare [Mo(dmpe)$_2$Cl$_2$] directly from [Mo(CO)$_4$Cl$_2$] without initially removing the CO. Reaction with dmpe in THF at 0 °C resulted in immediate CO evolution, but the product was the 18-electron cation [Mo(dmpe)$_2$(CO)$_2$Cl]$^+$, presumably because the complementary σ-donor and π-acceptor characteristics of the phosphane and carbonyl ligands results in increasingly tight binding of the CO ligands as the phosphanes are added to the metal center. The cation was initially formed as the chloride salt, which has been previously prepared by reaction of [Mo(dmpe)$_2$(CO)$_2$] with CCl$_4$,[13] but was isolated as the hexafluorophosphate salt.

Although seven-coordinate Mo(II) complexes of the type [Mo(L-L′)$_2$(CO)$_2$X]$^+$ (L-L′ = bis-chelate diphosphane, X = halide) have been prepared in several laboratories and their dynamic behavior has been investigated in detail,[22] there is surprisingly little structural data available on systems of this type. Spectroscopic studies indicate that [M(dmpe)$_2$(CO)$_2$I]$^+$ (M = Mo, W),[23] [Mo(Me$_2$PCH$_2$CH$_2$PEt$_2$)$_2$(CO)$_2$I]$^+$,[22] and a series of isoelectronic Ta(I) complexes[22,24] have trigonal-prismatic geom-

Table VI. Selected Bond Lengths (Å) and Angles (deg) within [Mo(dmpe)$_2$(CO)$_2$Cl][PF$_6$]^a

Mo–Cl	2.537 (1)	C(11)–C(21)	1.517 (6)
Mo–P(1)	2.529 (1)	Mo–P(2)	2.572 (1)
Mo–C(1)	1.943 (5)	Mo–C(2)	1.956 (5)
C(1)–O(1)	1.153 (6)	C(2)–O(2)	1.147 (6)
P(1)–C(11)	1.817 (4)	P(2)–C(21)	1.830 (4)
P(1)–C(12)	1.815 (4)	P(2)–C(22)	1.820 (4)
P(1)–C(13)	1.817 (4)	P(2)–C(23)	1.807 (4)
Cl–Mo–C(1)	135.0 (2)	Cl–Mo–C(2)	153.9 (1)
Cl–Mo–P(1)	79.7 (1)	Cl–Mo–P(2)	84.4 (1)
C(1)–Mo–C(2)	71.1 (2)	P(1)–Mo–P(2)	75.7 (1)
C(1)–Mo–P(1)	74.0 (1)	C(1)–Mo–P(2)	122.1 (1)
C(2)–Mo–P(1)	114.3 (1)	C(2)–Mo–P(2)	78.5 (1)
Mo–C(1)–O(1)	178.9 (5)	Mo–C(2)–O(2)	179.3 (4)
P(1)–Mo–P(1′)	106.6 (1)	P(2)–Mo–P(1′)	163.1 (1)
P(2)–Mo–P(2′)	97.3 (1)		

^{a} Primed atoms are symmetry generated by the mirror plane at y = 0.25.

etries with the odd ligand capping a P$_4$ face, but the closest structural model for which details have been published is [Mo-(diars)$_2$(CO)$_2$Cl]I$_3$ (diars = o-phenylenebis(dimethylarsine)).[25]

A single-crystal X-ray diffraction study of [Mo(dmpe)$_2$-(CO)$_2$Cl]PF$_6$ has confirmed the anticipated capped-trigonal-prismatic geometry with the cis arrangement of carbonyl ligands indicated by the IR data. The molecular structure of the cation is shown in Figure 3, and selected bond lengths and angles are listed in Table VI. The cis orientation of the carbonyls is retained when [Mo(dmpe)$_2$(CO)$_2$Cl]PF$_6$ is reduced with 40% sodium amalgam to give exclusively cis-[Mo(dmpe)$_2$(CO)$_2$].

Attempts To Prepare [Mo(dmpe)$_2$R$_2$] Complexes. An objective of this research was to prepare paramagnetic dialkyls of the type [Mo(dmpe)$_2$R$_2$] analogous to the complex [Cr(dmpe)$_2$(CH$_3$)$_2$] reported while this work was in progress.[5] Initial approaches involved attempts to alkylate [Mo(dmpe)$_2$Cl$_2$], but no conditions were found that gave tractable alkyl derivatives. The reducing alkylating agent t-BuLi led to formation of small yields of [Mo(dmpe)$_2$(N$_2$)$_2$] in pentane/benzene (solution IR), while unreacted starting material was recovered from attempts to react [Mo(dmpe)$_2$Cl$_2$] with less reactive alkylating agents such as MeLi and Me$_2$Cd. MeMgBr did react with the dichloride in toluene-/THF mixtures and in dioxane, but we have been unable to isolate any tractable materials from these reactions.

Attempts to prepare [Mo(dmpe)$_2$(CH$_3$)$_2$] by a route analogous to that used to prepare [Cr(dmpe)$_2$(CH$_3$)$_2$]^5 were unsuccessful. Treatment of a suspension of amorphous MoCl$_2$ in THF with CH$_3$MgBr or CH$_3$Li did result in dissolution of most of the suspended solid, but no tractable products were obtained in either case following addition of dmpe.

(18) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1983**, *2*, 185.
(19) Nardelli, M.; Pelizzi, G.; Predieri, G. *Gazz. Chim. Ital.* **1980**, *110*, 375.
(20) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1969**, 1674.
(21) Gunz, H. P.; Leigh, G. J. *J. Chem. Soc. A* **1971**, 2229.
(22) Brown, L. D.; Datta, S.; Kouba, J. K.; Smith, L. K.; Wreford, S. S. *Inorg. Chem.* **1978**, *17*, 729.
(23) Connor, J. A.; McEwen, G. K.; Rix, C. J. *J. Chem. Soc., Dalton Trans.* **1974**, 589.
(24) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134.

(25) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2664.

Table VII. Selected Bond Lengths (Å) and Angles (deg) within [Mo(dmpe)₂Cl₂][SnCl₃][a]

Sn–Cl(10)	2.422 (2)	Sn–Cl(11)	2.468 (2)
Sn–Cl(12)	2.470 (3)		
Mo(1)–Cl(1)	2.401 (2)	Mo(1)–P(11)	2.534 (1)
Mo(1)–P(12)	2.523 (2)	P(11)–Cₐ(1)	1.783 (8)
P(11)–Cₐ(2)	1.801 (12)	P(11)–Cₐ(3)	1.806 (9)
P(12)–C_b(1)	1.803 (8)	P(12)–C_b(2)	1.827 (15)
P(12)–C_b(3)	1.796 (9)	Cₐ(3)–C_b(3)	1.296 (15)
Mo(2)–Cl(2)	2.407 (2)	Mo(2)–P(21)	2.544 (1)
Mo(2)–P(22)	2.548 (2)	P(21)–C(11)	1.814 (6)
P(21)–C(12)	1.809 (7)	P(21)–C(13)	1.824 (6)
P(22)–C(21)	1.809 (6)	P(22)–C(22)	1.816 (8)
P(22)–C(23)	1.831 (5)	C(13)–C(23′)	1.529 (8)
Cl(10)–Sn–Cl(11)	92.4 (1)	Cl(10)–Sn–Cl(12)	97.5 (1)
Cl(11)–Sn–Cl(12)	92.7 (1)		
Cl(1)–Mo(1)–P(11)	90.8 (1)	Cl(2)–Mo(2)–P(21)	93.6 (1)
Cl(1)–Mo(1)–P(12)	89.7 (1)	Cl(2)–Mo(2)–P(22)	90.0 (1)
P(11)–Mo(1)–P(12)	79.1 (1)	P(21)–Mo(2)–P(22)	100.2 (1)

[a] Primed atoms are symmetry generated by a center of inversion.

Oxidation of [Mo(dmpe)₂Cl₂] and Characterization of [Mo(dmpe)₂Cl₂]⁺. The failure to alkylate [Mo(dmpe)₂Cl₂] led us to attempt to increase the lability of the Cl ligand by reaction with stannous chloride. Insertion of SnCl₂ into transition-metal–chloride bonds is a well-established reaction,[26] and the resulting [SnCl₃]⁻ ligands are often more labile than Cl⁻ ligands. Surprisingly, however, SnCl₂ oxidized the neutral complex into a Mo(III) compound shown by single-crystal X-ray diffraction to consist of discrete [Mo(dmpe)₂Cl₂]⁺ cations and [SnCl₃⁻] anions. There are two sets of crystallographically independent cations and four equivalent anions per unit cell, and the molecular structure of one of the cations and of its nearest-neighbor anion is shown in Figure 2. Selected bond lengths and angles are listed in Table VII, and although the second set of cations in the unit cell exhibit some disorder in the dmpe ligands, it is clear that they possess the same overall structure. The major distinction between the two independent types of cation is in their relation to the [SnCl₃]⁻ anions. The cations of the type shown in Figure 2 are closer to the anions, with nearest approach nonbonding contacts of 4.156 Å (Sn–Cl_Mo). The less ordered cations have nearest approach nonbonding contacts of 4.795 Å (Sn–Cl_Mo).

It was initially unclear whether SnCl₂ was the true oxidant in the formation of [Mo(dmpe)₂Cl₂][SnCl₃], although in aqueous solutions the potential of the Sn²⁺/Sn couple is quite close to that of the Sn⁴⁺/Sn²⁺ couple (–0.38 and –0.11 V vs. SCE respectively). We have, however, confirmed that [Mo(dmpe)₂Cl₂] is readily oxidized by examining cyclic voltammograms of the complex in CH₃CN. These show oxidation and reduction waves centered on –0.510 V (vs. SCE), with a peak to peak separation of 62 mV at a scan rate of 100 mV s⁻¹, indicating that the [Mo(dmpe)₂Cl₂]⁺/[Mo(dmpe)₂Cl₂] couple is essentially reversible under these conditions and that oxidation with SnCl₂ is not thermodynamically unreasonable.

Oxidation of [Mo(dmpe)₂Cl₂] can be carried out by using more rational reagents than SnCl₂, and [Mo(dmpe)₂Cl₂]⁺ can be isolated as its PF₆⁻ salt by oxidizing the neutral dichloride with AgPF₆ (this has been used previously to oxidize the analogous 1,2-bis(diphenylphosphino)ethane (dppe) complex to [Mo(dppe)₂Cl₂]PF₆[27]). The susceptibility of [Mo(dmpe)₂Cl₂]PF₆ in CH₃CN solution has been shown by the NMR method to correspond to an effective magnetic moment of 3.61 μ_B, close to the spin-only value of 3.87 μ_B, anticipated for a d³ complex with approximately octahedral coordination. The conductivity of [Mo(dmpe)₂Cl₂]SnCl₃ and of [Mo(dmpe)₂Cl₂]PF₆ in CH₃CN indicates[28] that both salts are 1:1 electrolytes in this solvent, as would be anticipated.

The electrophilic molybdenum in [Mo(dmpe)₂Cl₂]⁺ is water-sensitive, and treatment of the tin salt with H₂O for 24 h gave a purple solution from which purple plates could be isolated following solvent removal and low-temperature recrystallization from acetone. The compound analyzed as "Mo(dmpe)₂OCl₂", but since the conductivity of the material in CH₃CN indicated that it was a 1:1 electrolyte,[28] it has been formulated as [MoO(dmpe)₂Cl]Cl. This probably contains a *trans*-[MoO(dmpe)₂Cl]⁺ cation analogous to the structurally characterized [MoO(dppe)Cl]⁺ cation (dppe = Ph₂PCH₂CH₂PPh₂).[29,30] The Mo≡O unit gives rise to two strong IR absorptions, similar to those reported for a variety of salts of [MoO(dppe)Cl]⁺.[29,30]

Structural Comparison of [Mo(dmpe)₂Cl₂] with [Mo(dmpe)₂Cl₂]⁺. The availability of structural data for both [Mo(dmpe)₂Cl₂] and [Mo(dmpe)₂Cl₂][SnCl₃] allows a direct comparison of structural parameters for Mo(II) and Mo(III) complexes with the same ligand environment. The overall geometry of both complexes approximate octahedral coordination of the metal, and the most significant differences between the structures lie in the Mo–Cl and Mo–P distances. It is particularly interesting that while the average Mo–Cl distance decreases from 2.439 Å (2.435 (1) and 2.443 (1) Å) to 2.404 Å (2.401 (2) and 2.407 (2) Å) on changing from Mo(II) to Mo(III), the average Mo–P distance actually increases from 2.462 Å (range 2.460 (1)–2.464 (1) Å) to 2.537 Å (range 2.523 (2)–to 2.548 (2) Å). This could be interpreted in terms of an increase in the hardness of the Lewis acidity of the metal center, which leads to tighter binding of the harder Lewis base. Alternatively, removing one electron from the t₂g orbitals of the complex may allow increased π-donation from the Cl lone pairs into those orbitals and thereby strengthen the Mo–Cl bonds, while simultaneously reducing π-back-donation from the metal to the phosphine ligands and hence weakening the Mo–P bonds.

Reduction of [Mo(dmpe)₂Cl₂] under N₂ and CO. The dichloride complex has obvious potential as a substrate for the preparation of Mo(0) complexes, and we have examined its reduction in the presence of potential ligands including dinitrogen. Initial experiments involved the reaction of the dichloride in THF under dinitrogen with 1% sodium amalgam, but although ¹H NMR spectra of aliquots of the THF solution (recorded in benzene-d₆ after removal of the THF under vacuum) indicated that diamagnetic materials had been formed, the presence of the characteristic resonances of the dichloride showed that reduction was incomplete even after 24 h.

A more powerful reductant is required to achieve complete reaction, and a convenient reagent is 40% sodium amalgam: this is a liquid, and hence a kinetically effective reducing agent, at 20–30 °C.[8] Reaction of [Mo(dmpe)₂Cl₂] with 40% sodium amalgam for 24 h under 1.5 atm of N₂ results in complete consumption of the dichloride (¹H NMR) and formation of a brown solution. A material with a composition corresponding to that of [Mo(dmpe)₂(N₂)₂] can be isolated from this solution as flaky orange plates, and the formulation of the material as a dinitrogen complex is supported by the observation of N≡N stretching absorptions in the IR spectrum of the molecule.

The crystallized N₂ complex is stable indefinitely in the solid state, but has limited stability in solution. It can be crystallized from pentane at 0 °C by blowing off the solvent with a stream of N₂, but attempts to recrystallize the compound from pentane at low temperatures (–60 °C) resulted in formation of an amorphous material that would not redissolve in pentane, suggesting that a dinitrogen ligand dissociated readily. Decomposition was a more significant problem in pentane than in benzene: ³¹P NMR showed only partial (ca. 20%) decomposition of the complex after 2 weeks in benzene.

The presence of three bands in the N≡N stretching region suggests that the molecule has been formed as a mixture of the

(26) Young, J. F. *Adv. Inorg. Chem. Radiochem.* **1968**, *11*, 91.
(27) Eaborn, C.; Farrell, N.; Murphy, J. L.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1976**, 58.
(28) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(29) Adams, V. C.; Gregory, U. A.; Kilbourn, B. T. *J. Chem. Soc., Chem. Commun.* **1970**, 1400.
(30) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1603.

cis isomer (2037 (m) and 1982 (s) cm^{-1}) and trans isomer (1960 (s) cm^{-1}). The frequencies of these bands are similar to those in the literature for related *cis*- and *trans*-bis(dinitrogen) complexes of molybdenum.[31] The assignment of the 1960-cm^{-1} band rather than the 1982-cm^{-1} band to the trans isomer is confirmed by the observation that the 1960-cm^{-1} band increased in intensity relative to the other bands in later crops isolated during recrystallization.

The formation of [Mo(dmpe)$_2$(N$_2$)$_2$] as a mixture of cis and trans isomers was confirmed by the ^{31}P NMR spectrum of a freshly prepared THF solution of the complex. This contained a singlet, which could be assigned to the equivalent P nuclei of the trans isomer, together with two triplets assigned to the two sets of equivalent P nuclei of the cis isomer, which form an A$_2$B$_2$ coupling system.

Bis(dinitrogen) complexes of Mo(0) of the type [MoL$_4$(N$_2$)$_2$], where L is a phosphane ligand, have been prepared previously with a range of phosphanes[31] including L = PMe$_2$Ph, PPh$_2$Me, or PEt$_2$Ph and L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2 or 3) or Ph$_2$PCH= CHPPh$_2$, but most of the complexes have trans orientations of the N$_2$ ligands. The only exceptions to this are [Mo-(PMe$_2$Ph)$_4$(N$_2$)$_2$], formed as the cis isomer,[32] and [Mo-(Ph$_2$PCH=CHPPh$_2$)$_2$(N$_2$)$_2$], which has been reported to form initially as an unstable cis isomer that isomerizes to the characterized trans isomer.[1] [Mo(dmpe)$_2$(N$_2$)$_2$] is unique in being formed as a relatively stable mixture of cis and trans isomers, but this probably does not indicate that the isomers have similar thermodynamic stability. It is more probable that trapping of the low-valent molybdenum species formed in the reduction is rapid and indiscriminate. This is suggested by comparison with the reduction of [Mo(dmpe)$_2$Cl$_2$] under CO, which results in formation of an approximately 1.6:1 mixture of cis and trans isomers of [Mo(dmpe)$_2$(CO)$_2$]. Pure cis isomer could be isolated from this in 25% yield, and the trans isomer, contaminated with ca 11%

cis, could be isolated in 19% yield. Since it is well established that the cis isomer is more stable than the trans,[33] we know that the ratio of the dicarbonyl isomers is kinetically controlled, and it is reasonable to infer that the ratio of bis(dinitrogen) isomers is also kinetically controlled.

Conclusion

Reaction of amorphous molybdenum dichloride with dmpe affords a convenient route to [Mo(dmpe)$_2$Cl$_2$], establishing that this form of the dichloride behaves chemically as if it contains monomeric MoCl$_2$ and suggesting that it may be a convenient starting material for the preparation of other mononuclear Mo(II) complexes. The d^4 complex [Mo(dmpe)$_2$Cl$_2$] is surprisingly inert to alkylation, but is readily oxidized to the cationic d^3 complex [Mo(dmpe)$_2$Cl$_2$]$^+$.

Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen parameters, and bond lengths and angles for [Mo(dmpe)$_2$Cl$_2$], [Mo(dmpe)$_2$Cl$_2$][SnCl$_3$], and [Mo(dmpe)$_2$(CO)$_2$Cl]-PF$_6$, and thermal ellipsoid plots for the independent molecules in all three structures (14 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (27 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in·print. Inquiries for copies of these materials should be directed to the Editor.

(31) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
(32) George, T. A.; Seibold, C. D. *Inorg. Chem.* **1973**, *12*, 2544.

(33) Datta, S.; McNeese, T. J.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 2661.

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Oxygenated Titanium Sulfide Clusters. Synthesis and Structures of (CH$_3$C$_5$H$_4$)$_4$Ti$_4$S$_8$O$_x$ (x = 1, 2)

Gregg A. Zank,† Catherine A. Jones,† Thomas B. Rauchfuss,*† and Arnold L. Rheingold*‡

Received June 17, 1985

The reaction of Li$_2$S$_2$ with (CH$_3$C$_5$H$_4$)TiCl$_3$ followed by exposure to oxygen gives both (CH$_3$C$_5$H$_4$)$_4$Ti$_4$S$_8$O (**1**) and (CH$_3$C$_5$-H$_4$)$_4$Ti$_4$S$_8$O$_2$ (**2**). Also isolated was the mixed-ligand complex (C$_5$H$_5$)(CH$_3$C$_5$H$_4$)$_3$Ti$_4$S$_8$O$_2$ (**2″**), which arises from an impurity in the starting material. Compound **1** can be converted to **2** by using (NBu$_4$)IO$_4$, *m*-chloroperoxybenzoic acid, and *tert*-butyl hydroperoxide. Experiments with **1** and its (C$_5$H$_5$) analogue indicate that this transformation occurs without cluster fragmentation. The compounds were purified chromatographically and were characterized by spectroscopic and, for **2**, crystallographic methods. ^{1}H NMR studies over the temperature range −70 to +90 °C show that **1** is dynamic, as the methyl groups give rise to four resonances at low temperatures that merge into three resonances at higher temperatures. The ^{1}H NMR spectrum of **2**, which does not vary over the temperature range of +80 to −70 °C, shows two methyl resonances and eight cyclopentadienyl ring proton resonances, two of which are coincident. Relative to **2**, the ^{1}H NMR spectrum of **2″** shows the following differences: (i) one of the two methyl resonances is halved in intensity and is shifted upfield, (ii) three of the eight ring proton resonances are halved in intensity, and (iii) one of the eight ring proton resonances overlaps with the single C$_5$H$_5$ peak. Complex **2** crystallizes in the trigonal space group P3$_1$21 with a = 10.700 (2) Å, c = 22.530 (6) Å, V = 2233.9 (9) Å^3, and ρ_{obsd} = 1.75 g/cm^3 (ρ_{calcd} = 1.77 g/cm^3 for Z = 3). The structure was solved by direct methods leading to a final R = 0.0234 (R_w = 0.0246) with all non-hydrogen atoms anisotropic. The molecule possesses crystallographic C$_2$ symmetry and consists of a Ti$_4$(μ_4-O) core with two Ti atoms further bridged by an oxo ligand. Each of the four faces of the tetrahedral Ti$_4$O core is capped by a μ_3-S$_2$ ligand.

Introduction

Oxidation is a fundamental reaction type and is of current interest in metal sulfide chemistry.[1-5] The oxidation of certain μ_3-S-containing cluster compounds has been shown to give μ_3-SO

compounds whereas the μ-S ligand in an A-frame complex proceeds to the μ-SO$_2$ derivative.[2] Disulfur ligands can be oxidized

(1) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130–6.
(2) Balch, A. L.; Brenner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996. For a very recent discussion of the oxidation of bridging sulfides see: Lee, C.-L.; Besenyei, G.; James, B. R.; Nelson, D. A.; Lilga, M. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1175.

† University of Illinois.
‡ University of Delaware.