

external CCl_3F): ϕ -69.3 (s). ^1H NMR (CCl_4): δ 3.8-4.3 (AA', 2 H), 4.4-4.8 (BB', 2 H).

The similar reaction in the presence of sodium fluoride gave a mixture of **7** (36%) and **8** (31%) (^{19}F NMR assay).

The similar reaction in the presence of trimethylamine afforded only **7** in 79% yield.

Reaction of Amine 3 with Sulfur Tetrafluoride. Sulfur tetrafluoride (9.7 mmol) and trimethylamine (12.9 mmol) were condensed into the 75-mL Hoke cylinder containing amine **3** (610 mg, 3.2 mmol). The reaction mixture was warmed to room temperature and agitated for 10 h. The slightly volatile liquid was collected by removing the product under dynamic vacuum (10^{-2} torr) at 40 °C after the excess sulfur tetrafluoride and trimethylamine was pulled off at -78 °C. Trap-to-trap separation of this liquid at 33 °C gave the pure difluoride **11** (690 mg, 83%). IR (film): 2940 (w), 2030 (w), 1835 (w), 1422 (s), 1386 (s), 1281 (s), 1242 (s), 1227 (vs), 1197 (vs), 963 (m), 912 (m), 870 (w), 840 (m), 720 (m), 700 (s), 618 (m), 584 (w) cm^{-1} . Mass

spectrum (m/e): M^+ , 257; $\text{M} - \text{NSF}^+$, 192; $\text{M} - \text{NSF}_2^+$, 173; $\text{M} - \text{C}_3\text{H}_4\text{S}_2\text{F}^+$, 134; $\text{C}_3\text{H}_4\text{S}_2\text{F}^+$, 123; $\text{C}_2\text{H}_4\text{S}^+$, 60. ^{19}F NMR (neat, external CCl_3F): ϕ -75.5 (s, 3 F), 59.4 (s, 2 F). ^1H NMR (CDCl_3): δ 3.2-3.9 (A_2B_2). Anal. Calcd: C, 18.68; H, 1.57; N, 5.45. Found: C, 18.51; H, 1.49; N, 5.25

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New Seven-Coordinate Mixed Phosphine-Alkyl Isocyanide Complexes of Molybdenum(II) Obtained from the Reactions of Phosphine Dimers of the Type $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ and the $[\text{Mo}(\text{CNR})_7]^{2+}$ Cations

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The reactions of the tertiary phosphine complexes $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$, $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, and $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$, where dppm = bis(diphenylphosphino)methane and dppe = 1,2-bis(diphenylphosphino)ethane, with alkyl isocyanides RNC , where R = CH_3 , $\text{C}(\text{CH}_3)_3$, or C_6H_{11} , lead to the cleavage of the Mo-Mo quadruple bonds and the formation of the following cations: $[\text{Mo}(\text{CNR})_5(\text{dppm})]^{2+}$, $[\text{Mo}(\text{CNR})_5(\text{dppe})]^{2+}$, $[\text{Mo}(\text{CNR})_5(\text{PR}_3)_2]^{2+}$, and $[\text{Mo}(\text{CNR})_6(\text{PR}_3)]^{2+}$. These can all be isolated as their PF_6^- salts. These same products are formed upon reaction of the homoleptic seven-coordinate complexes $[\text{Mo}(\text{CNR})_7](\text{PF}_6)_2$ with the appropriate phosphines, thereby demonstrating the existence of a potentially extensive substitution chemistry for the 18-electron $[\text{Mo}(\text{CNR})_7]^{2+}$ ions. The spectroscopic characterization of these complexes has included measurement of their ^1H NMR, IR, electronic absorption, and X-ray photoelectron spectra. These data support the mixed-ligand complexes possessing seven-coordinate geometries since there is no evidence for unbound phosphine donor atoms (an obvious possibility in the case of the dppm and dppe ligands). These new complexes exhibit one-electron quasi-reversible electrochemical oxidations between +0.9 and +1.2 V.

Introduction

Reactions of compounds containing metal-metal quadruple bonds ($(\sigma)^2(\pi)^4(\delta)^2$ configuration) lead to products in which the quadruple bond is retained, decreased in order, or completely disrupted. The last of these three reaction pathways is important since it can provide a good synthetic route to either new or previously known compounds. Thus, it is one of the classes of reactions which are currently of interest to us in our investigations into the reaction chemistry of metal-metal multiple bonds.

Following our recent discovery that the phosphine complexes $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ ($\text{X} = \text{Cl}$, Br , or NCS) react with NO to produce the monomeric species $\text{Mo}(\text{NO})_2\text{X}_2(\text{PR}_3)_2$,¹ a reaction which proves to be an excellent general synthetic route to complexes of this type, we have sought to establish the factors which determine whether the metal-metal quadruple bond is cleaved. The possibility that this is the usual reaction course when π -acceptor ligands are used is supported by our recent studies on the reactions of the dimers $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{K}_4\text{Mo}_2\text{Cl}_8$ with alkyl isocyanides.² The seven-coordinate homoleptic cations $[\text{Mo}(\text{CNR})_7]^{2+}$ which are formed² turn out to be the

same class of molybdenum(II) isocyanide complexes which had first been reported by Lippard and co-workers.^{3,4}

An important question which emerges from our previous work^{1,2} concerns the generality of this reaction path when π -acceptor ligands are used since it could be maintained (by a "devil's advocate") that the two systems we have so far studied^{1,2} are in fact atypical. Accordingly we are, at the present time, focusing our attention on other such reactions and in the present report describe the reactions of the phosphine dimers $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$ with alkyl isocyanides. This work has led to (1) the isolation of a new class of seven-coordinate mixed phosphine-alkyl isocyanide complexes of molybdenum(II) and (2) the discovery that the $[\text{Mo}(\text{CNR})_7]^{2+}$ cations exhibit an interesting substitution chemistry with neutral donors.

Experimental Section

Starting Materials: The following compounds were prepared by standard literature procedures: CH_3NC ,⁵ $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$,⁶ α -

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(2) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 6588.

(3) Lain, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127.

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$\text{Mo}_2\text{Cl}_4(\text{dppe})_2$,⁶ $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$,⁶ $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$,⁷ $\text{Mo}_2\text{Cl}_4(\text{PEtPh}_2)_4$,⁷ $\text{Mo}_2\text{Cl}_4(\text{P}(n\text{-Pr})_3)_4$,⁷ $[\text{Mo}(\text{CNCH}_3)_7](\text{PF}_6)_2$,² $[\text{Mo}(\text{CN}-\text{C}_6\text{H}_{11})_7](\text{PF}_6)_2$,² and $[\text{Mo}(\text{CNCMe}_3)_7](\text{PF}_6)_2$. Cyclohexyl isocyanide, *tert*-butyl isocyanide, tertiary phosphines (including the bidentate phosphines bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe)), and other reagents and solvents were obtained from commercial sources and used as received.

Reaction Procedures. All reactions were carried out under a nitrogen atmosphere, and solvents were deoxygenated by purging with N_2 gas prior to use.

A. Reactions of $[\text{Mo}(\text{CNR})_7](\text{PF}_6)_2$. (i) $[\text{Mo}(\text{CNCH}_3)_5(\text{dppm})](\text{PF}_6)_2$. A mixture of $[\text{Mo}(\text{CNCH}_3)_7](\text{PF}_6)_2$ (0.507 g, 0.75 mmol) and dppm (0.579 g, 1.50 mmol) in 30 mL of deoxygenated methanol was refluxed for 24 h. After the reaction mixture was cooled, the orange product was filtered off and washed with diethyl ether. The orange-red solid was recrystallized from an acetone-diethyl ether mixture (4:1), washed with diethyl ether, and dried in vacuo; yield 0.609 g (83%). Anal. Calcd for $\text{C}_{35}\text{H}_{37}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 43.10; H, 3.82; N, 7.18. Found: C, 43.14; H, 4.00; N, 7.19. The complex is soluble in acetone, dichloromethane, methanol, and many other polar solvents.

(ii) $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{dppm})](\text{PF}_6)_2$. A mixture of $[\text{Mo}(\text{CNC}_6\text{H}_{11})_7](\text{PF}_6)_2$ (0.070 g, 0.061 mmol) and dppm (0.080 g, 0.21 mmol) in 30 mL of deoxygenated methanol was refluxed for 24 h. The solution was cooled to 0 °C and filtered to remove excess dppm. The filtrate was then taken to dryness, redissolved in dichloromethane, and filtered. The resulting orange solution was again taken to dryness and the orange residue redissolved in a small volume of acetone. This solution was chilled and diethyl ether added dropwise until an orange solid formed. The orange complex was separated by filtration and dried in vacuo; yield 0.076 g (95%). Anal. Calcd for $\text{C}_{60}\text{H}_{77}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 54.97; H, 5.92; N, 5.34. Found: C, 54.74; H, 5.80; N, 5.64.

(iii) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_5(\text{dppm})](\text{PF}_6)_2$. A bright orange complex was obtained by a procedure analogous to that in section A(ii) using $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_7](\text{PF}_6)_2$ as the starting material; yield 74%. Anal. Calcd for $\text{C}_{50}\text{H}_{67}\text{F}_4\text{MoN}_5\text{P}_4$: C, 50.64; H, 5.70; N, 5.91. Found: C, 48.58; H, 5.96; N, 6.07.

(iv) $[\text{Mo}(\text{CNCH}_3)_5(\text{dppe})](\text{PF}_6)_2$. A mixture of $[\text{Mo}(\text{CNC}-\text{H}_3)_7](\text{PF}_6)_2$ (0.414 g, 0.615 mmol) and dppe (0.520 g, 1.31 mmol) in 20 mL of deoxygenated methanol was refluxed for 14 h. The solution was cooled to 0 °C and filtered to separate a yellow precipitate from the yellow solution. The yellow precipitate was washed several times with diethyl ether and dried in vacuo. The filtrate was taken to dryness, redissolved in a small amount of acetone, and cooled to 0 °C. Diethyl ether was added dropwise until a further quantity of yellow product started to separate. It was filtered off, washed with ether and dried in vacuo. The two yellow solids were found by infrared and ¹H NMR spectroscopy to be identical; yield 0.565 g (93%). Anal. Calcd for $\text{C}_{36}\text{H}_{39}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 43.01; H, 3.92; N, 6.98. Found: C, 43.30; H, 4.14; N, 7.09.

(v) $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{dppe})](\text{PF}_6)_2$. This bright yellow complex was obtained by a procedure analogous to that in section A(ii); yield 58%. Anal. Calcd for $\text{C}_{61}\text{H}_{79}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 55.08; H, 5.99; N, 5.27. Found: C, 54.19; H, 5.99; N, 4.92.

(vi) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_5(\text{dppe})](\text{PF}_6)_2$. A bright yellow complex of this stoichiometry was obtained by a procedure analogous to that in section A(ii); yield 60%. Anal. Calcd for $\text{C}_{51}\text{H}_{69}\text{F}_4\text{MoN}_5\text{P}_4$: C, 51.05; H, 5.80; N, 5.84. Found: C, 50.17; H, 5.58; N, 5.83.

(vii) $[\text{Mo}(\text{CNCH}_3)_5(\text{P}(\text{C}_3\text{H}_7)_3)_2](\text{PF}_6)_2$. The reaction between $[\text{Mo}(\text{CNCH}_3)_7](\text{PF}_6)_2$ (0.145 g, 0.215 mmol) and tri-*n*-propylphosphine (0.60 mL, 3.0 mmol) in refluxing methanol was carried out for 1 h. The resulting orange solution was reduced to dryness in a stream of nitrogen gas and redissolved in a small volume of methanol. Several drops of diethyl ether were added, and the solution was stoppered and refrigerated. After 2 days a yellow-green solid was separated, washed with diethyl ether, and dried in vacuo; yield 0.162 g (87%). Anal. Calcd for $\text{C}_{28}\text{H}_{57}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 36.89; H, 6.30; N, 7.68. Found: C, 35.93; H, 6.36; N, 7.96.

(viii) $[\text{Mo}(\text{CNCH}_3)_5(\text{P}(\text{C}_6\text{H}_5)_3)_2](\text{PF}_6)_2$. This yellow complex was obtained by a procedure analogous to that in section A(vii); yield 59%. Anal. Calcd for $\text{C}_{34}\text{H}_{69}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 41.01; H, 6.99; N, 7.03.

Found: C, 38.34; H, 7.00; N, 6.99.

(ix) $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{P}(\text{C}_2\text{H}_5)_3)_2](\text{PF}_6)_2$. The reaction between a methanol solution of $[\text{Mo}(\text{CNC}_6\text{H}_{11})_7](\text{PF}_6)_2$ (0.401 g, 0.349 mmol) and triethylphosphine (1.0 mL, 6.8 mmol) was carried out under reflux conditions for 10 h. The orange solution was cooled and filtered to remove a small amount of brown-gray material which was discarded. After the solution was taken to dryness in a stream of nitrogen gas, the resulting solid was redissolved in a small volume of acetone, and 5 mL of ethanol was added. A small volume of acetone saturated with KPF_6 was added to this mixture and the solution gently heated. Once a solid began to precipitate, the reaction mixture was cooled, thereby producing a large quantity of yellow solid which was washed with diethyl ether and dried in vacuo. The product was recrystallized from an acetone-ether mixture (5:1); yield 0.339 g (83%). Anal. Calcd for $\text{C}_{47}\text{H}_{85}\text{F}_{12}\text{MoN}_5\text{P}_4$: C, 48.33; H, 7.34; N, 6.00. Found: C, 47.85; H, 7.32; N, 6.20.

(x) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_6(\text{P}(\text{C}_2\text{H}_5)_3)](\text{PF}_6)_2$. The reaction between a solution containing $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_7](\text{PF}_6)_2$ (0.395 g, 0.408 mmol) and triethylphosphine (1.0 mL, 6.8 mmol) in refluxing methanol was carried out for 10 h. The orange solution was evaporated to small volume and cooled to 0 °C. A yellow solid was produced which was separated by filtration, washed with diethyl ether and dried in vacuo; yield 0.342 g (81%). Anal. Calcd for $\text{C}_{36}\text{H}_{69}\text{F}_{12}\text{MoN}_6\text{P}_3$: C, 43.08; H, 6.94; N, 8.38. Found: C, 42.52; H, 7.08; N, 7.78.

(xi) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_6(\text{P}(\text{C}_3\text{H}_7)_3)](\text{PF}_6)_2$. A bright yellow complex was obtained by a procedure analogous to that in section A(ix); yield 67%. Anal. Calcd for $\text{C}_{39}\text{H}_{75}\text{F}_{12}\text{MoN}_6\text{P}_3$: C, 44.83; H, 7.24; N, 8.04. Found: C, 44.75; H, 7.41; N, 7.66.

B. Reactions of $\text{Mo}_2\text{Cl}_4(\text{LL})_2$. The reactions between these metal-metal bonded dimers, which contain the bidentate phosphines dppm or dppe, and the appropriate alkyl isocyanides were carried out in a variety of refluxing solvents. In general, $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ was found to react well with isocyanides in methanol, whereas $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ reacted best in methylene chloride, perhaps because of the slightly higher solubility of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ in the latter solvent. $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ was found to exhibit negligible reactivity toward isocyanides, presumably because of its exceedingly low solubility in all organic solvents.

(i) $[\text{Mo}(\text{CNCH}_3)_5(\text{dppm})](\text{PF}_6)_2$. Methyl isocyanide (1.3 mL, 23 mmol) was syringed into a stirred solution of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ (0.886 g, 0.80 mmol) in 30 mL of methanol. After the solution had been refluxed for 1 h, cooled, and filtered, 0.2 g of KPF_6 was added to the filtrate and the resulting solution was stirred and refrigerated. The solution was filtered to yield a quantity of brown-gray material which was discarded. The filtrate was taken to dryness and redissolved in a small volume of acetone, and 20 mL of methanol was added. An orange-brown precipitate (0.62 g) formed after the addition of a large volume of isopropyl alcohol. This was separated by filtration, washed with ether, and dried in vacuo. The product was found by ¹H NMR and infrared spectroscopy to be identical with the product isolated in section A(i); yield 40%.

(ii) $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{dppm})](\text{PF}_6)_2$. Cyclohexyl isocyanide (0.30 mL, 2.1 mmol) was syringed into a stirred solution of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ (0.47 g, 0.43 mmol) in methanol. The reaction mixture was refluxed overnight, cooled, and then filtered. The brown filtrate was taken to dryness and redissolved in a small volume of methanol. Several drops of a KPF_6 -saturated acetone solution were added, and the mixture was stirred and refrigerated. Red-orange crystals formed, and these were separated by filtration, washed with diethyl ether, and dried in vacuo. The product was shown by ¹H NMR and infrared spectroscopy to be identical with the product isolated in section A(ii); yield 25%.

(iii) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_5(\text{dppm})](\text{PF}_6)_2$. *tert*-Butyl isocyanide (0.50 mL, 4.73 mmol) was syringed into a stirred solution of $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ (0.412 g, 0.374 mmol) in 30 mL of deoxygenated methanol. After the reaction mixture was refluxed for 24 h, the solution was cooled and filtered. A quantity of KPF_6 (0.20 g) was added to the filtrate, and the mixture was stirred and cooled to 0 °C. A yellow solid (0.111 g) was separated by filtration and identified as $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_7](\text{PF}_6)_2$.⁷ The orange filtrate was taken to low volume, and diethyl ether was added dropwise. The resulting orange solid (0.401 g) was separated by filtration, washed with diethyl ether, and dried in vacuo. This product was identified by ¹H NMR and infrared spectroscopy to be identical with that isolated in section A(ii); yield 45%.

(iv) $[\text{Mo}(\text{CNCH}_3)_5(\text{dppe})](\text{PF}_6)_2$. Methyl isocyanide (0.80 mL, 26 mmol) was syringed into a stirred suspension of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$

(7) Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* 1976, 15, 2205.

(0.535 g, 0.47 mmol) in 20 mL of dichloromethane, and the reaction mixture was refluxed for 48 h. The solution was cooled, filtered, and taken to dryness. After the residue was redissolved in a small volume of acetone, several drops of a KPF_6 -saturated acetone solution were added, and the mixture was stirred and refrigerated. A product appeared which was separated by filtration, dried in vacuo, and found to be spectroscopically identical with that of section A(iv); yield 20%.

(v) $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{dppe})](\text{PF}_6)_2$. A bright yellow complex was obtained by a procedure analogous to that of section B(iv) and was found to have ^1H NMR and infrared spectroscopic properties identical with those of the product which was isolated in section A(v); yield 30%.

(vi) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_2(\text{dppe})](\text{PF}_6)_2$. A bright yellow complex was obtained by a procedure analogous to that of section B(iv) and was found by ^1H NMR and infrared spectroscopy to be identical with the product in section A(vi); yield 44%.

C. Reactions of Mo_2Cl_4 . (i) $[\text{Mo}(\text{CNCH}_3)_6(\text{P}(\text{C}_2\text{H}_5)_3)](\text{PF}_6)_2$. Methyl isocyanide (0.50 mL, 9.0 mmol) was syringed into a solution of $\text{Mo}_2\text{Cl}_4(\text{P}(\text{C}_2\text{H}_5)_3)_4$ (0.370 g, 0.459 mmol) in 30 mL of methanol. The solution was refluxed for 1 h and then cooled and filtered. The filtrate was taken to dryness and redissolved in a small volume of methanol, and KPF_6 (0.15 g) was added to the solution. The solution was stirred and cooled to 0 °C, thereby producing a yellow solid. The product was filtered off, washed with ether, and dried in vacuo; yield 0.375 g (50%). Anal. Calcd for $\text{C}_{18}\text{H}_{33}\text{F}_{12}\text{MoN}_6\text{P}_3$: C, 28.81; H, 4.43; N, 11.20. Found: C, 28.99; H, 4.61; N, 11.42.

(ii) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_2(\text{P}(\text{C}_2\text{H}_5)_3)](\text{PF}_6)_2$. A bright yellow complex of this stoichiometry was obtained by a procedure analogous to that of section C(i) and was found by infrared and ^1H NMR spectroscopy to be identical with the product isolated in section A(x). Anal. Calcd for $\text{C}_{36}\text{H}_{69}\text{F}_{12}\text{MoN}_6\text{P}_3$: C, 43.12; H, 6.94. Found: C, 42.05; H, 6.95.

(iii) $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_6(\text{P}(\text{C}_2\text{H}_5)_3)](\text{PF}_6)_2$. This bright yellow complex was obtained by a procedure analogous to that of section C(i) and was found by infrared and ^1H NMR spectroscopy to be identical with the product isolated in section A(xi). Anal. Calcd for $\text{C}_{39}\text{H}_{75}\text{F}_{12}\text{MoN}_6\text{P}_3$: C, 44.83; H, 7.24. Found: C, 44.75; H, 7.41.

(iv) $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5)_2](\text{PF}_6)_2$. A bright yellow complex was obtained by a procedure analogous to that of section C(i); yield 25%. Anal. Calcd for $\text{C}_{63}\text{H}_{85}\text{F}_{12}\text{MoN}_3\text{P}_4$: C, 55.63; H, 6.30; N, 5.15. Found: C, 55.30; H, 6.20; N, 5.10.

(v) $[\text{Mo}(\text{CNCH}_3)_7](\text{PF}_6)_2$. A quantity of methyl isocyanide (0.50 mL, 9.0 mmol) was syringed into a stirred solution of $\text{Mo}_2\text{Cl}_4(\text{PEtPh}_2)_4$ (0.446 g, 0.375 mmol) in 30 mL of methanol. The solution was refluxed for 48 h, cooled, and filtered to yield a small amount of an unidentified brown material. KPF_6 (0.20 g) was added to the filtrate, and the solution was stirred and cooled. A yellow precipitate (0.356 g) was washed with diethyl ether and recrystallized from an acetone-ether mixture (4:1). Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{F}_{12}\text{MoN}_7\text{P}_2$: C, 25.0; H, 3.14. Found: C, 25.73; H, 3.27. This product had infrared and ^1H NMR spectra which were identical with those exhibited by an authentic sample of $[\text{Mo}(\text{CNCH}_3)_7](\text{PF}_6)_2$.

Physical Measurements. Infrared spectra of Nujol mulls and methylene chloride or acetone solutions were recorded in the region 4000–200 cm^{-1} with a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded by using Cary 14 and Varian series 634 spectrophotometers. A Perkin-Elmer R32 NMR spectrometer was used to obtain the ^1H NMR spectra while ^{31}P spectra were recorded by using a Varian XL-100 spectrometer. Samples were dissolved in acetone- d_6 or dimethyl- d_6 sulfoxide, and peak resonances were internally referenced to Me_4Si in the case of the ^1H NMR spectra. X-ray photoelectron spectra were obtained by using a Hewlett-Packard 5950A ESCA spectrometer. Further experimental details are described elsewhere.⁸ Cyclic voltammetry experiments were performed by using the setup described previously.⁹

Results and Discussion

Reactivity Studies. Reactions of an excess of methyl, cyclohexyl, or *tert*-butyl isocyanide with the dimers $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ and $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$, $\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$ and $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$, in refluxing methanol or dichloromethane produce

yellow solutions from which the six monomeric orange-yellow complexes $[\text{Mo}(\text{CNR})_5(\text{dppm})](\text{PF}_6)_2$ and $[\text{Mo}(\text{CNR})_5(\text{dppe})](\text{PF}_6)_2$ can be produced upon the addition of KPF_6 . These complexes are isoelectronic with the homoleptic seven-coordinate cations $[\text{Mo}(\text{CNR})_7]^{2+}$ and may be considered as substitution derivatives thereof.

The starting materials $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ and $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ both possess Mo–Mo quadruple bonds⁶ although these complexes differ as regards the nature of the bidentate phosphine coordination; dppm bridges the two molybdenum atoms within the $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ dimer¹⁰ while with $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ the dppe ligands are present in their conventional chelating form.⁶ As with the reactions of $\text{Mo}_2(\text{O}_2\text{CC-H}_3)_4$ and $\text{K}_4\text{Mo}_2\text{Cl}_8$ with methanol solutions of alkyl isocyanides, in which the monomeric $[\text{Mo}(\text{CNR})_7]^{2+}$ cations are produced,² the Mo–Mo quadruple bond of these two phosphine derivatives is readily cleaved.

Our use of a solvent in the reactions between the Mo_2^{4+} derivatives and alkyl isocyanides and the addition of PF_6^- to the reaction mixtures prior to workup turn out to be very important in determining the nature of the reaction products. Following the publication of our original report² describing the Mo–Mo bond cleavage reactions induced by alkyl isocyanides, Girolami and Anderson¹¹ have described how treatment of crystalline samples of $\text{Mo}_2(\text{O}_2\text{CR})_4$ ($\text{R} = \text{CH}_3$ or CF_3), $\text{K}_4\text{Mo}_2\text{Cl}_8$, and $\text{Mo}_2\text{Cl}_4(\text{P}(n\text{-Bu})_3)_4$ with *neat tert*-butyl isocyanide affords either $\text{Mo}(\text{CNCMe}_3)_5\text{X}_2$ ($\text{X} = \text{O}_2\text{C-CF}_3$ or Cl) or $\text{Mo}(\text{CNCMe}_3)_4(\text{O}_2\text{CCH}_3)_2$. The latter complexes are convertible¹¹ to $[\text{Mo}(\text{CNCMe}_3)_7](\text{PF}_6)_2$ upon reaction with an excess of *tert*-butyl isocyanide and NH_4PF_6 .

Of particular note in the report by Girolami and Anderson¹¹ is their observation that treatment of $\text{Mo}_2\text{Cl}_4(\text{P}(n\text{-Bu})_3)_4$ with *neat tert*-butyl isocyanide leads to the loss of all the *tert*-butylphosphine ligands. We have also investigated the reactions between several molybdenum complexes of the type $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$ ($\text{PR}_3 = \text{PET}_3$, $\text{P}(n\text{-Pr})_3$, or PEtPh_2) and the three alkyl isocyanides. In all instances we find that these reactions afford mixed phosphine-alkyl isocyanide complexes with the stoichiometries $[\text{Mo}(\text{CNR})_5(\text{PR}_3)_2](\text{PF}_6)_2$ or $[\text{Mo}(\text{CNR})_6(\text{PR}_3)](\text{PF}_6)_2$ when carried out under our experimental conditions. While steric factors may be important in determining the stoichiometries of certain of the products (for example, with *tert*-butyl isocyanide we always get $[\text{Mo}(\text{CNCMe}_3)_6(\text{PR}_3)]^{2+}$), electronic factors (for example, basicity differences among the phosphine ligands) must also play an important role. Thus $\text{Mo}_2\text{Cl}_4(\text{PET}_3)_4$ reacts with methyl isocyanide to produce $[\text{Mo}(\text{CNCH}_3)_6(\text{PET}_3)_2]^{2+}$ whereas under comparable reaction conditions $\text{Mo}_2\text{Cl}_4(\text{PEtPh}_2)_4$ is converted to $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{PEtPh}_2)_2]^{2+}$ by cyclohexyl isocyanide.

During the course of our reactivity studies, there were two occasions when we isolated the homoleptic derivatives $[\text{Mo}(\text{CNR})_7]^{2+}$. $[\text{Mo}(\text{CNCMe}_3)_7](\text{PF}_6)_2$ was isolated as a minor product (20% or thereabouts) from the reaction between $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$ and *tert*-butyl isocyanide, and $[\text{Mo}(\text{CNC-H}_3)_7](\text{PF}_6)_2$ was formed upon reacting $\text{Mo}_2\text{Cl}_4(\text{PEtPh}_2)_4$ with methyl isocyanide. In both instances, a very large excess of the isocyanide had been added to the molybdenum dimer. However, on no occasions were we able to isolate a complex containing more than two phosphine donor atoms per molybdenum.

The preceding account of the reactions between phosphine complexes of Mo_2^{4+} and alkyl isocyanides leads to the expectation that the same mixed phosphine-alkyl isocyanide complexes of molybdenum(II) might be prepared directly from $[\text{Mo}(\text{CNR})_7](\text{PF}_6)_2$. This is indeed the case as evidenced by

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Table I. Selected Spectroscopic Properties of Mixed Phosphine-Alkyl Isocyanide Complexes of Molybdenum(II)

complex	P 2p XPS, eV		$I(\text{PF}_6^-)/I(\text{PR}_3)^a$	^1H chem shifts, δ			IR abs, $\nu(\text{N}\equiv\text{C})$, cm^{-1}
	PF_6^-	PR_3		alkyl ^c	P-(CH ₂) _n -P	phenyl	
[Mo(CNCH ₃) ₅ (dppm)](PF ₆) ₂	136.2	131.4	1.0:1.0	3.49	4.94 t ^d	~7.7 br	2220 m, 2185 ms, 2135 s
[Mo(CNCMe ₃) ₅ (dppm)](PF ₆) ₂	136.2	131.3	1.2:1.0	1.41	4.89 t ^d	~7.7 br	2195 m, 2150 s, 2115 s, 2080 sh
[Mo(CNC ₆ H ₁₁) ₅ (dppm)](PF ₆) ₂	136.2	131.5	1.1:1.0	4.15 br, 1.85 br, ~1.5 br	4.95 t ^d	~7.6 br	2190 ms, 2147 s, 2109 s, 2060 sh
[Mo(CNCH ₃) ₅ (dppe)](PF ₆) ₂	136.2	131.3	1.2:1.0	3.37	3.08, 2.87	~7.65 br	2220 mw, 2190 sh, 2150 s
[Mo(CNCMe ₃) ₅ (dppe)](PF ₆) ₂	136.4	131.7	1.0:1.0	1.37	3.11, 2.88	~7.8 br	2192 mw, 2135 s
[Mo(CNC ₆ H ₁₁) ₅ (dppe)](PF ₆) ₂	136.3	131.4	1.1:1.0	4.0 br, ~1.9 br, ~1.5 br	3.12, 2.90	~7.7 br	2188 mw, 2128 s
[Mo(CNCH ₃) ₅ (P(<i>n</i> -Pr) ₃) ₂](PF ₆) ₂				3.77, ~1.6 br, ~1.1 m*			2212 w, 2142 s
[Mo(CNCH ₃) ₅ (P(<i>n</i> -Bu) ₃) ₂](PF ₆) ₂							2220 w, 2145 s
[Mo(CNC ₆ H ₁₁) ₅ (PEt ₃) ₂](PF ₆) ₂				4.45 br ^e			
[Mo(CNC ₆ H ₁₁) ₅ (PEtPh ₂) ₂](PF ₆) ₂	136.2	131.2	1.2:1.0	4.0 br, ~1.5 br		~7.65 br	2190 vw, 2128 s
[Mo(CNCH ₃) ₅ (PEt ₃) ₂](PF ₆) ₂	136.4	131.3	2.1:1.0	3.69, 1.95 br*, ~1.1 p*			2235 w, 2160 s
[Mo(CNCH ₃) ₅ (PEt ₃) ₂](PF ₆) ₂	135.9	130.8	1.9:1.0	1.53, 1.93 br*, ~1.05 p*			2205 mw, 2180 sh, 2135 s, 2065 sh
[Mo(CNCMe ₃) ₅ (P(<i>n</i> -Pr) ₃) ₂](PF ₆) ₂	136.0	131.0	1.9:1.0	1.54, 1.88 br*, ~1.1 m*			2203 w, 2128 s, 2060 sh

^a Intensity ratio of the P 2p binding energy peaks associated with the PF₆⁻ anions and phosphine ligands. ^b All spectra were recorded in acetone-*d*₆ except for the use of Me₂SO-*d*₆ in the case of [Mo(CNCMe₃)₅(PR₃)₂](PF₆)₂ (R = Et or *n*-Pr). Abbreviations are as follows: br = broad, m = multiplet, p = pentet, t = triplet. ^c Resonances attributable to the alkyl groups of the phosphine ligands are marked with an asterisk. ^d $J_{\text{C}-\text{P}} = 11$ Hz. ^e Overlap of resonances due to the cyclohexyl and ethyl groups (δ ca. 1 to ca. 2) gives rise to a complex pattern which is not reported here.

our isolation of the hexafluorophosphate salts of [Mo(CNR)₅(dppm)]²⁺, [Mo(CNR)₅(dppe)]²⁺, [Mo(CNCH₃)₅(PR₃)₂]²⁺ (R = *n*-Pr or *n*-Bu), [Mo(CNC₆H₁₁)₅(PEt₃)₂]²⁺, and [Mo(CNCMe₃)₅(PR₃)₂]²⁺ (R = Et or *n*-Pr) in yields in excess of 60% (in most instances greater than 80%) by such a procedure. Note that the only examples of [Mo(CNR)₅(PR₃)₂]²⁺ species prepared by this method are the *tert*-butyl isocyanide derivatives. All complexes prepared by this route had spectroscopic properties which were identical with those of the complexes of these same stoichiometries which were prepared from Mo₂Cl₄(PR₃)₄.

Of the many reactions we carried out there was only one which did not yield a pure product and that involved the reaction between [Mo(CNCH₃)₇](PF₆)₂ and triphenylphosphine. The resulting orange solid had microanalyses and a ¹H NMR spectrum (in acetone-*d*₆)¹² which were consistent with it being a mixture (approximately 30:70) of unreacted starting material and [Mo(CNCH₃)₆(PPh₃)](PF₆)₂.

Spectroscopic Characterizations. A variety of spectroscopic measurements were carried out with the purpose of both establishing the structural integrity of the different complexes and providing information on whether they could be conveniently subdivided into structurally related groups.

The X-ray photoelectron spectra (XPS) of most of the complexes were recorded. All possessed Mo 3d_{5/2} binding energies (228.8 ± 0.3 eV) which were similar to those of other molybdenum(II) species, including halide^{6,13,14} and allyl¹⁵ derivatives and the previously characterized [Mo(CNR)₇](PF₆)₂.^{2,16} These measurements, furthermore, revealed the absence of any higher oxidation state molybdenum-containing contaminants. Two sets of P 2p binding energies were observed (Table I), those due to the PF₆⁻ anions being at the higher binding energy. The chemical shift was reasonably constant (4.9 ± 0.2 eV), and relative peak intensity ratios¹⁷ were in quite

good agreement with the expected stoichiometric ratios of PF₆⁻ to phosphine phosphorus (Table I).

In acetone-*d*₆ or dimethyl-*d*₆ sulfoxide, the room-temperature proton NMR spectra of most of the complexes were well-defined, and in the case of the dppm and dppe complexes and [Mo(CNC₆H₁₁)(PEtPh₂)₂](PF₆)₂, integration of the phenyl (δ ca. 7.6) and alkyl isocyanide resonances were in accord with the known stoichiometry of the complexes. Overlap of the *tert*-butyl (δ 1.53) and cyclohexyl (δ ca. 1.55 and ~1.9) resonances with those arising from the alkylphosphine ligands precluded meaningful integrations for these systems. A summary of the more important ¹H NMR data is presented in Table I. The ¹H NMR spectra of the dppm and dppe complexes were consistent with both phosphorus atoms of the bidentate phosphine ligands being coordinated.

The room-temperature ³¹P NMR spectra of [Mo(CNR)₅(dppm)](PF₆)₂, [Mo(CNR)₅(dppe)](PF₆)₂ (R = CH₃ or C₆H₁₁), and [Mo(CNC₆H₁₁)₅(PEtPh₂)₂](PF₆)₂ in acetone-*d*₆ at 40.5 MHz revealed that the chemical shifts of the coordinated phosphorus atoms of the phosphine ligands were about 5–50 ppm upfield of 85% H₃PO₄. On the NMR time scale the phosphorus atoms of the dppm and dppe ligands are magnetically equivalent, consistent, once again, with their bidentate coordination. In the complexes containing two phosphorus donor atoms the observation of a singlet in the ³¹P NMR spectra is in accord with the stereochemical nonrigidity often encountered with seven-coordinate species.

In most instances, both Nujol mull and solution IR spectra of the complexes were recorded, the spectral region of particular interest being that between 2250 and 2050 cm⁻¹ wherein the $\nu(\text{N}\equiv\text{C})$ modes of the coordinated alkyl cyanides are located. The appropriate data for acetone or dichloromethane solutions of the complexes are presented in Table I. We cannot of course hope to deduce the detailed stereochemistry of these complexes from such measurements, so that our objective was simply to ascertain whether there appeared to be any structure related correlations. The striking similarity of the IR spectra of certain of the mulls to those of the solutions indicated that in these instances there is no significant structural change upon dissolution. This was clearly the case for the four complexes [Mo(CNR)₅(dppm)](PF₆)₂ and [Mo(CNR)₅(dppe)](PF₆)₂ (R = CMe₃ or C₆H₁₁). For other complexes the simplification

(12) The ¹H NMR of [Mo(CNCH₃)₇](PF₆)₂ consists of a single sharp methyl resonance with δ 3.72, while for [Mo(CNCH₃)₆(PPh₃)](PF₆)₂ this resonance is shifted upfield to δ 3.43.

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(17) Carried out by using a Du Pont 310 curve resolver.

Table II. $E_{1/2}$ Values for Mixed-Ligand Phosphine-Alkyl Isocyanide Complexes of Molybdenum(II)^a

complex	$E_{1/2}$
[Mo(CNCH ₃) ₅ (dppm)](PF ₆) ₂	+0.99
[Mo(CNC ₆ H ₁₁) ₅ (dppm)](PF ₆) ₂	+1.08
[Mo(CNCMe ₃) ₅ (dppe)](PF ₆) ₂	+1.18
[Mo(CNC ₆ H ₁₁) ₅ (dppe)](PF ₆) ₂	+1.12
[Mo(CNCH ₃) ₅ (P(<i>n</i> -Pr) ₃) ₂](PF ₆) ₂	+0.90
[Mo(CNC ₆ H ₁₁) ₅ (PEt ₃) ₂](PF ₆) ₂	+1.00
[Mo(CNCH ₃) ₆ (PEt ₃)](PF ₆) ₂	+1.04
[Mo(CNCMe ₃) ₆ (PEt ₃)](PF ₆) ₂	+1.12
[Mo(CNCMe ₃) ₆ (P(<i>n</i> -Pr) ₃)](PF ₆) ₂	+1.12

^a In volts vs. SCE with a Pt-bead working electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte.

of the IR spectra in the $\nu(\text{N}\equiv\text{C})$ region upon dissolving them in acetone or dichloromethane is probably due, at least in part, to the elimination of solid-state splitting effects; most of the complexes containing monodentate phosphines fall into this category. However, a structural difference between a complex in the solid state and solution is a very real possibility, particularly with seven-coordinate species where the different coordination geometries may be very close in energy. This is possibly the case with the methyl isocyanide complexes [Mo(CNCH₃)₅(dppm)](PF₆)₂ and [Mo(CNCH₃)₅(dppe)](PF₆)₂, for which the solution spectra are much simpler than those of the solids and an intense band which is present in the mulls (2099 cm⁻¹ for the dppm complex and 2132 cm⁻¹ for its dppe analogue) is no longer a characteristic of the solution species.

An examination of the IR data (both the $\nu(\text{N}\equiv\text{C})$ energies and band profiles) permits us to conclude that there are certain pairs of complexes which probably bear a close structural relationship to one another in *both* the solid and solution states. These are the following: [Mo(CNR)₅(dppm)](PF₆)₂ for R = CMe₃ or C₆H₁₁, [Mo(CNR)₅(dppe)](PF₆)₂ for R = CMe₃ or C₆H₁₁, [Mo(CNCH₃)₅(PR₃)₂](PF₆)₂ for R = *n*-Pr or *n*-Bu, and [Mo(CNCMe₃)₆(PR₃)](PF₆)₂ for R = Et or *n*-Pr. However, the structural relationships which exist between pairs are unknown at present although we note that the solution spectra of the four complexes [Mo(CNR)₅(dppe)](PF₆)₂, where R = CMe₃ or C₆H₁₁, and [Mo(CNCH₃)₅(PR₃)₂](PF₆)₂, where R = *n*-Pr or *n*-Bu, are very similar, perhaps hinting at a close similarity in structure.

Electronic absorption spectral measurements on methanol solutions of all thirteen mixed-ligand complexes have been carried out. In the region between 210 and 450 nm the complexes exhibit five or six absorptions (several as shoulders), the three at highest energy occurring over relatively narrow energy ranges (310–280, 260–250, and 235–217 nm) and clearly being charge transfer in origin ($\epsilon > 5 \times 10^3$). The dppm complexes possess an absorption at 320 (± 3) nm which has no counterpart in the spectra of the other complexes. The two remaining absorption bands are located at 437–392 and 375–330 nm and are significantly weaker ($\epsilon \approx (0.4\text{--}0.9) \times 10^3$ and $(1.2\text{--}2.2) \times 10^3$, respectively) than the other absorptions. The lowest energy band at 420 (± 20) nm is most likely analogous to the band at 410 (± 5) nm which is present² in the spectra of methanol solutions of [Mo(CNR)₇]²⁺ and which has been assigned by Lippard and co-workers³ to a metal-based transition.

Oxidation of [Mo(CNR)_{7-x}(PR₃)_x]²⁺. The electrochemical properties of these seven-coordinate mixed-ligand complexes were investigated by the cyclic voltammetry technique. Voltammetric half-wave potentials vs. SCE for dichloromethane solutions of a representative group of these complexes are presented in Table II. The cyclic voltammogram of [Mo(CNCH₃)₅(P(*n*-Pr)₃)₂](PF₆)₂ is shown in Figure 1a. In

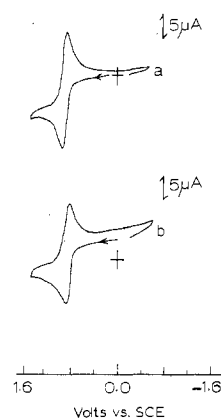


Figure 1. Cyclic voltammograms in 0.2 M TBAH–dichloromethane of [Mo(CNCH₃)₅(P(*n*-Pr)₃)₂](PF₆)₂ (a) before and (b) after exhaustive electrolysis at +1.2 V.

all instances, the complexes exhibit a single oxidation, [Mo(CNR)_{7-x}(PR₃)_x]²⁺ → [Mo(CNR)_{7-x}(PR₃)_x]³⁺ + e⁻. For sweep rates (*v*) between 100 and 300 mV/s, $i_{p,a}/i_{p,c} \approx 1$ and the ratio $i_p/v^{1/2}$ was constant in accord with diffusion control. The potential separation between the anodic and cathodic peaks, ΔE_p , was greater than 60 mV, being in the range 80–100 mV for a sweep rate of 200 mV/s, and increased slightly with an increase in sweep rate, a clear indication of this being a quasi-reversible electron-transfer process.^{18,19}

In no instance did we observe irreversible waves in the vicinity of +1.1 V which we could attribute to the presence of uncomplexed phosphine groups.²⁰ This is further support for our contention that in the dppm and dppe complexes both phosphine donor atoms are coordinated.

Exhaustive electrolyses were performed on dichloromethane solutions of the complexes by using potentials in the neighborhood of +1.2 V. The resulting pink–pale purple solutions exhibited cyclic voltammograms (Figure 1b) which were the same as those obtained prior to oxidation.²¹ For these oxidations we obtained *n* values very close to 1 (e.g., *n* = 1.02 for [Mo(CNCH₃)₆(PEt₃)](PF₆)₂ and 1.09 for [Mo(CNC₆H₁₁)₅(PEt₃)₂](PF₆)₂). The X-band ESR spectra of CH₂Cl₂ glasses (–180 °C) of these oxidized solutions showed that the seven-coordinate molybdenum(III) species were not ESR active under these conditions.

Some General Comments. The facile cleavage of the Mo–Mo quadruple bond of the phosphine dimers Mo₂Cl₄(dppm)₂, Mo₂Cl₄(dppe)₂, and Mo₂Cl₄(PR₃)₄ by alkyl isocyanides provides good support for our belief that this will be the general reaction pathway with π -acceptor ligands. In dimers of these types, sterically unhindered ligands such as C≡N–R (or NO) can be expected to bind to the vacant “axial” coordination sites (collinear with the M–M bond), producing intermediates of the type M₂Cl₄L₄L’₂.²² This may well be the reason for the eventual cleavage of the metal–metal bond since the overlap between the antibonding orbitals of π symmetry on CNR and the metal-based π -bonding orbitals may lead to the weakening

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(20) Under our experimental conditions dichloromethane solutions of P(*n*-Pr)₃, PPh₃, dppm, and dppe exhibit oxidation waves with $E_{p,a}$ values in the vicinity of +1.1 V.

(21) This is true provided the cyclic voltammograms of the oxidized solutions are measured immediately after they have been generated. However, when the solutions are kept under a nitrogen atmosphere and periodically monitored by cyclic voltammetry, they are observed to undergo a slow chemical change without the molybdenum being oxidized beyond the 3+ state. These coupled electrochemical–chemical reactions are currently being investigated in more detail.

(22) Up to the present time we have been unable to detect spectroscopically such an intermediate or isolate it. If formed, it must be extremely labile.

of the π -bonding component of the metal-metal bond.

The tertiary phosphine-isocyanide complexes of the types $[\text{Mo}(\text{CNR})_6(\text{PR}_3)]^{2+}$ and $[\text{Mo}(\text{CNR})_5(\text{PR}_3)_2]^{2+}$ are electronically related to the mixed halide-isocyanides $[\text{Mo}(\text{CNR})_6\text{X}]^+$ and $[\text{Mo}(\text{CNR})_5\text{X}_2]$ which have previously been isolated by Lippard and co-workers³ and Bonati and Minghetti.²³ While the latter halogen-containing species have been used as intermediates^{3,11} on the way to homoleptic $[\text{Mo}(\text{CNR})_7]^{2+}$, our discovery that the $[\text{Mo}(\text{CNR})_7]^{2+}$ cations react with phosphine to give mixed-ligand species points to the existence of an extensive substitution chemistry for $[\text{Mo}(\text{CNR})_7]^{2+}$ in their reactions with neutral donors.²⁴ This is of particular significance bearing in mind the formal "isoelectronic" relationship between $[\text{Mo}(\text{CNR})_7]^{2+}$, $\text{Mo}(\text{C}-\text{NAr})_6$ (Ar = aryl), and $\text{Mo}(\text{CO})_6$; i.e., all are 18-electron systems.

With the current interest in the structures of seven-coordinate isocyanide complexes of molybdenum(II) and tungsten(II)^{2-4,25-27} and the need to assess those factors which favor one geometry over another (capped trigonal prism,^{3,4,25} capped octahedron,² and 4:3 piano stool²⁶) our isolation of four dif-

ferent groups of mixed-ligand complexes, viz., $[\text{Mo}(\text{CNR})_5(\text{dppm})]^{2+}$, $[\text{Mo}(\text{CNR})_5(\text{dppe})]^{2+}$, $[\text{Mo}(\text{CNR})_5(\text{PR}_3)]^{2+}$, and $[\text{Mo}(\text{CNR})_6(\text{PR}_3)]^{2+}$, provides an excellent opportunity to pursue further the structures of such complexes. Accordingly, we plan to carry out single-crystal X-ray structure determinations on representatives of these groups in the very near future.

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Registry No. $[\text{Mo}(\text{CNCH}_3)_5(\text{dppm})](\text{PF}_6)_2$, 74081-65-5; $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_5(\text{dppm})](\text{PF}_6)_2$, 74096-43-8; $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{dppm})](\text{PF}_6)_2$, 74096-45-0; $[\text{Mo}(\text{CNCH}_3)_5(\text{dppe})](\text{PF}_6)_2$, 74096-47-2; $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_5(\text{dppe})](\text{PF}_6)_2$, 74096-49-4; $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{dppe})](\text{PF}_6)_2$, 74096-51-8; $[\text{Mo}(\text{CNCH}_3)_5(\text{P}(\text{C}_3\text{H}_7)_3)_2](\text{PF}_6)_2$, 74081-67-7; $[\text{Mo}(\text{CNCH}_3)_5(\text{P}(\text{C}_4\text{H}_9)_3)_2](\text{PF}_6)_2$, 74096-53-0; $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{P}(\text{C}_2\text{H}_5)_3)_2](\text{PF}_6)_2$, 74096-55-2; $[\text{Mo}(\text{CNC}_6\text{H}_{11})_5(\text{P}(\text{C}_6\text{H}_5)_3)_2](\text{PF}_6)_2$, 74096-57-4; $[\text{Mo}(\text{CNC}_6\text{H}_5)_6(\text{P}(\text{C}_2\text{H}_5)_3)](\text{PF}_6)_2$, 74096-59-6; $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_6(\text{P}(\text{C}_2\text{H}_5)_3)](\text{PF}_6)_2$, 74096-61-0; $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_6(\text{P}(\text{C}_3\text{H}_7)_3)](\text{PF}_6)_2$, 74096-63-2; $[\text{Mo}(\text{CNCH}_3)_7](\text{PF}_6)_2$, 66632-84-6; $[\text{Mo}(\text{CNC}_6\text{H}_{11})_7](\text{PF}_6)_2$, 72155-82-9; $[\text{Mo}(\text{CNC}(\text{CH}_3)_3)_7](\text{PF}_6)_2$, 41982-05-2; $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$, 64508-35-6; $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$, 64490-77-3; $\text{Mo}_2\text{Cl}_4(\text{P}(\text{C}_2\text{H}_5)_3)_4$, 59780-36-8; $\text{Mo}_2\text{Cl}_4(\text{PEtPh}_2)_4$, 59752-92-0; $\text{Mo}_2\text{Cl}_4(\text{P}(n\text{-Pr})_3)_4$, 59780-37-9.

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Complexes of d^8 Metals with Tetrathiomolybdate and Tetrathiotungstate Ions. Synthesis, Spectroscopy, and Electrochemistry¹

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The synthesis of $\text{Pd}(\text{MoS}_4)_2^{2-}$, $\text{Pd}(\text{WS}_4)_2^{2-}$, and $\text{Pt}(\text{MoS}_4)_2^{2-}$ has been achieved, and improved methods for the Ni analogues and $\text{Pt}(\text{WS}_4)_2^{2-}$ have been developed. Infrared spectra of these compounds reflect the effects of changing the central d^8 metal. These complexes undergo reversible electrochemical reductions (Ni, Pd) quite sensitive to the nature of the d^8 metal but less so to the ligand. Two well-separated one-electron reversible reductions are seen for the nickel complexes. These move closer together in the Pd species and the second reduction becomes irreversible. Only one reduction wave is observed for the Pt complexes, but it appears to be an overlap of two different electrode processes. The electrochemical results are consistent with a decreased separation of the a_g and b_{1g} orbitals as the mass of the central metal increases. All compounds show irreversible, multielectron oxidations, probably localized on the terminal sulfur atoms of the ligands.

Introduction

Complexes of bidentate sulfur ligands with transition metals having d^8 electronic configurations have been of continuing interest for nearly 20 years.^{2,3} Only recently, however, have the disputes as to the nature of the redox processes which some of these species exhibit been apparently resolved.^{4,5} An example of this situation is $\text{Ni}(\text{mnt})_2^2$, where mnt is the ma-

leonitriedithiolate ion and z ranges from 0 to 3-; it now seems established that the sequential reductions of the neutral complex occur both on the ligand and at the metal, the exact location being a function of the particular one-electron redox couple.⁵ We have studied a series of complexes in which the bidentate sulfur ligand also possesses a potentially electroactive metal and report the details of this system. A preliminary account has already appeared.⁶

Synthesis

Müller⁷⁻⁹ originally reported the preparation of $\text{Ni}(\text{MoS}_4)_2^{2-}$, $\text{Ni}(\text{WS}_4)_2^{2-}$, and later $\text{Pt}(\text{WS}_4)_2^{2-}$. We have extended this

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