Reactions of Homoleptic (Alkyl Isocyanide)molybdenum(II) Cations [Mo(CNR)₇]²⁺ with 2,2'-Bipyridine and Related Ligands (N–N). Substitution Chemistry and Dealkylation To Form Cyano-Bridged Complexes of the Type [{Mo(CNCMe₃)₄(N–N)}₂(μ-CN)](PF₆)₃

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Reactions of the homoleptic cyclohexyl isocyanide complex $[Mo(CNC_6H_{11})_7](PF_6)_2$ with bidentate nitrogen ligands 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), and 1,10-phenanthroline (phen) in 1-propanol lead to substitution of two isocyanide ligands and formation of mononuclear seven-coordinate complexes $[Mo(CNC_6H_{11})_5(N-N)](PF_6)_2$. On the other hand, $[Mo(CNCMe_3)_7](PF_6)_2$ reacts under these same conditions to give a cyano-bridged dimolybdenum(II) species $[\{Mo(CNCMe_3)_4(N-N)\}_2(\mu\text{-}CN)](PF_6)_3$, the identity of which has been confirmed by a crystal structure determination on the bpy derivative. The compound $[\{Mo(CNCMe_3)_4(bpy)\}_2(\mu\text{-}CN)](PF_6)_3$ crystallizes in monoclinic space group C_{2h}^5—$P2_1/n$ with $a = 13.964$ (2) Å, $b = 37.734$ (4) Å, $c = 16.933$ (2) Å, $\beta = 104.17$ (1)°, and $Z = 4$. The structure has been refined to $R = 0.079$ for 4177 reflections and 515 variable parameters. The cyano-bridged cation has approximate C_2 symmetry. Each molybdenum atom has capped trigonal-prismatic stereochemistry with a bipyridine ligand, Mo–N$_{av}$ = 2.220 (17) Å, and two isocyanide ligands, Mo–C$_{av}$ = 2.07 (2) Å, occupying the capped rectangular face, two isocyanide groups, Mo–C$_{av}$ = 2.04 (2) Å, on the unique edge, and a disordered bridging cyanide ligand, Mo–C(N) = 2.19 (2) Å, at the capping position. The electrochemical properties of $[\{Mo(CNCMe_3)_4(N-N)\}_2(\mu\text{-}CN)](PF_6)_3$ are consistent with the presence of two chemically inequivalent $[Mo(CNCMe_3)_4(N-N)]$ moieties, and the ¹H NMR spectra are also indicative of a binuclear species in solution. The reaction of *tert*-butyl chloride with $[\{Mo(CNCMe_3)_4(bpy)\}_2(\mu\text{-}CN)](PF_6)_3$ leads to $[Mo(CNCMe_3)_4(bpy)Cl]PF_6$. Subsequent reaction of this chloro species with *tert*-butyl isocyanide gives rise to $[Mo(CNCMe_3)_5(bpy)](PF_6)_2$. Dealkylation of $[Mo(CNCMe_3)_5(bpy)](PF_6)_2$ occurs in refluxing 1-propanol to regenerate $[\{Mo(CNCMe_3)_4(bpy)\}_2(\mu\text{-}CN)](PF_6)_3$. The reactions between $[Mo(CNCMe_3)_7](PF_6)_2$ and N,N'-di-*tert*-butylethylenediimine, N,N'-diisopropylethylenediimine, and pyrazine resulted in dealkylation of one of the coordinated *tert*-butyl isocyanide ligands to yield $[Mo(CNCMe_3)_6(CN)]PF_6$, but otherwise did not yield substitution products. Reactions of the binuclear compounds $Mo_2Cl_4(bpy)_2$ and $Mo_2Cl_4(py)_4$ with *tert*-butyl isocyanide lead to cleavage of the Mo–Mo quadruple bond and the formation of $[Mo(CNCMe_3)_4(bpy)Cl]PF_6$ and $[Mo(CNCMe_3)_6(py)](PF_6)_2$, respectively.

Introduction

Seven-coordinate homoleptic alkyl isocyanide complexes of molybdenum(II) and tungsten(II) of the type [M-(CNR)₇](PF₆)₂ react with monodentate and bidentate tertiary phosphines to substitute up to two isocyanide ligands and form a variety of seven-coordinate mixed isocyanide–phosphine complexes of stoichiometry [M-(CNR)₆(PR₃)](PF₆)₂, [M(CNR)₅(PR₃)₂](PF₆)₂, [M-(CNR)₅(dppe)](PF₆)₂, or [M(CNR)₅(dppm)](PF₆)₂, where PR₃ = PEt₃, P-*n*-Pr₃, P-*n*-Bu₃, or PEtPh₂, dppe = Ph₂PCH₂CH₂PPh₂, and dppm = Ph₂PCH₂PPh₂.[2-5] In order to examine more fully the scope of the substitution chemistry of [M(CNR)₇](PF₆)₂, we have studied the reactions of these molybdenum(II) complexes with heterocyclic amines, in particular, 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), and 1,10-phenanthroline (phen). As described in the present report, this work has led to the isolation of the seven-coordinate species [Mo(CNR)₅(N–N)](PF₆)₂ (N–N = bpy, Me₂bpy, and phen) and, in the case of the *tert*-butyl isocyanide

derivatives, the novel dimolybdenum(II) cyano-bridged complexes [{Mo(CNCMe₃)₄(N–N)}₂(μ-CN)](PF₆)₃. These results not only expand considerably the chemistry of high coordinate isocyanide complexes of the early transition series but further stress the importance of dealkylation reactions of isocyanide ligands.[6] Although alkylation of coordinated cyanide ligands is a well-known route to isocyanide complexes,[7] the reverse reaction has not been fully appreciated. Dealkylation of coordinated alkyl isocyanide is probably involved in the metal-mediated hydrocyanation of α,β-unsaturated carbonyl compounds by *tert*-butyl isocyanide.[8] Dealkylation to form a cyanide-bridged bimetallic complex is reported for the first time here.

Experimental Section

Starting Materials. The following compounds were prepared by standard literature procedures: methyl isocyanide,[9] *tert*-butyl isocyanide,[10] cyclohexyl isocyanide,[10] isopropyl isocyanide,[10] N,N'-diisopropylethylenediimine (DAP),[11] N,N'-di-*tert*-butyl-

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(1) (a) Purdue University. (b) Massachusetts Institute of Technology.
(2) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* 1980, *19*, 2614.
(3) Mialki, W. S.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* 1981, *20*, 1380.
(4) Dewan, J. C.; Wood, T. E.; Walton, R. A.; Lippard, S. J. *Inorg. Chem.* 1982, *21*, 1854.
(5) Corfield, P. W. R.; Dewan, J. C.; Lippard, S. J. *Inorg. Chem.*, in press.

(6) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* 1982, *1*, 142.
(7) Malatesta, L.; Bonati, F. "Isocyanide Complexes of Metals"; Wiley Interscience: New York, 1969; pp 3-4.
(8) Ito, Y.; Kato, H.; Imai, H.; Saegusa, T. *J. Am. Chem. Soc.* 1982, *104*, 6449 and references cited therein.
(9) Casanova, J., Jr.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* 1963, 4280.
(10) Weber, W. D.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* 1972, *11*, 530.

ethylenediimine (DAB),[11] $Mo_2Cl_4(bpy)_2$,[12] $Mo_2Cl_4(py)_4$,[12] and [Mo(CNR)$_7$](PF$_6$)$_2$,[13] where R = CH$_3$, CHMe$_2$, CMe$_3$, and C$_6$H$_{11}$. 2,2'-Bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me$_2$bpy), 1,10-phenanthroline (phen), 1,10-phenanthroline monohydrate (phen·H$_2$O), and pyrazine were obtained from commercial sources as were all other reagents and solvents. Solvents were used as received with the exception of pyridine which was redistilled twice before use. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was obtained from the reaction of tetra-*n*-butylammonium iodide with KPF$_6$ in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo.

Reaction Procedures. All reactions were carried out in a nitrogen atmosphere; all solvents were dried over molecular sieves and deoxygenated by purging with N$_2$ gas prior to use. In general, KPF$_6$ was always added to the reaction mixtures, where the reacting species started as their PF$_6^-$ salts, in order to prevent formation of products containing the [HPO$_4$]$^{2-}$ counteranion.[6]

A. Reactions of [Mo(CNR)$_7$](PF$_6$)$_2$. (i) [{Mo(CNCMe$_3$)$_4$-(bpy)}$_2$(μ-CN)](PF$_6$)$_3$. A mixture of [Mo(CNCMe$_3$)$_7$](PF$_6$)$_2$ (1.0 g, 1.03 mmol), bpy (1.0 g, 6.41 mmol), and KPF$_6$ (0.25 g, 1.36 mmol) in 30 mL of deoxygenated 1-propanol was refluxed for 24 h. The solution was cooled to 0 °C and filtered to remove a dark red solid from the red filtrate. The addition of 30 mL of a diethyl ether–petroleum ether mixture (1:1) to the filtrate followed by its refrigeration led to a further quantity of red product. The combined red solid was washed with diethyl ether and after being dried in vacuo was redissolved in 15 mL of dichloromethane and filtered to removed any excess KPF$_6$. The red filtrate was reduced in volume under a stream of nitrogen gas, and the addition of diethyl ether precipitated a red crystalline product that was separated by filtration, washed with diethyl ether, and dried in vacuo; yield 0.60 g (72%). Anal. Calcd for C$_{61}$H$_{88}$F$_{18}$Mo$_2$N$_{13}$P$_3$: C, 44.94; H, 5.44; N, 11.17. Found: C, 44.09; H, 5.39; N, 10.63.

Other preparative procedures also produced this complex albeit usually in much lower yields (40% or less). Thus, use of refluxing methanol or toluene gave a low yield of [{Mo(CNCMe$_3$)$_4$-(bpy)}$_2$(μ-CN)](PF$_6$)$_3$ after inconveniently long reflux periods (3 days or more). With acetonitrile as reaction solvent, the desired product was obtained in quite high yield (admixed with starting material) but only after a reaction time of 12 days. On the other hand, 1-pentanol turned out to be as convenient a solvent as 1-propanol, but since it offered no advantage over the latter, it was not used further.

(ii) [{Mo(CNCMe$_3$)$_4$(Me$_2$bpy)}$_2$(μ-CN)](PF$_6$)$_3$. The reaction between [Mo(CNCMe$_3$)$_7$](PF$_6$)$_2$ (0.5 g, 0.517 mmol), Me$_2$bpy (0.5 g, 2.71 mmol), and KPF$_6$ (0.2 g, 1.09 mmol) in refluxing 1-propanol (30 mL) was carried out for 24 h. The resulting red solution was cooled to 0 °C, and toluene (40 mL) was syringed into the reaction mixture. The red-purple solid was collected by filtration, washed with toluene (10 mL) and diethyl ether (20 mL), and dried in vacuo. Any excess of KPF$_6$ was removed by redissolving the red solid in a minimum volume of dichloromethane and filtering. Addition of diethyl ether to the deep red filtrate resulted in the separation of a purple solid that was collected by filtration, washed with diethyl ether, and dried in vacuo; yield 0.26 g (60%). Anal. Calcd for C$_{65}$H$_{96}$F$_{18}$Mo$_2$N$_{13}$P$_3$: C, 46.30; H, 5.74. Found: C, 46.26; H, 5.65.

(iii) [{Mo(CNCMe$_3$)$_4$(phen)}$_2$(μ-CN)](PF$_6$)$_3$. This dark red complex was obtained by a procedure analogous to that in section A(i); yield 70%. Anal. Calcd for C$_{65}$H$_{88}$Mo$_2$N$_{13}$P$_3$F$_{18}$: C, 46.52; H, 5.29; N, 10.85. Found: C, 45.80; H, 5.51; N, 9.79.

(iv) [Mo(CNC$_6$H$_{11}$)$_5$(bpy)](PF$_6$)$_2$. A mixture of [Mo(CN-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$ (1.0 g, 0.920 mmol), bpy (1.0 g, 6.41 mmol), and KPF$_6$ (0.25 g, 1.03 mmol) in 30 mL of deoxygenated 1-propanol was refluxed for 13 h. The solution was cooled to −10 °C in an acetone/ice slush bath, and 30 mL of diethyl ether was syringed into the flask. The orange-red solid that separated was filtered, washed with diethyl ether, and dried in vacuo. The dark red reaction filtrate was reduced in volume to afford a dark red crystalline product. The initial insoluble orange-red reaction

product was washed with 10 mL of methanol to leave a residue of unreacted [Mo(CNC$_6$H$_{11}$)$_7$](PF$_6$)$_2$ (0.74 g). The red-brown methanol filtrate was taken to dryness under a stream of nitrogen gas, and the red solid that resulted was dissolved in 10 mL of dichloromethane. This solution was filtered from small quantities of KPF$_6$ and diethyl ether added to the filtrate to afford a further yield of the dark red product; combined yield 0.16 g (62%). Anal. Calcd for C$_{45}$H$_{63}$F$_{12}$MoN$_7$P$_2$: C, 49.68; H, 5.84. Found: C, 48.80; H, 5.90.

When this same reaction was carried out in refluxing acetonitrile for 24 h, the resulting product was shown by cyclic voltammetry and spectroscopy to be an approximately 40:60 mixture of unreacted [Mo(CNC$_6$H$_{11}$)$_7$](PF$_6$)$_2$ and [Mo(CNC$_6$H$_{11}$)$_5$(bpy)](PF$_6$)$_2$. Similar results were obtained by using 1-butanol or 1-pentanol as reaction solvents. Isolation of spectroscopically pure [Mo-(CNC$_6$H$_{11}$)$_5$(bpy)](PF$_6$)$_2$ could be effected by using column chromatography. However, these procedures offered no advantages over that developed by using 1-propanol as reaction solvent and so they were not pursued further.

(v) [Mo(CNC$_6$H$_{11}$)$_5$(Me$_2$bpy)](PF$_6$)$_2$. A mixture of [Mo(C-NC$_6$H$_{11}$)$_7$](PF$_6$)$_2$ (0.5 g, 0.46 mmol), Me$_2$bpy (0.5 g, 2.71 mmol), and KPF$_6$ (0.2 g, 1.09 mmol) in 40 mL of deoxygenated 1-propanol was refluxed for 60 h. The resulting orange solution was cooled to 0 °C and evaporated to dryness under vacuum. The red solid obtained after successive washing with toluene (100 mL), diethyl ether (50 mL), and petroleum ether (50 mL) was finally collected by filtration, washed with petroleum ether, and dried in vacuo. The cyclic voltammogram of the red powder showed it to be a 60:40 mixture of [Mo(CNC$_6$H$_{11}$)$_5$(Me$_2$bpy)](PF$_6$)$_2$ and [Mo(CN-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$. To isolate the desired reaction product, the mixture was stirred in 125 mL of deoxygenated 1-propanol, thereby dissolving any [Mo(CNC$_6$H$_{11}$)$_5$(Me$_2$bpy)](PF$_6$)$_2$ and leaving as an insoluble residue the unreacted starting material (0.2 g). The orange solution was taken to dryness under vacuum to leave a deep red powder that was washed with toluene (15 mL), diethyl ether (15 mL), petroleum ether (15 mL), and dried in vacuo; yield 0.15 g (53%). Anal. Calcd for C$_{47}$H$_{67}$F$_{12}$MoN$_7$P$_2$: C, 50.59; H, 6.05; N, 8.79. Found: C, 50.65; H, 6.37; N, 8.72.

(vi) [Mo(CNC$_6$H$_{11}$)$_5$(phen)](PF$_6$)$_2$. A mixture of [Mo(CN-C$_6$H$_{11}$)$_7$](PF$_6$)$_2$ (0.2 g, 0.188 mmol), phen (0.3 g, 1.67 mmol), and KPF$_6$ (0.2 g, 1.09 mmol) in 25 mL of deoxygenated 1-propanol was refluxed for 20 h. The reaction mixture was cooled to 0 °C and filtered to remove a dark purple solid from the dark red solution. The isolated solid was washed with diethyl ether and then dissolved in dichloromethane, and the solution was filtered into 20 mL of diethyl ether. The resulting bronze plates that precipitated were filtered, washed with diethyl ether, and dried in vacuo; yield 0.12 g (58%). Anal. Calcd for C$_{47}$H$_{63}$F$_{12}$MoN$_7$P$_2$: C, 50.77; H, 5.71. Found: C, 51.10; H, 5.93.

This complex could be obtained in the same yield by using a procedure similar to that described above but substituting phen·H$_2$O (0.36 g, 1.84 mmol) for phen. The product was found by ^{1}H NMR, IR, and electronic absorption spectroscopy and by cyclic voltammetry to be identical with the product isolated above.

(vii) [Mo(CNCHMe$_2$)$_5$(bpy)](PF$_6$)$_2$. A mixture of [Mo-(CNCHMe$_2$)$_7$](PF$_6$)$_2$ (0.5 g, 0.575 mmol), bpy (0.5 g, 3.20 mmol), and KPF$_6$ (0.2 g, 1.09 mmol) in 40 mL of 1-propanol was refluxed for 24 h. The resulting red solution was cooled to −10 °C and filtered to remove a dark red solid. The product was washed with copious amounts of water, diethyl ether, and petroleum ether and dried in vacuo; yield 0.26 g. This product was shown by cyclic voltammetry (see Results and Discussion) to be a 70:30 mixture of [Mo(CNCHMe$_2$)$_5$(bpy)](PF$_6$)$_2$ ($E_{1/2}$ = +0.87 V, $E_{p,a}$ = +1.64 V and $E_{p,c}$ = −1.20 V) and [Mo(CNCHMe$_2$)$_7$](PF$_6$)$_2$ ($E_{1/2}$ = +1.07 V). No attempt was made to separate the components of this mixture.

(viii) [Mo(CNCH$_3$)$_5$(bpy)](PF$_6$)$_2$. A mixture of [Mo(CN-CH$_3$)$_7$](PF$_6$)$_2$ (0.38 g, 0.391 mmol), bpy (0.38 g, 2.44 mmol), and KPF$_6$ (0.19 g, 1.03 mmol) in 35 mL of deoxygenated 1-propanol was refluxed for 26 h. The orange solution was cooled to 0 °C and filtered to remove a red solid. This product was deduced, on the basis of cyclic voltammetric measurements, to be a 60:40 mixture of the unreacted starting material [Mo(CNCH$_3$)$_7$](PF$_6$)$_2$ ($E_{1/2}$ = +1.01 V) and [Mo(CNCH$_3$)$_5$(bpy)](PF$_6$)$_2$ ($E_{1/2}$ = +0.86 V, $E_{p,c}$ = −1.21 V). No attempt was made to separate the components of this mixture.

(11) Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555.

(12) San Filippo, J., Jr.; Sniadoch, H. J.; Grayson, R. L. *Inorg. Chem.* **1974**, *13*, 2121.

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

B. Reactions of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃. (i) *tert*-Butyl Chloride. The reaction between [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ (0.2 g, 0.123 mmol), KPF₆ (0.5 g, 2.72 mmol), and Me₃CCl (12.6 g, 0.136 mol) in refluxing methanol (15 mL) was carried out for 6 h. The purple solution was cooled to 0 °C and filtered and the filtrate taken to dryness under a stream of nitrogen. The pale purple powder was washed with water and diethyl ether and dried in vacuo. The resulting complex [Mo-(CNCMe₃)₄(bpy)Cl]PF₆ was recrystallized from an acetone–diethyl ether mixture (1:2) and then from a dichloromethane–diethyl ether mixture (1:2); yield 0.15 g (80%). Anal. Calcd for C₃₀H₄₄ClF₆MoN₆P: C, 47.10; H, 5.80; Cl, 4.63. Found: C, 46.68; H, 5.98; Cl, 5.20.

(ii) *tert*-Butyl Isocyanide. A quantity of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ (0.1 g, 0.062 mmol) was dissolved in 10 mL of warm methanol. The addition of various quantities of *tert*-butyl isocyanide to the reaction vessel (stoichiometric ratios of 1:1 to 1:10 for complex to *tert*-butyl isocyanide) always resulted in an immediate color change to orange. Subsequent workup of the reaction mixtures after refluxing them for periods of 1–3 h always yielded complex mixtures. The composition of the mixtures was monitored by cyclic voltammetry of CH₂Cl₂–0.2 M TBAH solutions. The major components were shown to be unreacted starting material, [Mo(CNCMe₃)₇](PF₆)₂, [Mo(CNCMe₃)₅(bpy)](PF₆)₂ (see section C), and what we believe to be [Mo(CNCMe₃)₄(bpy)(CN)]PF₆ ($E_{1/2}$ at +0.54 V vs. SCE).

C. Reaction of [Mo(CNCMe₃)₄(bpy)Cl]PF₆ with *tert*-Butyl Isocyanide. A mixture of [Mo(CNCMe₃)₄(bpy)Cl]PF₆ (0.1 g, 0.131 mmol) and KPF₆ (0.1 g, 0.544 mmol) in 10 mL of methanol was warmed until the solids dissolved. The addition of *tert*-butyl isocyanide (0.02 mL, 0.131 mmol) to the reaction vessel caused the purple solution to change color immediately to a dark red-orange. The reaction mixture was heated for 1 h, cooled to 0 °C, and taken to dryness under a stream of nitrogen. The red solid was collected, washed with water and diethyl ether, and recrystallized from a dichloromethane diethyl ether mixture (1:2); yield 0.11 g (84%). Anal. Calcd for C₃₅H₅₃F₁₂MoN₇P₂: C, 43.89; H, 5.58. Found: C, 43.45; H, 5.60.

D. Formation of the Cyano-Bridged Complex [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ via Dealkylation of a *tert*-Butyl Isocyanide Ligand in [Mo(CNCMe₃)₅(bpy)](PF₆)₂. A mixture of [Mo(CNCMe₃)₅(bpy)](PF₆)₂ (0.185 g, 0.193 mmol) and KPF₆ (0.185 g, 1.01 mmol) in 12 mL of 1-propanol was heated at reflux for 12 h. The solution was cooled to 0 °C and filtered, and the dark red crystalline product was washed with copious amounts of water, diethyl ether, and petroleum ether before drying in vacuo. The product was recrystallized from a dichloromethane–diethyl ether mixture (1:2), yield 0.11 g (70%). Anal. Calcd for C₆₁H₈₈F₁₈Mo₂N₁₃P₃: C, 44.94; H, 5.44. Found: C, 44.53; H, 5.21. The spectroscopic and electrochemical properties of this product were identical with those of samples prepared by using the procedure described in section A(i).

E. Reactions of Mo₂Cl₄(bpy)₂ and Mo₂Cl₄(py)₄ with *tert*-Butyl Isocyanide. (i) [Mo(CNCMe₃)₄(bpy)Cl]PF₆. A quantity of *tert*-butyl isocyanide (0.8 mL, 3.36 mmol) was syringed into a suspension of Mo₂Cl₄(bpy)₂ (0.5 g, 0.79 mmol) in 25 mL of deoxygenated 1-propanol, and the mixture was refluxed for 23 h. The dark red mixture was cooled to 0 °C and filtered to removed a gray residue, and KPF₆ (0.56 g, 3.05 mmol) was then added to the filtrate. This solution was taken to dryness under a stream of nitrogen gas, redissolved in a minimum volume of dichloromethane, and filtered to remove any unreacted KPF₆, and the filtrate was added dropwise to diethyl ether (30 mL). The dark red-purple solid was collected by filtration, washed with diethyl ether, and dried in vacuo. The product was recrystallized from a dichloromethane–diethyl ether mixture (1:2) and twice from an acetone–diethyl ether mixture (1:2) to give a purple solid; yield 0.11 g (15%). Anal. Calcd for C₃₀H₄₄ClF₆MoN₆P: C, 47.10; H, 5.80. Found: C, 45.12; H, 5.80. Although the carbon microanalysis indicated that this product was slightly impure, its spectroscopic and electrochemical properties were identical with those exhibited by samples of this complex prepared as described in section B(i).

In subsequent attempts to repeat this preparation, using the exact procedure described above, the product was always found to be a mixture of [Mo(CNCMe₃)₄(bpy)Cl]PF₆ and [{Mo-(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃.

(ii) [Mo(CNCMe₃)₆(py)](PF₆)₂. This complex was isolated by using a procedure similar to that described in section E(i), but with Mo₂Cl₄(py)₄ in place of Mo₂Cl₄(bpy)₂. The crude yellow powder was recrystallized from a dichloromethane–diethyl ether mixture (2:1) and an acetone–diethyl ether mixture (2:1), washed with diethyl ether, and dried in vacuo; yield 0.24 g (16%). Anal. Calcd for C₃₅H₅₉F₁₂MoN₇P₂: C, 43.62; H, 6.12. Found: C, 43.27; H, 6.45.

F. Reactions of [Mo(CNR)₇](PF₆)₂ (R = CH₃, C₆H₁₁, and CMe₃) with Other Nitrogen Donors. Selected reactions of [Mo(CNR)₇](PF₆)₂ with the nitrogen donors pyrazine (pyz), N,N′-diisopropylethylenediimine (DAP), and N,N′-di-*tert*-butylethylenediimine (DAB) were attempted but in no instance was a complex isolated that contained these ligands. Thus, [Mo(CNCH₃)₇](PF₆)₂ and [Mo(CNC₆H₁₁)₇](PF₆)₂ failed to react with DAB in refluxing 1-propanol with reaction periods up to 12 h. In the case of the reactions between [Mo(CNCMe₃)₇](PF₆)₂ and pyz, DAP, and DAB, dealkylation occurred to give [Mo-(CNCMe₃)₆(CN)]PF₆. A typical procedure is as follows. A mixture of [Mo(CNCMe₃)₇](PF₆)₂ (0.5 g, 0.517 mmol) and DAB (0.75 g, 4.46 mmol) in 25 mL of deoxygenated 1-propanol was refluxed for 15 h. The yellow solution was cooled to 0 °C and filtered, and the pale yellow precipitate obtained was washed several times with diethyl ether. The solid was recrystallized from a mixture of acetone–diethyl ether (1:2) and was collected by filtration, washed with diethyl ether, and dried in vacuo, yield 0.37 g (94%). Anal. Calcd for C₃₁H₅₄F₆MoN₇P: C, 48.63; H, 7.11. Found: C, 47.49; H, 6.75. The identity of this complex was confirmed by comparison of its spectroscopic and electrochemical properties with those exhibited by an authentic sample of [Mo(CNCMe₃)₆(CN)]PF₆.[6,14]

Preparation of Single Crystals of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃. Crystals suitable for an X-ray crystallographic study were obtained by refluxing a mixture of [Mo(CNCMe₃)₇](PF₆)₂, bpy, and KPF₆ in 1-propanol using the recipe described in section A(i) with the exception that a white birch boiling stick ("Puritan Applicator") was added to the contents of the reaction flask. During the course of the reaction (24-h reflux period) the boiling stick not only prevented bumping of the reaction mixture but also, more importantly, served as a means of nucleating crystal growth. Dark red crystals grew on the stick and were harvested by removing it from the reaction flask upon completion of the reaction (24 h). The crystals were washed with water and then diethyl ether but were otherwise untreated.

X-ray Crystallography. The dark red crystal of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ used for the diffraction study was of approximate dimensions 0.15 mm × 0.20 mm × 0.37 mm bounded by the faces {021}, {120}, (010), and (01̄0). Study on the diffractometer and Weissenberg photographs showed the crystal to belong to the monoclinic system, space group $P2_1/n$ (C_{2h}^5, No. 14, in a nonstandard setting). Data collection and reduction proceeded by methods standard in our laboratory,[15] the details of which are presented in Table I. Because of the large value of b, data were collected by using Cu radiation to avoid overlapping of peaks in the counter window.

The positions of the molybdenum atoms were found by using direct methods. All the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Although inspection of the positional parameters of these atoms showed them to be approximately related by a twofold symmetry axis parallel to b, a systematic search failed to reveal an alternative space group with higher symmetry. Anisotropic thermal parameters were used in the refinement of the molybdenum and bridging cyanide atoms. All other atoms were refined with isotropic thermal parameters. The hydrogen atoms of the N,N′-bipyridine rings were placed at calculated positions [d(C–H) = 0.95 Å] and constrained to "ride" on the carbon atoms to which they are attached. Owing to the very large size of the structure (97 non-hydrogen atoms in the asymmetric unit), no hydrogen atoms were assigned to the *tert*-butyl groups nor was there any attempt made to account for

(14) Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860.

(15) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

Table I. Experimental Details of the X-ray Diffraction
Study of [{Mo(CNCMe$_3$)$_4$(bpy)}$_2$(μ-CN)](PF$_6$)$_3$
(Mo$_2$P$_3$F$_{18}$N$_{13}$C$_{61}$H$_{80}$)

(A) Crystal Parameters[a] at 23 °C

a = 13.964 (2) Å	space group = $P2_1/n$
b = 37.734 (4) Å	fw = 1630.2
c = 16.933 (2) Å	Z = 4
β = 104.17 (1)°	ρ calcd = 1.252 g/cm^3
V = 8650.8 Å^3	ρ obsd[b] = 1.30 (1) g/cm^3

(B) Measurement and Treatment of Intensity Data[c]

instrument:	Enraf-Nonius CAD-4F kappa geometry diffractometer
radiation:	Cu Kα ($\lambda_{\bar{\alpha}}$ = 1.5418 Å), nickel filtered
scan range:	3° < 2θ < 110°
check reflctns:	(2,0,$\bar{2}$), (1,1,2), and (1,$\bar{5}$,$\bar{1}$), monitored every 9000 s, varied randomly with a net 1% decay
no. of unique data collected:	10764, 4177 of which has $I > 2\sigma(I)$
abs correct:	
cryst size:	0.15 × 0.20 × 0.37 mm
linear abs coeff:	37.9 cm^{-1}
transmissn factors:	0.45–0.65

(C) Final Model in the Least-Squares Refinement[d]

final R values:[e]	R_1 = 0.079; R_2 = 0.092
no. of observn:	4177
no. of parameters:	515
highest peak in final difference map:	0.8 e/Å^3

[a] From a least-squares fit to the setting angles of 25 reflections with 2θ in the range 50–100°. [b] By neutral buoyancy in toluene–carbon tetrachloride. [c] For procedures used in our laboratory, see ref 15. [d] Refinements were carried out with unit weights and the use of G. Sheldrick's SHELX program. Anisotropic thermal parameters for Mo, P, F, and bridging CN group atoms only were used. Positions of H atoms were refined, "riding" at C–H distances of 0.95 Å. [e] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$; $R_2 = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w|F_o|^2]^{1/2}$.

their disorder, evident on difference Fourier maps. The hydrogen atoms of the bipyridine rings were refined with a common isotropic thermal parameter. A final difference Fourier map showed peaks ~0.8 e/Å^3 that could have been due to the presence of residual solvent, since the crystals were washed with ether and water. Additional mass would bring the calculated density into better agreement with that observed (Table I). No attempt was made to account for this possibility in the model, however.

Least-squares refinement converged to the R indices listed in Table I. Final positional and thermal parameters are given in Table II, and details of the molecular geometry are supplied in Table III. A listing of observed and calculated structure factors is provided as Table S1.[16]

Physical Measurements. IR spectra of Nujol mulls were recorded in the region 4000–400 cm^{-1} between KBr plates on a Beckman IR-12 spectrophotometer. Solution IR spectra were taken in dichloromethane in the 2200–1550 cm^{-1} region. Nuclear magnetic resonance spectra were recorded by using Perkin-Elmer R-32 and Varian XL-200 spectrometers. Resonances were referenced internally, usually to impurities in the deuterated solvents used. Electronic absorption spectra were recorded on methanol solutions by using a Varian series 634 spectrophotometer.

Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, taken as $(E_{p,a} + E_{p,c})/2$, were referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7015B x-y recorder. All voltammetric measurements were made at a

platinum bead electrode in solutions deaerated in a stream of nitrogen.

Elemental microanalyses were performed by Dr. H. D. Lee and Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

The reactions of the homoleptic species [Mo(CNR)$_7$]$^{2+}$ (R = alkyl group) with monodentate and bidentate tertiary phosphines produce yellow or orange colored seven-coordinate substitution products in which up to two isocyanide ligands have been replaced.[2-4] While the corresponding thermal reactions with pyridine do not appear to proceed within reasonable periods of time (up to 2 days), the reactions with 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (Me$_2$bpy), and 1,10-phenanthroline (phen) lead to intense red-purple solutions which upon workup afford products whose identity depends upon the nature of the alkyl ligand in the [Mo(CNR)$_7$](PF$_6$)$_2$ starting material.

Reactions of [Mo(CNCy)$_7$](PF$_6$)$_2$ with bpy, Me$_2$bpy, and phen. The dark red-purple products formed when these reactions are carried out in refluxing 1-propanol were, in all instances, identified as being of stoichiometry [Mo(CNC$_6$H$_{11}$)$_5$(N–N)](PF$_6$)$_2$ (N–N represents bpy, Me$_2$bpy, or phen). The complexes prepared by this procedure are listed in Table IV along with certain of their IR and electronic absorption spectral properties. An especially noteworthy feature is the occurrence of an intense Mo(4d) → N–N(π^*) electronic transition at ca. 510 nm, the existence of which explains the striking color difference between these complexes and their phosphine analogues.[2,3] The ^{1}H NMR spectra of all three complexes (Table V) are typical of normal chelating bpy, Me$_2$bpy, and phen groups.[17] Integration of these resonances and those arising from the cyclohexyl isocyanide ligands showed excellent agreement with the expected stoichiometric ratios of these ligands.

The reactions of the methyl isocyanide and isopropyl isocyanide complexes [Mo(CNR)$_7$](PF$_6$)$_2$ with bpy proceeded in a similar fashion to those described above, but these reactions were slower than that between [Mo(CNCy)$_7$](PF$_6$)$_2$ and bpy. The products were identified on the basis of the similarity of their electrochemical properties (see Experimental Section) to those of authentic complexes of the type [Mo(CNR)$_5$(N–N)](PF$_6$)$_2$.

The synthesis of [Mo(CNCy)$_5$(N–N)](PF$_6$)$_2$ by the one-pot procedure outlined above contrasts with the only previous report on a complex of the type [Mo(CNR)$_5$-(N–N)]X$_2$, viz., [Mo(CNEt)$_5$(bpy)](BF$_4$)$_2$.[18] The latter compound was prepared from Mo(CO)$_2$(bpy)$_2$ via the intermediate formation of [Mo(CO)$_2$(bpy)$_2$(NCMe)](BF$_4$)$_2$.

Reactions of [Mo(CNCMe$_3$)$_7$](PF$_6$)$_2$ with bpy, Me$_2$bpy, and phen. The products emanating from reactions carried out under conditions similar to those already described for [Mo(CNCy)$_7$](PF$_6$)$_2$ had spectroscopic and electrochemical properties (vide infra) that were inconsistent with the formulation [Mo(CNCMe$_3$)$_5$(N–N)](PF$_6$)$_2$, even though the microanalytical elemental analyses were in close agreement with such a stoichiometry. Although the C≡N stretching bands in the IR spectra of these complexes were somewhat different from those of [Mo(CNCy)$_5$(N–N)](PF$_6$)$_2$ (Table IV), these differences could not be interpreted in terms of any obvious structural dissimilarities. Both sets of complexes possess similar electronic absorption spectra, with the exception that the

(16) Supplementary material.

(17) See, for example: Kitagaiwa, S.; Munakata, M.; Miyaji, N. *Inorg. Chem.* **1982**, *21*, 3842.
(18) Connor, J. A.; James, E. J.; Overton, C. *J. Organomet. Chem.* **1981**, *218*, C31.

Table II. Final Positional and Thermal Parameters for [{Mo(CN-t-Bu)₄(bpy)}₂(μ-CN)](PF₆)₃^{a,b}

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	0.35949 (12)	0.35962 (5)	0.64897 (9)	0.0424 (12)	0.0472 (11)	0.0376 (10)	0.0045 (10)	0.0077 (9)	0.0001 (9)
Mo(2)	0.64730 (12)	0.35453 (5)	0.93832 (9)	0.0421 (11)	0.0472 (10)	0.0383 (10)	-0.0055 (10)	0.0098 (8)	0.0015 (9)
P(1)	0.5039 (8)	0.2144 (2)	0.2941 (6)	0.084 (5)	0.107 (7)	0.081 (5)	-0.009 (6)	0.017 (5)	-0.001 (5)
P(2)	0.7092 (7)	0.4359 (3)	0.4857 (6)	0.085 (7)	0.147 (9)	0.089 (7)	0.038 (7)	0.025 (6)	0.020 (6)
P(3)	0.2939 (7)	0.4311 (3)	0.1036 (5)	0.094 (7)	0.135 (8)	0.069 (6)	-0.037 (6)	0.025 (5)	0.001 (6)
F(1)	0.5942 (19)	0.2159 (10)	0.3575 (18)	0.13 (2)	0.41 (5)	0.24 (3)	-0.01 (3)	-0.06 (2)	0.00 (3)
F(2)	0.559 (2)	0.2124 (7)	0.2276 (16)	0.31 (4)	0.25 (3)	0.21 (3)	-0.08 (2)	0.20 (3)	-0.04 (2)
F(3)	0.507 (2)	0.1732 (5)	0.300 (2)	0.27 (3)	0.106 (16)	0.33 (3)	0.02 (2)	0.15 (3)	0.01 (2)
F(4)	0.502 (3)	0.2530 (5)	0.2914 (19)	0.36 (4)	0.082 (15)	0.29 (3)	-0.01 (2)	0.00 (3)	0.01 (2)
F(5)	0.4133 (19)	0.2114 (9)	0.2297 (16)	0.16 (2)	0.32 (4)	0.21 (3)	-0.04 (2)	-0.08 (2)	-0.03 (3)
F(6)	0.446 (2)	0.2139 (7)	0.3595 (16)	0.29 (3)	0.25 (3)	0.21 (3)	0.06 (2)	0.17 (3)	0.04 (2)
F(7)	0.6238 (19)	0.4288 (9)	0.420 (2)	0.15 (2)	0.30 (4)	0.29 (4)	0.04 (2)	-0.11 (3)	-0.05 (3)
F(8)	0.663 (2)	0.4693 (6)	0.5053 (16)	0.33 (4)	0.17 (2)	0.21 (2)	0.10 (2)	0.13 (3)	-0.015 (19)
F(9)	0.7506 (20)	0.4004 (7)	0.4622 (17)	0.21 (3)	0.22 (3)	0.25 (3)	0.08 (2)	0.11 (2)	0.05 (2)
F(10)	0.656 (3)	0.4146 (7)	0.5389 (19)	0.33 (4)	0.20 (3)	0.28 (3)	0.03 (2)	0.24 (3)	0.04 (2)
F(11)	0.797 (2)	0.4381 (10)	0.5523 (18)	0.23 (3)	0.39 (5)	0.19 (3)	-0.10 (3)	-0.09 (3)	-0.04 (3)
F(12)	0.758 (3)	0.4531 (8)	0.4286 (18)	0.36 (4)	0.26 (3)	0.24 (3)	0.03 (3)	0.19 (3)	0.03 (2)
F(13)	0.283 (2)	0.3988 (6)	0.1521 (13)	0.42 (4)	0.150 (19)	0.149 (19)	-0.03 (2)	0.15 (2)	0.040 (16)
F(14)	0.3001 (16)	0.4644 (6)	0.0501 (13)	0.18 (2)	0.17 (2)	0.173 (20)	-0.006 (16)	0.054 (16)	0.051 (17)
F(15)	0.3938 (20)	0.4237 (13)	0.100 (2)	0.113 (20)	0.67 (8)	0.34 (5)	0.12 (3)	0.11 (3)	0.27 (5)
F(16)	0.329 (4)	0.4506 (8)	0.1773 (14)	0.62 (7)	0.28 (3)	0.096 (17)	-0.28 (4)	0.09 (3)	-0.054 (19)
F(17)	0.264 (3)	0.4101 (7)	0.0297 (12)	0.52 (6)	0.17 (2)	0.079 (15)	-0.07 (3)	0.00 (2)	-0.026 (14)
F(18)	0.196 (2)	0.4388 (9)	0.103 (3)	0.15 (3)	0.24 (4)	0.68 (8)	0.05 (3)	0.20 (4)	0.07 (5)
CN(1)	0.9722 (14)	0.1467 (5)	0.2628 (11)	0.065 (13)	0.037 (11)	0.043 (10)	0.001 (11)	0.006 (10)	-0.010 (11)
CN(2)	0.0328 (13)	0.1500 (5)	0.3230 (11)	0.044 (12)	0.053 (13)	0.045 (11)	-0.002 (11)	0.019 (9)	-0.012 (10)

atom	x	y	z	U, Å²	atom	x	y	z	U, Å²
N(1B)	0.9112 (11)	0.0846 (4)	0.1619 (9)	0.043 (4)	C(71)	0.2093 (17)	0.2637 (6)	0.3881 (14)	0.070 (7)
N(2B)	0.7839 (11)	0.1138 (4)	0.2338 (9)	0.044 (4)	C(72)	0.124 (2)	0.2862 (8)	0.4097 (17)	0.111 (10)
N(3B)	0.7221 (12)	0.3831 (4)	-0.1443 (9)	0.050 (4)	C(73)	0.205 (2)	0.2668 (7)	0.2971 (17)	0.103 (9)
N(4B)	0.0899 (12)	0.0904 (4)	0.4238 (9)	0.051 (4)	C(74)	0.312 (2)	0.2754 (7)	0.4375 (17)	0.102 (9)
N(11)	0.6277 (14)	0.1437 (5)	0.0666 (10)	0.073 (5)	C(81)	0.8923 (17)	0.1998 (6)	0.5320 (14)	0.065 (6)
N(21)	0.3788 (13)	0.1499 (5)	0.5235 (10)	0.064 (5)	C(82)	0.907 (2)	0.1892 (7)	0.6239 (16)	0.098 (9)
N(31)	0.1755 (14)	0.1201 (5)	0.6236 (12)	0.072 (6)	C(83)	0.803 (2)	0.1860 (8)	0.4717 (17)	0.107 (10)
N(41)	0.8270 (14)	0.1123 (5)	-0.0332 (13)	0.080 (6)	C(84)	0.904 (2)	0.2408 (8)	0.5270 (17)	0.103 (9)
N(51)	0.0253 (14)	0.1790 (5)	0.0751 (10)	0.066 (5)	C(1B)	0.9805 (15)	0.0714 (6)	0.1282 (12)	0.060 (6)
N(61)	0.8107 (13)	0.2221 (5)	0.1740 (11)	0.068 (5)	H(1B)	0.0157 (15)	0.0873 (6)	0.1022 (12)	0.074 (7)
N(71)	0.1949 (13)	0.2266 (5)	0.4059 (10)	0.064 (5)	C(2B)	0.0034 (18)	0.0353 (6)	0.1291 (14)	0.13 (3)
N(81)	0.9817 (13)	0.1853 (5)	0.5073 (10)	0.062 (5)	H(2B)	0.0544 (18)	0.0268 (6)	0.1058 (14)	0.083 (8)
C(1)	0.7116 (16)	0.1437 (6)	0.0918 (12)	0.062 (16)	C(3B)	0.9515 (18)	0.0132 (7)	0.1641 (14)	0.13 (3)
C(2)	0.2921 (15)	0.1476 (6)	0.4947 (12)	0.056 (6)	H(3B)	0.9629 (18)	-0.0116 (7)	0.1617 (14)	0.073 (7)
C(3)	0.1681 (16)	0.1295 (6)	0.5572 (14)	0.064 (6)	C(4B)	0.8837 (17)	0.0246 (6)	0.2025 (14)	0.13 (3)
C(4)	0.8369 (15)	0.1241 (6)	0.0316 (13)	0.059 (6)	H(4B)	0.8484 (17)	0.0086 (6)	0.2283 (14)	0.053 (6)
C(5)	0.9643 (17)	0.1660 (6)	0.0993 (14)	0.065 (7)	C(5B)	0.8672 (15)	0.0620 (5)	0.2025 (12)	0.056 (6)
C(6)	0.8289 (15)	0.1930 (6)	0.1620 (12)	0.055 (6)	C(6B)	0.7984 (15)	0.0789 (6)	0.2431 (12)	0.071 (7)
C(7)	0.1784 (15)	0.1972 (6)	0.4195 (12)	0.059 (6)	C(7B)	0.7539 (17)	0.0603 (6)	0.2983 (13)	0.13 (3)
C(8)	0.0413 (16)	0.1717 (5)	0.4852 (12)	0.054 (6)	H(7B)	0.7645 (17)	0.0356 (6)	0.3067 (13)	0.083 (8)
C(11)	0.5241 (19)	0.1323 (7)	0.0415 (15)	0.079 (7)	C(8B)	0.6969 (19)	0.0782 (7)	0.3381 (15)	0.13 (3)
C(12)	0.515 (3)	0.1089 (9)	-0.030 (2)	0.143 (13)	H(8B)	0.6676 (19)	0.0657 (7)	0.3747 (15)	0.13 (3)
C(13)	0.502 (3)	0.1131 (10)	0.114 (2)	0.169 (15)	C(9B)	0.6795 (18)	0.1137 (7)	0.3280 (14)	0.081 (8)
C(14)	0.461 (3)	0.1634 (12)	0.029 (3)	0.184 (17)	H(9B)	0.6378 (18)	0.1261 (7)	0.3553 (14)	0.13 (3)

Atom				B
C(10B)	0.7283(16)	0.1311(6)	0.2734(13)	0.066(7)
H(10B)	0.7205(16)	0.1559(6)	0.2657(13)	0.13(3)
C(11B)	0.7850(16)	0.3670(6)	-0.1797(12)	0.062(6)
H(11B)	0.8265(16)	0.3502(6)	-0.1968(12)	0.13(2)
C(12B)	0.3310(18)	0.1146(7)	0.2634(14)	0.083(8)
H(12B)	0.3589(18)	0.1376(7)	0.2642(14)	0.13(2)
C(13B)	0.3048(20)	0.0806(8)	0.2487(16)	0.096(9)
H(13B)	0.3323(20)	0.0676(8)	0.2114(16)	0.13(2)
C(14B)	0.2425(20)	0.0641(7)	0.2842(15)	0.089(8)
H(14B)	0.2009(20)	0.0475(7)	0.3018(15)	0.13(2)
C(15B)	0.7007(15)	0.4171(5)	-0.1607(12)	0.054(6)
C(16B)	0.1256(16)	0.0681(6)	0.3761(13)	0.062(6)
C(17B)	0.0893(17)	0.0329(6)	0.3648(14)	0.077(7)
H(17B)	0.1164(17)	0.0170(6)	0.3325(14)	0.13(2)
C(18B)	0.0175(18)	0.0213(7)	0.3988(14)	0.083(8)
H(18B)	0.9962(18)	-0.0027(7)	0.3925(14)	0.13(2)
C(19B)	0.9750(19)	0.0448(7)	0.4431(15)	0.086(8)
H(19B)	0.9211(19)	0.0382(7)	0.4649(15)	0.13(2)
C(20B)	0.0160(15)	0.0789(6)	0.4537(12)	0.061(6)
H(20B)	0.9888(15)	0.0952(6)	0.4851(12)	0.13(2)
C(21)	0.4839(18)	0.1372(7)	0.5479(14)	0.078(7)
C(22)	0.497(3)	0.1191(9)	0.627(2)	0.139(12)
C(23)	0.505(3)	0.1172(9)	0.481(2)	0.137(12)
C(24)	0.547(3)	0.1687(10)	0.556(2)	0.151(13)
C(31)	0.1828(17)	0.1057(6)	0.7053(14)	0.067(6)
C(32)	0.110(2)	0.1264(8)	0.7416(18)	0.120(11)
C(33)	0.150(2)	0.0678(9)	0.6950(19)	0.122(11)
C(34)	0.286(2)	0.1131(8)	0.7553(18)	0.107(10)
C(41)	0.819(2)	0.0962(7)	-0.1142(16)	0.089(8)
C(42)	0.895(3)	0.1154(9)	-0.150(2)	0.138(12)
C(43)	0.712(2)	0.1031(8)	-0.1663(18)	0.107(9)
C(44)	0.847(3)	0.0594(10)	-0.106(2)	0.142(13)
C(51)	0.1107(19)	0.1944(7)	0.0488(15)	0.081(8)
C(52)	0.104(2)	0.1836(7)	-0.0362(17)	0.102(9)
C(53)	0.102(2)	0.2345(8)	0.0598(18)	0.111(10)
C(54)	0.204(2)	0.1791(8)	0.1071(18)	0.113(10)
C(61)	0.7978(18)	0.2591(7)	0.1950(14)	0.075(7)
C(62)	0.878(2)	0.2808(8)	0.1690(17)	0.109(10)
C(63)	0.8018(20)	0.2614(7)	0.2870(16)	0.097(9)
C(64)	0.693(2)	0.2706(8)	0.1437(17)	0.108(10)

a Numbers in parentheses are errors in the last significant digit(s). See Figures 3 and 4 for atom labeling scheme. b Anisotropic thermal parameters are of the form exp$[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

Mo(4d) → N–N(π^*) electronic transition at ca. 520 nm in the spectra of the tert-butyl isocyanide complexes had an extinction coefficient that was approximately twice that of the corresponding band in the spectra of [Mo-(CNCy)$_5$(N–N)](PF$_6$)$_2$ (Table IV). The most striking spectroscopic difference between these two groups of complexes, however, was seen in a comparison of their ^{1}H NMR spectra (Figure 1 and Table V). The more complicated spectra of the tert-butyl isocyanide products (see parts a and c of Figure 1 in the case of the bpy and Me$_2$bpy complexes) led us to suspect the presence of two inequivalent pyridine rings in these ligands, which could result from monodentate coordination, an unsymmetrical binuclear complex, or the presence of inequivalent halves of a single coordinated bidentate ligand. The first possibility seemed unlikely since the complexes containing the rigid phen ligand showed these same characteristics. Spin decoupling experiments carried out on the tert-butyl isocyanide derivative containing the Me$_2$bpy ligand revealed resonances due either to two inequivalent Me$_2$bpy ligands or to inequivalent halves of the Me$_2$bpy ligand. These resonances are labeled A and B in Figure 1c and consist of a characteristic doublet, singlet, doublet pattern. The doublet farthest upfield (δ 7.76) in Figure 1c has twice the relative intensity compared to the singlets and doublets at lower fields and arises from the accidental coincidence of separate doublets due to ligands A and B. Since the ^{1}H NMR spectral results could be interpreted only in terms of tert-butyl isocyanide complexes possessing two inequivalent pyridine rings of the bidentate nitrogen donors, a binuclear structure seemed to be the only reasonable alternative in the light of the microanalytical data we had obtained. This interpretation was supported by the electrochemical properties of these complexes.

Electrochemical Properties. The electrochemical properties of the cyclohexyl isocyanide complexes [Mo-(CNCy)$_5$(N–N)](PF$_6$)$_2$ are in accord with those expected on the basis of existing data for [Mo(CNR)$_7$](PF$_6$)$_2$ and various mixed isocyanide–phosphine complexes of molybdenum(II).[2,3,14] The voltammetric half-wave potentials vs. SCE for 0.2 M TBAH–dichloromethane solutions, as measured by the cyclic voltammetric technique, are presented in Table VI, and the cyclic voltammogram of [Mo(CNC$_6$H$_{11}$)$_7$(bpy)](PF$_6$)$_2$ is shown in Figure 2b. Each complex exhibits a couple at ca. +0.9 V, corresponding to a one-electron oxidation (as determined by coulometry) which is characterized by $i_{p,a}/i_{p,c} = 1$ and a constant $i_p/\nu^{1/2}$ ratio for sweep rates between 50 and 400 mV/s. The potential separation between the anodic and cathodic peaks, ΔE_p, was close to 75 mV for a sweep rate of 200 mV/s and increased slightly with increase in sweep rate. These observations are in accord with this being a quasi-reversible electron-transfer process. Additionally, these complexes show an irreversible oxidation close to +1.7 V and an irreversible reduction at ca. –1.3 V. The latter reduction is followed, on the reverse sweep, by the appearance of product waves at ca. –0.9 and –0.15 V vs. SCE. Similar electrochemical properties were found for the methyl and isopropyl isocyanide complexes [Mo(CNR)$_5$-(bpy)](PF$_6$)$_2$ (see Experimental Section).

In striking contrast to this behavior, the tert-butyl isocyanide complexes have cyclic voltammograms that display two very close reversible oxidations in the vicinity of the single reversible oxidation of [Mo(CNCy)$_5$(N–N)](PF$_6$)$_2$, plus two irreversible reductions ($E_{p,c} \simeq$ –1.4 and –1.6 V). These data are given in Table VI, and the cyclic voltammogram of the bpy derivative is shown in Figure 2a. These observations, along with the ^{1}H NMR spectral results,

Table III. Interatomic Distances (A) and Angles (deg) for [{Mo(CNCMe$_3$)$_4$(bpy)}$_2$(μ-CN)](PF$_6$)$_3$ [a]

Coordination Sphere
Bond Distances

Mo(1)-C(1)	2.059 (20)	Mo(2)-C(2)	2.015 (20)
Mo(1)-C(4)	2.030 (22)	Mo(2)-C(3)	2.053 (23)
Mo(1)-C(5)	2.094 (26)	Mo(2)-C(7)	2.043 (22)
Mo(1)-C(6)	2.056 (21)	Mo(2)-C(8)	2.092 (23)
Mo(1)-CN(1)	2.182 (17)	Mo(2)-CN(2)	2.208 (16)
Mo(1)-N(1B)	2.220 (15)	Mo(2)-N(3B)	2.220 (17)
Mo(1)-N(2B)	2.219 (17)	Mo(2)-N(4B)	2.220 (16)

Bond Angles

C(6)-Mo(1)-N(1B)	167.8 (6)	C(7)-Mo(2)-N(4B)	164.3 (6)
C(5)-Mo(1)-N(2B)	163.4 (7)	C(8)-Mo(2)-N(3B)	162.7 (6)
C(1)-Mo(1)-CN(1)	146.3 (8)	C(2)-Mo(2)-CN(2)	147.3 (8)
C(4)-Mo(1)-CN(1)	143.4 (8)	C(3)-Mo(2)-CN(2)	142.1 (8)
C(4)-Mo(1)-N(2B)	120.8 (7)	C(2)-Mo(2)-C(8)	121.5 (8)
C(1)-Mo(1)-C(5)	120.2 (9)	C(3)-Mo(2)-N(3B)	120.0 (7)
C(4)-Mo(1)-C(6)	114.3 (8)	C(7)-Mo(2)-C(3)	116.7 (8)
C(1)-Mo(1)-N(1B)	111.6 (7)	C(2)-Mo(2)-N(4B)	112.5 (7)
C(5)-Mo(1)-N(1B)	103.6 (8)	C(8)-Mo(2)-N(4B)	102.5 (7)
C(6)-Mo(1)-N(2B)	102.9 (7)	C(7)-Mo(2)-N(3B)	102.4 (8)
C(6)-Mo(1)-CN(1)	85.6 (7)	C(7)-Mo(2)-CN(2)	85.6 (7)
C(5)-Mo(1)-CN(1)	83.2 (8)	C(8)-Mo(2)-CN(2)	82.7 (7)
CN(1)-Mo(1)-N(1B)	82.5 (6)	C(3B)-Mo(2)-CN(2)	80.3 (6)
CN(1)-Mo(1)-N(2B)	80.3 (6)	N(4B)-Mo(2)-CN(2)	79.1 (6)
C(6)-Mo(1)-C(1)	77.4 (8)	C(2)-Mo(2)-C(7)	79.0 (8)
C(6)-Mo(1)-C(5)	77.4 (9)	C(7)-Mo(2)-C(8)	78.7 (9)
C(4)-Mo(1)-N(1B)	77.2 (7)	C(3)-Mo(2)-N(4B)	78.2 (7)
C(1)-Mo(1)-N(2B)	75.5 (7)	C(2)-Mo(2)-N(3B)	75.2 (7)
C(4)-Mo(1)-C(5)	72.7 (9)	C(3)-Mo(2)-C(8)	73.2 (8)
N(2B)-Mo(1)-N(1B)	72.7 (6)	N(3B)-Mo(2)-N(4B)	71.8 (6)
C(4)-Mo(1)-C(1)	70.1 (9)	C(2)-Mo(2)-C(3)	70.3 (9)

Ligand Geometry
(i) *tert*-Butyl Isocyanide Groups
Bond Distances

min C-N	1.12 (3)	min N-C	1.46 (3)
max C-N	1.19 (3)	max N-C	1.51 (3)
mean C-N	1.15 (1)	mean N-C	1.48 (1)
min C-C(methyl)	1.44 (5)		
max C-C(methyl)	1.57 (4)		
mean C-C(methyl)	1.516 (8)		

Bond Angles

min Mo-C-N	173.1 (20)	min C-N-C	156.1 (20)
max Mo-C-N	177.7 (17)	max C-N-C	177.1 (22)
mean Mo-C-N	175.9 (7)	mean C-N-C	171.3 (7)
min N-C-C(methyl)	104.0 (20)	min C-C-C(methyl)	105.6 (27)
max N-C-C(methyl)	110.8 (23)	max C-C-C(methyl)	118.4 (22)
mean N-C-C(methyl)	107.2 (4)	mean C-C-C(methyl)	111.6 (5)

(ii) *N,N'*-Bipyridine Groups
Bond Distances

min N-C	1.32 (3)	min C-C	1.33 (4)
max N-C	1.34 (3)	max C-C	1.46 (3)
mean N-C	1.331 (11)	mean C-C	1.393 (7)

Bond Angles

min Mo-N-C	116.0 (14)	min C-N-C	117.2 (17)
max Mo-N-C	124.2 (13)	max C-N-C	121.2 (19)
mean Mo-N-C	120.5 (5)	mean C-N-C	118.8 (9)
min N-C-C	113.7 (18)	min C-C-C	115.5 (24)
max N-C-C	125.4 (22)	max C-C-C	124.9 (21)
mean N-C-C	119.8 (6)	mean C-C-C	120.2 (6)

(iii) Bridging Cyanide Group
Bond Distances

CN(1)-CN(2)	1.16 (2)		
Mo(1)-CN(1)-CN(2)	179.4 (19)	Mo(2)-CN(2)-CN(1)	169.3 (17)

Anion Geometry
Group 1
Bond Distances

min P-F	1.44 (3)
max P-F	1.56 (2)
mean P-F	1.49 (1)

Table III *(Continued)*

Bond Angles

min cis-F-P-F	86.7 (16)	min trans-F-P-F	176.1 (16)
max cis-F-P-F	92.8 (18)	max trans-F-P-F	178.4 (18)
mean cis-F-P-F	90.0 (5)	mean trans-F-P-F	177.4 (11)

Group 2

Bond Distances

min P-F	1.44 (3)
max P-F	1.55 (3)
mean P-F	1.49 (1)

Bond Angles

min cis-F-P-F	85.7 (19)	min trans-F-P-F	172.5 (22)
max cis-F-P-F	96.1 (19)	max trans-F-P-F	176.5 (16)
mean cis-F-P-F	89.9 (5)	mean trans-F-P-F	174.2 (11)

Group 3

Bond Distances

min P-F	1.39 (4)
max P-F	1.56 (2)
mean P-F	1.46 (1)

Bond Angles

min cis-F-P-F	86.2 (24)	min trans-F-P-F	176.3 (25)
max cis-F-P-F	95.7 (23)	max trans-F-P-F	176.9 (15)
mean cis-F-P-F	90.0 (6)	mean trans-F-P-F	176.7 (13)

a Standard deviations quoted for mean values are obtained by dividing the average of the individual standard deviations by the square root of the number of observations being averaged.

suggested that the different properties and behavior of the cyclohexyl isocyanide vs. *tert*-butyl isocyanide systems arose because the latter possessed ligand-bridged dimolybdenum(II) units in which each metal was coordinated by one bidentate nitrogen donor and the requisite number of isocyanides. The only feasible bridging ligand was cyanide, formed by the dealkylation of one of the *tert*-butyl isocyanide ligands. Such a dealkylation process has been recognized previously[6] in the conversion of [M-(CNCMe₃)₇]²⁺ cations (M = Mo or W) to [M(CNCMe₃)₆-(CN)]⁺. The formulation that appeared most consistent with the spectroscopic, electrochemical, and microanalytical data was [{Mo(CNCMe₃)₄(N-N)}₂(μ-CN)](PF₆)₃, and this conclusion was confirmed by a crystal structure determination of the bpy derivative.

Crystal Structure of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃. As shown in Figure 3, the structure consists of two Mo(CNCMe₃)₄(bpy) fragments joined by a bridging cyanide ligand. The end-for-end disorder of the latter could not be resolved in the structure analysis so both atoms of the cyanide group were assigned a composite carbon–nitrogen scattering factor. Although the [{Mo-(CNCMe₃)₄(bpy)}₂(μ-CN)]³⁺ cation has no crystallographically required symmetry, an approximate twofold axis passes through the midpoint of the bridging cyano ligand. A view of the cation approximately perpendicular to this pseudotwofold axis is given in Figure 4.

Comparison of the angles at both molybdenum atoms with values for various idealized seven-coordinate polyhedra[19] reveals the coordination geometry to be best described as capped trigonal prismatic. In this reference geometry the μ-cyano ligand is in the capping position, the bpy and two isocyanide ligands comprise the capped quadrilateral, and the unique edges contain *tert*-butyl isocyanide ligands C(2)/C(3) or C(1)/C(4) (Figure 3). The individual molybdenum atom environments are thus very much like that found in the [Mo(CNCMe₃)₆(CN)]⁺ cation, which has a C₂ᵥ capped trigonal-prismatic stereochemis-

try.[20] The Mo–CNCMe₃ and Mo–CN bond lengths of 2.050 (10)–2.114 (6) and 2.191 (9) Å, respectively, in this mononuclear cyanide capped complex may be compared with corresponding values of 2.02 (2)–2.09 (3) and 2.19 (2) Å in the present binuclear structure. Other structural features are summarized in Table III.

From Figures 3 and 4 it is evident that the two pyridyl rings of each bpy ligand in [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)]³⁺ are in distinctly different environments in the solid state. If this geometry were to persist in solution it could account for the observed ¹H NMR results presented above, assuming that rotation about the Mo(1)—C≡N—Mo(2) bonds were slow on the NMR time scale and that Mo–C vs. Mo–N coordination did not affect the chemical shifts of the protons on the bpy ligands. Alternatively, Mo(1)--C≡N—Mo(2) bond rotation might be rapid and the inequivalencies found in the ¹H NMR spectra could be the result of the two different environments produced by the bridging cyano ligand.

A measure of the extent to which the two molybdenum capped trigonal-prismatic coordination spheres are rotated about the Mo(1)—C≡N—Mo(2) bonds is provided by the dihedral angle of 39.6° between planes defined by C(2)–Mo(2)–C(3) and C(1)–Mo(1)–C(4). The two bpy ligands are canted toward one another (Figure 3) by 31.8°.

Bond lengths and angles within the ligands are normal except for the unusually bent C–N–C angles of 156.1 (20)° and 162.6 (23)° in *tert*-butyl isocyanide groups C2 and C1, respectively. Although uncommon, values this small have been previously reported[21] for coordinated alkyl isocyanide ligands.

Reactions of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ with *tert*-Butyl Chloride and *tert*-Butyl Isocyanide. Although the title complex is unreactive toward an excess of 2,2′-bipyridine, it could be converted to [Mo-(CNCMe₃)₄(bpy)Cl]PF₆, albeit in a rather impure state, upon reaction with various chloride salts, viz, LiCl, KCl,

(19) Giandomenico, C. M.; Dewan, J. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1407.

(20) Szalda, D. J.; Dewan, J. C.; Lippard, S. *J. Inorg. Chem.* **1981**, *20*, 3851.

(21) Chatt, J.; Pombeiro, A. J. L.; Richards, R. L.; Royston, G. H. D.; Muir, K. W.; Walker, R. *J. Chem. Soc., Chem. Commun.* **1975**, 708.

Table IV. Spectroscopic Properties of Mixed Nitrogen Donor Ligand–Alkyl Isocyanide Complexes of Molybdenum(II)

complex	IR absorptions,^{a} cm^{-1}		elect abs spectra,^{c} nm
	ν(C≡N)	ν(C=N)^b	
[Mo(CNC$_6$H$_{11}$)$_5$(bpy)](PF$_6$)$_2$	2204 (m), 2169 (s), 2119 (vs), 2050 (vw, sh)	1600 (m)	518 (4900), 335 (7600)
[Mo(CNC$_6$H$_{11}$)$_5$(Me$_2$bpy)](PF$_6$)$_2$	2190 (m, sh), 2150 (s, sh), 2120 (vs), 2044 (m, sh)	1618 (m)	502 (4900), 330 (7600)
[Mo(CNC$_6$H$_{11}$)$_5$(phen)](PF$_6$)$_2$	2192 (m, sh), 2144 (s, sh), 2120 (vs), 2050 (w, sh) ^{d} 2192 (m),^{d} 2144 (vs, sh),^{d} 2120 (vs)^d	1633 (w), 1605 (w), 1580 (w)	512 (4300), 410 (3100), 320 (5600)
[Mo(CNCMe$_3$)$_5$(bpy)](PF$_6$)$_2$	2185 (m, sh), 2140 (vs, sh), 2113 (vs), 2052 (m, sh)	1602 (m)	512 (4800), 310 (7000)
[{Mo(CNCMe$_3$)$_4$(bpy)}$_2$(μ-CN)](PF$_6$)$_3$	2160 (s), 2100 (vs), 2050 (s, sh)	1600 (m)	525 (10 700), 325 (11 600)
[{Mo(CNCMe$_3$)$_4$(Me$_2$bpy)}$_2$(μ-CN)](PF$_6$)$_3$	2160 (s), 2104 (vs), 2050 (s, sh)	1622 (m)	512 (10 400), 335 (11 400)
[{Mo(CNCMe$_3$)$_4$(phen)}$_2$(μ-CN)](PF$_6$)$_3$	2160 (s), 2100 (vs), 2058 (s, sh)	1633 (w), 1602 (w), 1580 (w)	528 (10 300), 327 (sh)
[Mo(CNCMe$_3$)$_6$(py)](PF$_6$)$_2$	2208 (w, sh), 2142 (vs), 2062 (w, sh)	1612 (w)	400 (sh)
[Mo(CNCMe$_3$)$_4$(bpy)Cl]PF$_6$	2160 (s), 2100 (vs), 2060 (vs, sh) ^{d} 2158 (s),^{d} 2100 (vs),^{d} 2060 (s, sh)^d	1606 (m)	528 (4700), 343 (4800)

^{a} IR spectra recorded as Nujol mulls unless stated otherwise (see footnote *d*). ^{b} Vibrations associated with bpy, Me$_2$bpy, or phen ligands. ^{c} Data recorded in methanol. ^{d} Data recorded in dichloromethane. ε_{max} values (M^{-1} cm^{-1}) when recorded are given in parentheses.
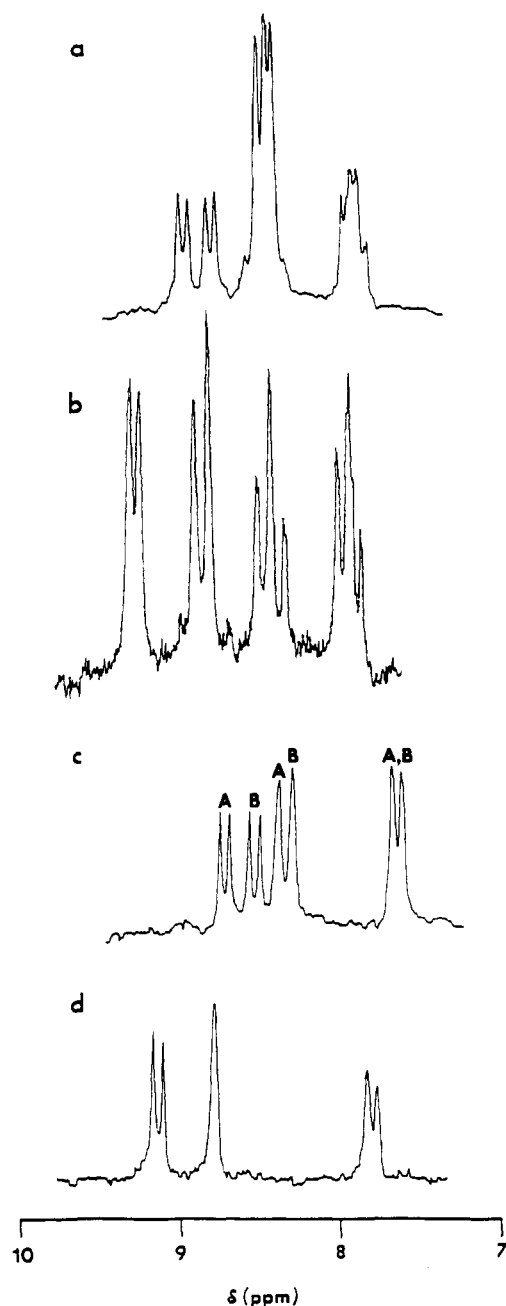
Figure 1. The aromatic region of the 90-MHz ^{1}H NMR spectrum of (a) [{Mo(CNCMe$_3$)$_4$(bpy)}$_2$(μ-CN)](PF$_6$)$_3$, (b) [Mo(CNC$_6$H$_{11}$)$_5$(bpy)](PF$_6$)$_2$, (c) [{Mo(CNCMe$_3$)$_4$(Me$_2$bpy)}$_2$(μ-CN)](PF$_6$)$_3$, and (d) [Mo(CNC$_6$H$_{11}$)$_5$(Me$_2$bpy)](PF$_6$)$_2$ recorded at ambient temperature in acetone-d_6. Spectrum a was found to be unchanged over the temperature range -20 to +120 °C.

NH$_4$Cl, (Me$_4$N)Cl, and (PhCH$_2$NEt$_3$)Cl. A much more effective synthetic procedure utilized *tert*-butyl chloride as the chloride source and refluxing methanol as the reaction solvent. By this means [Mo(CNCMe$_3$)$_4$(bpy)Cl]PF$_6$ could be isoalted in yields of 80%. The properties of this complex, which is a substitution derivative of [Mo(CNCMe$_3$)$_6$Cl]PF$_6$, are summarized in Tables IV–VI, and a cyclic voltammogram of a solution in 0.2 M TBAH–dichloromethane is presented in Figure 2c. Like other molybdenum(II) isocyanide complexes, it exhibits a reversible one-electron oxidation ($E_{1/2}$ = +0.50 V vs. SCE), the value of which is ca. 0.40 V more negative than the corresponding redox process for [Mo(CNR)$_5$(N–N)](PF$_6$)$_2$; this difference is very similar to that between the corresponding $E_{1/2}$(ox) values for [Mo(CNCMe$_3$)$_7$](PF$_6$)$_2$ and [Mo-

Table V. ¹H NMR Chemical Shifts of Mixed Nitrogen Donor Ligand-Alkyl Isocyanide Complexes of Molybdenum(II)

complex	chemical shifts,[a] δ	
	alkyl	aromatic
[Mo(CNC₆H₁₁)₅(bpy)](PF₆)₂	1.41 br, 1.82 br, 4.35 br	7.90 t, 8.40 t, 8.83 d, 9.26 d
[Mo(CNC₆H₁₁)₅(Me₂bpy)](PF₆)₂	1.50 br, 1.90 br, 2.90 s, 4.38 br	7.80 d, 8.78 s, 9.12 d
[Mo(CNC₆H₁₁)₅(phen)](PF₆)₂	1.42 br, 1.83 br, 4.35 br	8.27 m, 8.43 s, 9.05 dd, 9.69 dd
[Mo(CNCMe₃)₅(bpy)](PF₆)₂	1.53 s	7.90 t, 8.37 t, 8.79 d, 9.16 d
[{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃	1.57 s	7.84 m, 8.40 m, 8.72 d, 8.91 d
[{Mo(CNCMe₃)₄(Me₂bpy)}₂(μ-CN)](PF₆)₃	1.54 s, 2.76 s	7.76 d, 8.31 s, 8.40 s, 8.54 d, 8.73 d
[{Mo(CNCMe₃)₄(phen)}₂(μ-CN)](PF₆)₃	1.39 s, 1.41 s	7.86 m, ~8.10 m, 8.54 m, 8.74 d
[Mo(CNCMe₃)₆(py)](PF₆)₂	1.62 s	7.85 t, 8.21 t, 8.78 d
[Mo(CNCMe₃)₄(bpy)Cl]PF₆	1.58 s	7.75 t, 8.22 t, 8.71 d, 9.24 d

[a] All spectra were recorded in acetone-d_6. Abbreviations are as follows: br = broad, d = doublet, dd = doublet of doublets, m = multiplet, s = singlet, t = triplet.

Table VI. Voltammetric Half-Wave Potentials for Mixed Nitrogen Donor Ligand-Alkyl Isocyanide Complexes of Molybdenum(II) in Dichloromethane[a]

complex	$E_{p,a}$	$E_{1/2}(ox)$	$E_{p,c}$
[Mo(CNC₆H₁₁)₅(bpy)](PF₆)₂	+1.73	+0.90	−1.22
[Mo(CNC₆H₁₁)₅(Me₂bpy)](PF₆)₂	+1.72	+0.85	−1.32
[Mo(CNC₆H₁₁)₅(phen)](PF₆)₂	+1.75	+0.90	−1.24
[Mo(CNCMe₃)₅(bpy)](PF₆)₂	+1.75	+0.90	−1.20
[{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃	+1.65	+0.70, +0.85	−1.38, −1.57
[{Mo(CNCMe₃)₄(Me₂bpy)}₂(μ-CN)](PF₆)₃	+1.62	+0.66, +0.81	−1.41, −1.63
[{Mo(CNCMe₃)₄(phen)}₂(μ-CN)](PF₆)₃	+1.67	+0.74, +0.88	−1.36, −1.56
[Mo(CNCMe₃)₆(py)](PF₆)₂		+1.06	
[Mo(CNCMe₃)₄(bpy)Cl]PF₆	+1.42	+0.50	−1.42

[a] In volts vs. SCE with a Pt bead electrode and 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte.
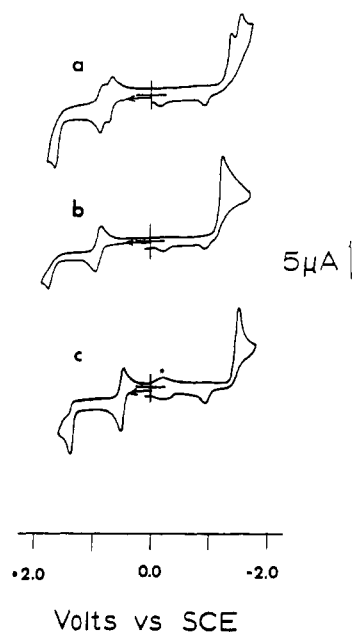
Figure 2. Cyclic voltammograms in 0.2 M tetra-n-butylammonium hexafluorophosphate–dichloromethane solutions of (a) [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃, (b) [Mo(CNC₆H₁₁)₅(bpy)](PF₆)₂, and (c) [Mo(CNCMe₃)₄(bpy)Cl]PF₆ recorded at 200 mV/s. The appearance of the wave at ca. −0.25 V (marked with an asterisk) in the CV of (c) signifies the formation of a chemical product following the irreversible oxidation at +1.42 V.

(CNCMe₃)₆Cl]PF₆[14,22] and reflects the fact that the $E_{1/2}$ values are much more sensitive to substitution of RNC by Cl⁻ than by phosphine or amine ligands.

Whereas the reaction of [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ with tert-butyl isocyanide did not prove to be a viable synthetic route to the elusive [Mo(CNCMe₃)₅(bpy)](PF₆)₂ compound (see Experimental Section), the

(22) Bell, A.; Klendworth, D. D.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* 1981, 20, 4456.
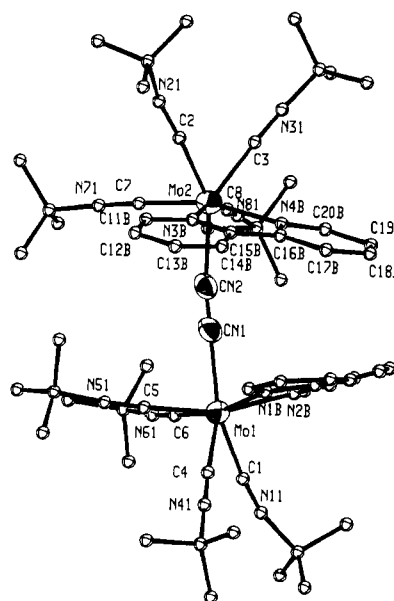
Figure 3. Structure of the [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)]³⁺ cation showing the atom labeling scheme.

corresponding reaction of [Mo(CNCMe₃)₄(bpy)Cl]PF₆ with a 1:1 stoichiometric quantity of tert-butyl isocyanide in methanol (containing an excess of KPF₆) produced red crystalline [Mo(CNCMe₃)₅(bpy)](PF₆)₂ in very high yield. Its spectroscopic and electrochemical properties were in excellent accord with comparable data for [Mo(CNCy)₅(bpy)](PF₆)₂ (Tables IV–VI) and so will not be discussed further. If, in this reaction, more than 2 equiv of isocyanide ligand are used, then the homoleptic species [Mo(CNCMe₃)₇](PF₆)₂ is the principal reaction product.

Dealkylation of [Mo(CNCMe₃)₅(bpy)](PF₆)₂. When [Mo(CNCMe₃)₅(bpy)](PF₆)₂ is refluxed in 1-propanol for 12 h, it is converted into the dealkylation product [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃. This result implies that the [Mo(CNCMe₃)₅(bpy)]²⁺ cation is the precursor to the
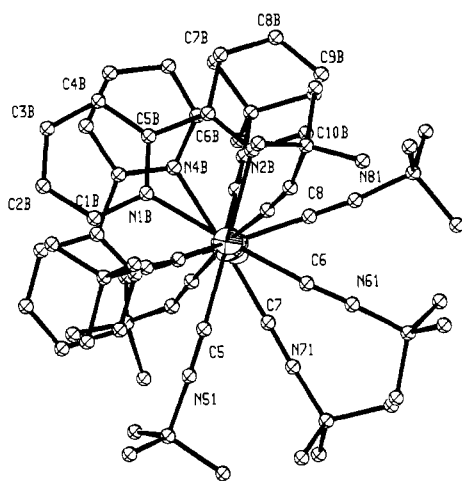
Figure 4. View of the [{Mo(CNCMe₃)₄(bpy)}₂(μ-CN)]³⁺ cation down the Mo—C≡N—Mo axis showing further details of the atom labeling scheme. An approximate twofold axis passes through the midpoint of the C≡N bond and relates C(6) to C(7), N(1B) to N(4B), C(5) to C(8), etc.

cyano-bridged species in the reaction of [Mo-(CNCMe₃)₇](PF₆)₂ with bpy. In a timed study, the reaction between [Mo(CNCMe₃)₇](PF₆)₂ and bpy in 1-propanol was monitored by cyclic voltammetry. Initially, the formation of [Mo(CNCMe₃)₅(bpy)](PF₆)₂ could be clearly seen; subsequently, dealkylation of one of the isocyanide ligands occurs with the creation of the cyanide-bridged species which in time becomes the dominant product in the system.

In attempting to understand the conditions under which the species [{Mo(CNCMe₃)₄(N–N)}₂(μ-CN)](PF₆)₃ are formed and in the hope of producing other mixed nitrogen donor–alkyl isocyanide molybdenum(II) complexes, the reactions between the homoleptic molybdenum isocyanide complexes and two *N,N′*-dialkylethylenediimine (diazadiene) ligands, DAB (R = *t*-Bu) and DAP (R = *i*-Pr), were studied. These ligands have the capability of stabilizing low oxidation states of metals, but like bpy, Me₂bpy, and phen they are also quite good σ donors. Previous studies[23] of mixed isocyanide–diazadiene molybdenum(II) complexes have shown that diazadiene ligands exhibit appreciable π-accepting ability.

In our investigation of the reactions between [Mo-(CNCMe₃)₇](PF₆)₂ and DAB or DAP, the products were not substitution products containing the diazadiene moiety but rather the dealkylation product [Mo(CNCMe₃)₆-(CN)]PF₆.[6] The same reaction product formed when [Mo(CNCMe₃)₇](PF₆)₂ was allowed to react with pyrazine. Dealkylation of coordinated *tert*-butyl isocyanide has been previously reported,[6] and it is clear that with [Mo-(CNCMe₃)₇](PF₆)₂ dealkylation is competitive with sub-

stitution by σ-nitrogen donors. Only bpy, Me₂bpy, and phen show any propensity for substituting the RNC ligands in [Mo(CNR)₇](PF₆)₂, since even in refluxing 1-propanol [Mo(CNCy)₇](PF₆)₂, which does not dealkylate,[6] fails to react with DAB and DAP. In the light of the preceding reactions, [Mo(CNCMe₃)₇](PF₆)₂ was heated alone at reflux in 1-propanol for a period of 24 h; the result was the formation of the dealkylation product [Mo-(CNCMe₃)₆(CN)]PF₆. In the lower boiling ethanol solvent, dealkylation required 3 days and proceeded in rather low yield.[6]

Reactions of Mo₂Cl₄(bpy)₂ and Mo₂Cl₄(py)₄ with *tert*-Butyl Isocyanide. The reactions of these quadruply bonded dimolybdenum(II) complexes[24] with *tert*-butyl isocyanide led to low yields (ca. 15%) of [Mo-(CNCMe₃)₄(bpy)Cl]PF₆ and [Mo(CNCMe₃)₆(py)](PF₆)₂. While these reactions provide further examples of the cleavage of metal–metal multiple bonds by π-acceptor ligands,[25] the first one does not afford a useful synthetic strategy since a far superior procedure already exists for the synthesis of [Mo(CNCMe₃)₄(bpy)Cl]PF₆ (vide supra). On the other hand, the synthesis of the yellow complex [Mo(CNCMe₃)₆(py)](PF₆)₂ is noteworthy since we were unable to prepare it from the direct reaction of pyridine with [Mo(CNCMe₃)₇](PF₆)₂. Its properties (Tables IV–VI) resemble closely those of phosphine complexes of the type [Mo(CNR)₆(PR₃)](PF₆)₂.[2]

Supplementary Material Available: Table S1, listing of observed and calculated structure factor amplitudes for [{Mo-(CNCMe₃)₄(bpy)}₂(μ-CN)](PF₆)₃ (18 pages). Ordering information is given on any masthead page.

(23) Pombeiro, A. J. L.; Richards, R. L. *Transition Met. Chem. (Weinheim, Ger.)* 1981, 6, 255.

(24) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(25) Walton, R. A. "Reactivity of Metal-Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, D.C., 1981; *ACS Symp. Ser. No. 155*, p 207.