Reductive Coupling of Isocyanide Ligands in Seven-Coordinate Molybdenum(II) Mixed Isocyanide–Bipyridine Complexes[1,2]

Steve Warner and Stephen J. Lippard*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received January 29, 1986

Seven-coordinate [Mo(CN-*t*-Bu)$_4$(bpy)Cl]$^+$ reacts with zinc in wet THF to afford red and purple products. The red complex is the previously known [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNHBu-*t*)Cl]$^+$ cation (**1**) containing a coordinated bis(*tert*-butylamino)acetylene ligand formed by the reductive coupling of two isocyanide ligands. The purple compound is the new species [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNHBu-*t*)(bpy)]$^{2+}$, which contains both coupled ligand and 2,2′-bipyridine. The identity of this complex has been established by single-crystal X-ray determinations of two of its salts, **2** and **3**. The synthesis of a family of [Mo(CNR)$_3$(RHNCCNHR)(bpy)](PF$_6$)$_2$ compounds [R = *tert*-butyl (**4**), methyl (**5**), ethyl (**6**), isopropyl (**7**), cyclohexyl (**8**), and benzyl (**9**)] was accomplished by zinc reduction of seven-coordinate [Mo(CNR)$_5$(bpy)](PF$_6$)$_2$ complexes. This chemistry represents the successful extension of reductive coupling of isocyanides to systems containing the chelating ligand bipyridine. Compounds **4**–**9** were characterized by infrared, UV–vis, and ^{1}H NMR spectroscopies as well as elemental analyses. Cyclic voltammetry of methylene chloride solutions of these complexes indicate that the coupled ligand is not as good at removing electron density from the molybdenum(II) center as are two (uncoupled) isocyanide ligands. Some mechanistic aspects of the reductive coupling reaction are reviewed and discussed in light of these new data. Compound **2**, [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNHBu-*t*)(bpy)](PF$_6$)(H$_2$PO$_4$)·0.5CH$_2$Cl$_2$, crystallizes in orthorhombic space group D_{2h}^{12}—*Pnnm* with $a = 14.727$ (4) Å, $b = 21.024$ (3) Å, $c = 16.581$ (4) Å, and $Z = 4$. The structure was refined to $R_1 = 0.088$ for 2087 reflections and 279 variable parameters. Compound **3**, [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNHBu-*t*)(bpy)](PF$_6$)$_2$·[N(Me)$_4$](PF$_6$)·0.5CH$_2$Cl$_2$, crystallizes in triclinic space group C_i^1—$P\bar{1}$ with $a = 11.742$ (2) Å, $b = 18.894$ (3) Å, $c = 14.770$ (3) Å, $\alpha = 108.84$ (1)°, $\beta = 92.25$ (1)°, $\gamma = 76.06$ (1)°, and $Z = 2$. The structure was refined to $R_1 = 0.084$ for 6068 reflections and 587 variable parameters. The seven-coordinate dictations in both crystal structures have approximately pentagonal-bipyramidal geometry with the coupled ligand occupying two equatorial sites and bipyridine spanning an equatorial and an axial site.

Introduction

The reductive coupling of two alkyl isocyanide ligands in seven-coordinate Mo(II) and W(II) complexes [M(CNR)$_6$X]$^+$ has been reported previously (eq. 1).[34] Several

$$[\mathrm{M(CNR)_6X}]^+ + \mathrm{Zn(s)} \xrightarrow[\mathrm{H^+}]{\mathrm{THF}} [\mathrm{M(CNR)_4(RHNCCNHR)X}]^+ \quad (1)$$

$$\mathrm{M = Mo, W;\ X = halide, CN^-;\ R = alkyl}$$

factors have been identified as important in promoting this reductive coupling reaction, including the high coordination number of the metal atom,[3,5] the need for a Lewis acid (H$^+$ or Zn^{2+}) to bind the heteroatom of the linear ligand (nitrogen in the case of isocyanides),[3,6] high electron density at the metal center,[7] and proper orbital alignment of the metal and two ligands forming the carbon–carbon bond.[8] Moreover, it was found that the (*N*,*N*′-dialkyldiamino)acetylene ligand formed by reductive coupling of isocyanides could be oxidatively removed as an oxamide, with the newly formed carbon–carbon bond intact (eq 2).[3] Two

$$[\mathrm{Mo(CNR)_4(RHNCCNHR)I}] \xrightarrow[\text{or Ag}^+]{\mathrm{H_2O_2}} \mathrm{RNHC(O)C(O)NHR} \quad (2)$$

$$\mathrm{R} = tert\text{-butyl}$$

other examples are known in which isocyanide ligands have been coupled in a carbon–carbon bond-forming reaction, M$_2$Cl$_6$(CN-*t*-Bu)$_4$(μ-*t*-BuNCCN-*t*-Bu) (M = Nb, Ta)[9] and Cp$_2$Mo$_2$(CO)$_4$(μ-F$_3$CNCCNCF$_3$),[10] although the factors promoting these reactions are unknown and the ligands have not been removed from the metal centers.

Recently, we have been exploring the extent to which the reductive coupling reaction can be generalized to complexes with mixed-ligand systems, other transition metals, higher coordination numbers, and other C$_1$ substrates, particularly carbon monoxide. In this work we have found that [CpNb(CN-*t*-Bu)$_4$Cl]$^+$ does not yield coupled ligand products under the conditions of eq 1[11] and that [M(CNR)$_6$X]$^{2+}$ cations (M = Tc, R = *t*-Bu, X = Cl, Br; M = Tc, R = CH$_3$, X = Br; or M = Re, R = *t*-Bu, Me, X = Br) give only [M(CNR)$_6$]$^+$ by reductive elimination under these conditions,[2] but that [Ta(CO)$_2$(dmpe)$_2$Cl] can be reductively coupled to yield coordinated bis(trimethylsiloxy)ethyne (eq 3).[12] In the present study we have

$$[\mathrm{Ta(CO)_2(dmpe)_2Cl}] \xrightarrow{\mathrm{Mg/HgCl_2}} \xrightarrow[\mathrm{THF}]{\mathrm{(C_5Me_5)_2ZrCl_2}} \xrightarrow{\mathrm{Me_3SiCl}} [\mathrm{Ta(Me_3SiOCCOSiMe_3)(dmpe)_2Cl}] \quad (3)$$

---

(1) Part 23 of a continuing series on higher coordinate complexes. For part 22, see ref 2.

(2) Farr, J. P.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139.

(3) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263.

(4) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617.

(5) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *16*, 511.

(6) Bianconi, P. A.; Lippard, S. J., unpublished results.

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

(8) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.

(9) (a) Cotton, F. A.; Roth, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3734. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 6987.

(10) Lentz, D.; Brüdgam, I.; Hartl, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 525.

(11) Aspinall, H. C.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1782.

0276-7333/86/2305-1716$01.50/0

extended the reductive coupling of isocyanides to other Mo complexes containing mixed bipyridine–alkyl isocyanide ligands in order to probe further the electronic and steric factors that promote reaction 1 and to provide new complexes from which the (dialkyldiamino)acetylene ligand might be removed in a productive manner. In particular, $[Mo(CNR)_5(bpy)]^{2+}$ cations, in which the coordinated carbon atoms of the isocyanide ligands have a close nonbonded contact of ~2.25 Å,[13] reductively couple to form $[Mo(CNR)_3(RHNCCNHR)(bpy)]^{2+}$ complexes, the synthesis and characterization of which are described in this report.

Experimental Section

Materials and Methods. Methyl isocyanide,[14] ethyl isocyanide,[14] isopropyl isocyanide,[15] *tert*-butyl isocyanide,[15] $[Mo(CN\text{-}t\text{-}Bu)_4(bpy)Cl](PF_6)$,[16] and $[Mo(CNR)_5(bpy)](PF_6)_2$ (R = Me, Et, *i*-Pr, *t*-Bu, Cy, benzyl)[17] were prepared by literature procedures. Cyclohexyl isocyanide (Aldrich), benzyl isocyanide (Aldrich), zinc (Fisher), zinc chloride (Matheson, Coleman and Bell, MCB), potassium hexafluorophosphate (Aldrich), tetra-*n*-butylammonium hexafluorophosphate (TBAH, Southwestern Analytical Chemicals), and tetramethylammonium hexafluorophosphate (Strem) were obtained from commercial sources and used without further purification. 2,2′-Bipyridine (bpy) from MCB was recrystallized from hexane prior to use. Dichloromethane used for electrochemical measurements was obtained from Burdick and Jackson Laboratories and used as received. Tetrahydrofuran was predried over potassium hydroxide and then distilled from dipotassium benzophenone under nitrogen. All other solvents were deoxygenated with dry nitrogen prior to use. Reactions and all manipulations were carried out by using standard Schlenk techniques or in a Vacuum Atmospheres drybox, all under nitrogen. Except for procedure A below, KPF_6 was added to reaction mixtures to suppress formation of the $H_2PO_4^-$ counterion.[18]

(A) Reaction of $[Mo(CN\text{-}t\text{-}Bu)_4(bpy)Cl](PF_6)$ with Zinc To Form $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Cl](PF_6)$ (1), $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)(H_2PO_4)\cdot 0.5CH_2Cl_2$(2), and $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)_2\cdot[N(CH_3)_4](PF_6)\cdot 0.5CH_2Cl_2$ (3). A mixture containing 0.774 g (1.01 mmol) of $[Mo(CN\text{-}t\text{-}Bu)_4(bpy)Cl](PF_6)$, 0.200 g (3.06 mmol) of Zn, 2 mL of H_2O, 0.01 g (0.07 mmol) of $ZnCl_2$, 30 mL of THF, and a magnetic stir bar in a 200-mL, two-necked round-bottom flask was stirred and heated at reflux for 69 h. The reaction, monitored by thin-layer chromatography on silica using 1:1 diethyl ether/chloroform as the eluant, was judged to be complete when no starting material remained and only orange and purple product bands were present. The mixture was filtered and the solvent removed under reduced pressure. The dark purple residue was dissolved in 5 mL of dichloromethane, transferred to the drybox, and loaded onto a 2 cm × 15 cm silica gel column. Using a 1:1 diethyl ether/chloroform mixture, a red-orange band was eluted from the column. After evaporation of the solvents under reduced pressure, this red product was recrystallized by vapor diffusion of diethyl ether into a concentrated dichloromethane solution at −40 °C. This compound (0.20 g, 25%) was identified as $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Cl](PF_6)$ (1) by its spectroscopic properties, which are identical with those of the known chloride salt of this cation:[3] ^1H NMR (CD_3CN) δ 1.46 (s, 36 H), 1.58 (s, 18 H), 9.88 (s, br, 2 H); IR (KBr) 3298 (m), 3241 (m), 3190 (w), 2978 (m), 2932 (sh), 2190 (m), 2140 (m), 2070 (sh), 1579 (s), 1515 (m), 1470 (w), 1460 (w), 1402 (w), 1392 (m), 1370 (s), 1235 (m), 1208 (s), 1090 (w), 1075 (m), 850 (s), 570 (m), 538 (m) cm^{-1}.

By using 1:1 chloroform/methanol as the eluant, a purple band was removed from the column and the solvent evaporated under reduced pressure. Purple crystals of **2** (0.25 g, 26%) were obtained by layering pentane onto a concentrated dichloromethane solution of the complex and allowing the liquids to diffuse together slowly at −40 °C for several days. The crystals were crushed, washed with pentane and ether, and dried under reduced pressure: ^1H NMR (CD_3CN) δ 1.17 (s, 18 H), 1.51 (s, 27 H), 7.25–8.87 (m, 10 H); IR (KBr) 3306 (m), 3175 (m), 3091 (w), 2972 (s), 2930 (sh), 2177 (m), 2146 (s), 2120 (sh), 1606 (m), 1593 (s), 1522 (m), 1477 (m), 1450 (m), 1425 (w), 1400 (w), 1378 (m), 1324 (w), 1231 (sh), 1201 (s), 1093 (s), 851 (s), 782 (m), 572 (s) cm^{-1}. Anal. Calcd for $C_{35}H_{57}H_7MoP_2F_6O_4$ (**2** without $0.5CH_2Cl_2$): C, 46.11; H, 6.30; N, 10.75. Found: C, 46.04; H, 6.09; N, 10.68.

When the above reaction was carried out in the presence of 1 equiv of KPF_6 and the purple product recrystallized, after chromatography, from a methylene chloride solution saturated with tetramethylammonium hexafluorophosphate at −20 °C, compound **3** was isolated: ^1H NMR (CD_3CN) δ 1.16 (s, 18 H), 1.50 (s, 27 H), 3.07 (s, 12 H), 7.22–8.85 (m, 10 H); IR (KBr) 3335 (m), 2983 (m), 2940 (m), 2178 (s), 2146 (s), 2127 (s), 1607 (s), 1601 (m), 1591 (s), 1503 (sh), 1492 (s), 1472 (m), 1445 (m), 1423 (m), 1374 (m), 1197 (s), 893 (m), 840 (s), 771 (m), 559 (s) cm^{-1}. Anal. Calcd for $C_{39}H_{67}N_8MoP_3F_{18}$ (**3** without $0.5CH_2Cl_2$): C, 39.74; H, 5.73; N, 9.51. Found: C, 39.81; H, 5.62; N, 9.64.

(B) Reaction of $[Mo(CNR)_5(bpy)](PF_6)_2$ Complexes with Zinc To Form $[Mo(CNR)_3(RHNCCNHR)(bpy)](PF_6)_2$ [R = $t\text{-}C_4H_9$ (4), CH_3 (5), C_2H_5 (6), $i\text{-}C_3H_7$ (7), $c\text{-}C_6H_{11}$ (8), $PhCH_2$ (9)]. (i) R = *tert*-Butyl (4). A mixture of $[Mo(CN\text{-}t\text{-}Bu)_5(bpy)](PF_6)_2$ (2.52 g, 2.63 mmol), Zn (0.568 g, 2.69 mmol), $ZnCl_2$ (0.050 g, 0.367 mmol), KPF_6 (0.484 g, 2.63 mmol), H_2O (1 mL), THF (85 mL), and a magnetic stir bar were placed in a three-necked 250-mL round-bottom flask and refluxed with stirring for 30 h, during which time the solution color changed from orange-red to deep purple. The solution was filtered, the solvents were removed under reduced pressure, and the purple residue extracted with methylene chloride. After the volume of the solution was reduced to ~10 mL, the sample was chromatographed on silica gel (3 cm × 10 cm, 15% H_2O by weight). Elution with 1:1 ether/dichloromethane removed a yellow material identified as $[Mo(CN\text{-}t\text{-}Bu)_7](PF_6)_2$ (~20% yield) by its spectroscopic properties. Elution with dichloromethane and/or 2:1 CH_2Cl_2/MeOH gave a purple solution. After the solvents were removed under reduced pressure, the residue was recrystallized from 1:2 methanol/ether at −20 °C overnight. After two or three more such recrystallizations, dark purple crystals of **4** were isolated. These were crushed, washed with pentane and ether, and dried under vacuum: yield, 0.595 g (24%); ^1H NMR (CD_3CN) δ 1.15 (s, 18 H), 1.49 (s, 27 H), 7.18–8.52 (m, 8 H), 8.81 (s, br, 2 H); IR (KBr) 3315 (m), 2984 (m), 2944 (w), 2178 (s), 2146 (s), 2126 (sh), 1610 (m), 1596 (m), 1584 (m), 1522 (m), 1472 (m), 1445 (m), 1392 (m), 1226 (sh), 1184 (s), 840 (s), 777 (m), 558 (s) cm^{-1}; UV–vis (CH_2Cl_2, 6.25×10^{-5} M) 600 (sh), 536 (3183), 356 (11 850), 306 (28 500), 298 nm (27 900 $M^{-1}\,cm^{-1}$). Cyclic voltammetry (CH_2Cl_2, V vs. Ag/AgCl): $E_{1/2}$(ox.), +0.704; $E_{p,c}$, −1.30, −1.55. Anal. Calcd for $C_{35}H_{55}N_7MoP_2F_{12}$: C, 43.80; H, 5.78; N, 10.22. Found: C, 43.21; H, 5.59; N, 10.05.

The synthesis was carried out as described above but with the addition of 3 equiv of bipyridine to the reaction mixture in order to check whether the low yield of **4** might be due to depletion of bpy by formation of $[Zn(bpy)_3]^{2+}$. A cyclic voltammogram of the product prior to column chromatography revealed the presence of $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)]^{2+}$, $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$, and $[Mo(CN\text{-}t\text{-}Bu)_5(bpy)]^{2+}$ in a 7.7:2:1 ratio. The isolated yield of **4** following column chromatography and recrystallization as described above was 44%. The resulting purple crystals were identified by ^1H NMR spectroscopy and cyclic voltammetry.

(ii) R = Methyl (5). The procedure was identical with that for **4** except as noted. The starting mixture contained $[Mo(CNMe)_5(bpy)](PF_6)_2$ (2.07 g, 2.77 mmol), Zn (0.599 g, 9.16 mmol), $ZnCl_2$ (0.136 g, 1.00 mmol), H_2O (1 mL), KPF_6 (0.512 g, 2.78 mmol), and THF (100 mL). The mixture was refluxed for 16 h,

---

(12) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311.

(13) Warner, S., unpublished results for $[Mo(CNEt)_5(bpy)](PF_6)_2$.

(14) Casanova, J., Jr.; Schuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.

(15) (a) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530. (b) Gokel, G. W.; Widera, R. P.; Weber, W. P. *Organic Synthesis*; Wiley: New York, 1976; Vol. 55, pp 96–99.

(16) Bell, A.; Lippard, S. J.; Roberts, M. M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562.

(17) (a) Bell, A.; Walton, R. A. *J. Organomet. Chem.* **1984**, *263*, 359. (b) Minelli, M.; Enemark, J. H.; Bell, A.; Walton, R. A. *J. Organomet. Chem.* **1985**, *284*, 25.

(18) Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142.

and the products were separated on a 2 cm × 15 cm silica gel column. The isolated yield of 5 was 0.16 g (8%): ^{1}H NMR (CD_3CN) δ 3.56 (s, 9 H), 3.63 (s, 6 H), 7.16–8.65 (m, 10 H); IR (KBr) 3400 (m), 2950 (w), 2207 (sh), 2178 (s), 1687 (m), 1607 (m), 1514 (w), 1473 (m), 1445 (m), 1414 (m), 1361 (w), 839 (s), 764 (m, br), 559 (s) cm^{-1}; UV-vis (CH_2Cl_2, 2.9 × 10^{-5} M) 600 (sh), 529 (2276), 349 (8172), 306 (22170), 297 nm (25790 M^{-1} cm^{-1}). Cyclic voltammetry (CH_2Cl_2, V vs. Ag/AgCl): $E_{1/2}$(ox.), + 0.538 V; $E_{p,c}$, −1.36, −1.57. Anal. Calcd for $C_{20}H_{25}N_7MoP_2F_{12}$: C, 32.06; H, 3.36; N, 13.08. Found: C, 31.56; H, 3.07; N, 13.29.

As described above for 4, the reaction was repeated with the addition of 3 equiv of bpy, but the isolated yield of 5 only increased to 10%.

(iii) R = Ethyl (6). The procedure used was the same as that used to prepare 4. The starting mixture consisted of 4.72 g (5.77 mmol) of $[Mo(CNEt)_5(bpy)](PF_6)_2$, 1.25 g (19.1 mmol) of Zn, 0.157 g (1.15 mmol) of $ZnCl_2$, 1.06 g (5.76 mmol) of KPF_6, 1.5 mL of H_2O, and 150 mL of THF, which was refluxed for 5 h to yield, ultimately, 0.814 g (17%) of product: ^{1}H NMR (CD_3CN) δ 1.29 (t, 6 H, J = 7.2 Hz), 1.38 (t, 9 H, J = 7.1 Hz), 3.86 (q, 4 H, J = 7.2 Hz), 3.97 (q, 6 H, J = 7.2 Hz), 7.3–9.2 (m, 10 H); IR (KBr) 3369 (m), 3208 (m), 3139 (m), 2980 (m), 2937 (m), 2871 (w), 2197 (m), 2163 (s), 2097 (sh), 1681 (s), 1655 (s), 1605 (m), 1518 (m), 1472 (s), 1445 (s), 1383 (m), 1344 (s), 1317 (w), 1095 (m), 844 (s), 769 (s), 733 (m), 559 (s) cm^{-1}; UV-vis (CH_2Cl_2, 3.66 × 10^{-5} M) 602 (sh), 532 (3962), 351 (14153), 307 (36200), 298 nm (34700 M^{-1} cm^{-1}). Cyclic voltammetry (CH_2Cl_2, V vs. Ag/AgCl): $E_{1/2}$(ox), +0.594; $E_{p,c}$, −1.37, −1.58. Anal. Calcd for $C_{25}H_{35}N_7MoP_2F_{12}$: C, 36.64; H, 4.31; N, 11.96. Found: C, 37.03; H, 4.31; N, 11.95.

(iv) R = Isopropyl (7). The procedure used was the same as that to prepare 4 in which the starting mixture consisted of 6.80 g (7.66 mmol) of $[Mo(CN\text{-}i\text{-}Pr)_5(bpy)](PF_6)_2$, 1.65 g (25.2 mmol) of Zn, 0.145 g (1.06 mmol) of $ZnCl_2$, 1.41 g (7.66 mmol) of KPF_6, 1 mL of H_2O, and 100 mL of THF. After the mixture was refluxed for 36 h, 1.1 g (16%) of 7 was isolated: ^{1}H NMR (CD_2Cl_2) δ 1.10 (d, 6 H, J = 6.1 Hz), 1.13 (d, 6 H, J = 6.1 Hz), 1.36 (d, 12 H, J = 6.5 Hz), 1.42 (d, 6 H, J = 6.5 Hz), 3.93 (spt, 2 H, J = 6.6 Hz), 4.11 (br spt, 2 H), 4.30 (spt, 1 H, J = 6.6 Hz), 7.22 (t, 1 H, J = 6.6 Hz), 7.63 (d, 1 H, J = 4.6 Hz), 7.83–7.94 (m, 2 H), 8.25–8.33 (m, 2 H), 8.45 (d, 1 H, J = 8.2 Hz), 8.57 (d, 1 H, J = 5.5 Hz), 9.66 (d, 2 H, J = 7.8 Hz); IR (KBr) 3347 (m), 3203 (m), 3132 (m), 2982 (m), 2941 (m), 2877 (w), 2184 (s), 2153 (s), 2120 (sh), 1672 (m, br), 1639 (m), 1606 (m), 1511 (m), 1472 (m), 1445 (m), 1393 (m), 1372 (m), 1338 (s), 1317 (w), 1166 (m), 1047 (s), 843 (s), 769 (m), 559 (s) cm^{-1}; UV-vis (CH_2Cl_2, 2.24 × 10^{-5} M) 607 (sh), 537 (3440), 354 (13440), 307 (34330), 299 nm (33300 M^{-1} cm^{-1}). Cyclic voltammetry (CH_2Cl_2, V vs. Ag/AgCl): $E_{1/2}$(ox.), +0.636; $E_{p,c}$, −1.43, −1.60. Anal. Calcd for $C_{30}H_{45}N_7MoP_2F_{12}$: C, 40.50; H, 5.10; N, 11.02. Found: C, 40.43; H, 5.13; N, 11.03.

(v) R = Cyclohexyl (8). Using the procedure for 4, a mixture of $[Mo(CNCy)_5(bpy)](PF_6)_2$ (0.59 g, 3.21 mmol), Zn (0.691 g, 10.6 mmol), $ZnCl_2$ (0.087 g, 0.64 mmol), KPF_6 (0.59 g, 3.21 mmol), 1 mL of H_2O, and 100 mL of THF was refluxed for 15 h to yield 0.94 g (27%) of 8: ^{1}H NMR (CD_3CN) δ 0.89–2.12 (m, 50 H), 3.63–4.39 (br, 5 H), 7.10–8.73 (m, 10 H); IR (KBr) 3339 (m), 2935 (s), 2858 (m), 2175 (sh), 2152 (s), 2127 (sh), 1651 (m, br), 1604 (m), 1511 (m), 1471 (w), 1452 (m), 1421 (w), 1365 (m), 1352 (m), 1320 (m), 1264 (w), 1127 (w), 1021 (w), 841 (s), 773 (m), 558 (s) cm^{-1}; UV-vis (CH_2Cl_2, 2.84 × 10^{-5} M) 625 (sh), 540 (3310), 355 (13200), 307 (33350), 298 nm (32570 M^{-1} cm^{-1}). Cyclic voltammetry (CH_2Cl_2, V vs. Ag/AgCl): $E_{1/2}$(ox.), +0.654; $E_{p,c}$, −1.36, −1.63. Anal. Calcd for $C_{45}H_{65}N_7MoP_2F_{12}$: C, 49.59; H, 6.01; N, 9.00. Found: C, 50.04; H, 6.15; N, 8.89.

(vi) R = Benzyl (9). The initial mixture contained $[Mo(CNBz)_5(bpy)](PF_6)_2$ (4.49 g, 3.98 mmol), Zn (0.867 g, 13.3 mmol), $ZnCl_2$ (0.273 g, 2.00 mmol), KPF_6 (0.739 g, 4.01 mmol), 1.5 mL of H_2O, and 150 mL of THF. After the mixture was refluxed for 16 h, 0.561 g (12%) of 9 was isolated by following the procedure for 4: ^{1}H NMR (CD_3CN) δ 4.38 (s, 4 H), 4.63 (s, 6 H), 6.62–8.80 (m, 36 H); IR (KBr) 3380 (m), 3188 (w), 3033 (w), 2935 (w), 2192 (m), 2159 (s), 2131 (sh), 1676 (s, br), 1605 (m), 1497 (m), 1470 (m), 1456 (m), 1444 (m), 1349 (s), 841 (s), 732 (m), 698 (m), 604 (m), 558 (s) cm^{-1}; UV-vis (CH_2Cl_2, 3.8 × 10^{-5} M) 608 (sh), 525 (3450), 352 (17820), 307 (40760), 299 nm (41760 M^{-1} cm^{-1}). Cyclic voltammetry (CH_2Cl_2, V vs. Ag/AgCl): $E_{1/2}$(ox.), +0.737; $E_{p,c}$, −1.29, −1.54. Anal. Calcd for $C_{50}H_{45}N_7MoP_2F_{12}$: C, 53.15; H, 4.01; N, 8.68. Found: C, 53.70; H, 4.20; N, 8.67.

Attempted Reaction of $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)_2$ with 2,2′-Bipyridine. A solution containing 0.145 g (0.15 mmol) of 4 and 0.071 g (0.45 mmol) of bpy in 40 mL of THF was stirred and refluxed under N_2 for 5 h. After evaporation of the solvent the solid residue was washed with two 25-mL portions of ether, dried, dissolved in CH_2Cl_2, and examined by cyclic voltammetry. Only starting material was observed.

Reaction of Zn^{2+} with $[Mo(CNCy)_5(bpy)](PF_6)_2$/$[Mo(CNCy)_3(CyHNCCNHCy)(bpy)](PF_6)_2$. A solution of 0.043 g (0.04 mmol) of $[Mo(CNCy)_5(bpy)](PF_6)_2$ and 0.043 g (0.04 mmol) of 8 in 25 mL of THF was stirred and refluxed under N_2 for 17 h. Thin-layer chromatography and a cyclic voltammogram of an aliquot revealed that there was no reaction. A 0.035-g (0.12-mmol) portion of $ZnSO_4$ was then added and the mixture stirred and refluxed for an additional 17 h. Thin layer chromatography on silica using 1:1 dichloromethane/diethyl ether showed the presence of a new yellow compound. The reaction mixture was filtered, and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with ~5 mL of CH_2Cl_2, and the crude product was precipitated with a 1:1 mixture of ether and pentane. A cyclic voltammogram of the precipitate, dissolved in CH_2Cl_2, revealed the presence of $[Mo(CNCy)_5(bpy)](PF_6)_2$, 8, and $[Mo(CNCy)_7](PF_6)_2$.

Physical Measurements. Proton NMR spectra were recorded on a JEOL-90X or Bruker WM-250 Fourier transform instrument using the residual proton resonances of acetonitrile-d_3 (δ 1.93 vs. Me_4Si) or dichloromethane-d_2 (δ 5.28 vs. Me_4Si) as internal calibrant. Infrared spectra were recorded in the 4000–400 cm^{-1} range on an IBM IR/32 FTIR spectrometer or a Beckman Acculab 10 grating spectrometer using samples prepared as KBr pellets and calibrated with polystyrene film. Electronic spectra were measured from 250 to 800 nm on a Perkin-Elmer Lambda 7 UV-visible spectrophotometer. Electrochemical measurements were made at 21 ± 2 °C on (~0.5–2) × 10^{-3} M dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. The $E_{1/2}$ values, taken as $(E_{p,a} + E_{p,c})/2$, were referenced to Ag/AgCl and are uncorrected for junction potential. Cyclic voltammetry experiments were carried out by using Princeton Applied Research Model 173 potentiostat, Model 179 digital coulometer, and Model 175 universal programmer and recorded on a Houston Instruments Omnigraphic 2000 X-Y recorder. Voltammetry was done at a platinum disk (1-mm diameter) electrode in deoxygenated solutions. Controlled potential coulometry was carried out on $[Mo(CNCy)_3(CyHNCCNHCy)(bpy)](PF_6)_2$ at +0.9 V using a Pt wire basket with a Pt coil immersed in a 0.2 M quinone/CH_2Cl_2 solution as the auxiliary electrode. Two trials showed this redox process to be a one-electron oxidation, with 0.934 and 0.912 electrons being passed per mole of cation. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

Collection and Reduction of X-ray Data. $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)(H_2PO_4)\cdot 0.5CH_2Cl_2$ (2). A dark purple crystal grown by slow diffusion of a layer of pentane into a dichloromethane solution of 2 was used for the diffraction study. The crystal, a parallelepiped of approximate dimensions 0.42 mm × 0.23 mm × 0.12 mm and bounded by {100}, {010}, and {001}, was mounted on a glass fiber and coated with epoxy to avoid solvent loss. Study on the diffractometer showed *mmm* Laue symmetry and systematic absences ($0kl$, $k + l \neq 2n$; $h0l$, $l + h \neq 2n$) consistent with space groups *Pnnm* (D_{2h}^{12}, No. 58) or *Pnn*2 (C_{2v}^{10}, No. 34).[19a] Open counter ω-scans of several strong, low-angle reflections showed no structure ($\Delta\bar{\omega}_{1/2}$ = 0.15°), and the crystal quality was deemed acceptable. Data collection and reduction proceeded by methods standard in our laboratory,[20] the details of which are presented in Table I.

$[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)_2\cdot[N(CH_3)_4](PF_6)\cdot 0.5CH_2Cl_2$ (3). A dark purple crystal grown by the

---

(19) *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, Holland; 1983; Vol. A: (a) pp 278–9; 226–7; (b) pp 102–5.

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

(21) SHELX-76, a package of crystallographic programs written by G. M. Sheldrick. All computations were prepared on a DEC VAX 11/780 computer.

Table I. Experimental Details of the X-ray Diffraction Study of $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)(H_2PO_4)\bullet 0.5CH_2Cl_2$ ($MoClP_2F_6O_4N_7C_{35.5}H_{58}$, 2) and $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)_2\bullet[N(CH_3)_4](PF_6)$ ($MoClP_3F_{18}N_8C_{39.5}H_{68}$, 3)

(A) Crystal Parameters[a]

2		3	
a = 14.727 (4) Å	space group *Pnnm*	a = 11.742 (2) Å	space group $P\bar{1}$
b = 21.024 (3)Å	fw = 954.23	b = 18.894 (3) Å	fw = 1221.31
c = 16.581 (4) Å	Z = 4	c = 14.770 (3) Å	Z = 2
V = 5133.6 Å^3	ρ_{calcd} = 1.234 g/cm^3	α = 108.84 (1) Å	ρ_{calcd} = 1.349 g/cm^3
	ρ_{obsd}[b] = 1.25 (1) g/cm^3	β = 92.25 (1)°	ρ_{obsd}[b] = 1.34 (1) g/cm^3
		γ = 76.06 (1)°	
		V = 3007.2 Å^3	

	2	3
(B) Measurement and Treatment of Intensity Data[c]		
instrument	Enraf-Nonius CAD-4F κ geometry diffractometer	
radiation	Mo K$\bar{\alpha}$ (0.710 69 Å), graphite monochromator	
takeoff angle	2.3°	
scan technique	ω(crystal)–2θ (counter)	
scan range	$3° \geqslant 2\theta \geqslant 45°$	$3° \geqslant 2\theta \geqslant 45°$
check reflections	$(16\bar{4})$, $(34\bar{2})$, and (031) monitored every 3600 s of exposure time, varies randomly with a net 3.3% decay	$(\bar{2}\bar{7}1)$, $(31\bar{4})$, and $(1\bar{7}\bar{2})$ monitored every 3600 s of exposure time. A fall-off correction was applied as the standards decayed by 23% over the course of data collection
no. of unique data collected	3481, 2087 of which have $F > 4\sigma(F)$	7596, 6068 of which have $F > 4\sigma(F)$
abs correct[d]		
cryst size	0.42 mm × 0.23 mm × 0.12 mm	0.12 mm × 0.47 mm × 0.20 mm
linear abs coeff	3.74 cm^{-1}	3.73 cm^{-1}
transmissn factors	empirical	0.85–0.92
(C) Final Model in the Least-Squares Refinement[e]		
final R values[f]	R_1 = 0.088; R_2 = 0.122	R_1 = 0.084; R_2 = 0.113
no. of observns	2087	6068
no. of parameters	279	587

[a] From a least-squares fit of the setting angles of 25 reflections with $2\theta > 30°$ for compound **2** (T = 22.5 °C) and $2\theta > 15°$ for compound **3** (T = 19 °C). [b] By neutral buoyancy in heptane–carbon tetrachloride. [c] For procedures used in our lab, see ref 20. [d] Absorption corrections were performed either empirically from psi scans or with the Wehe–Busing–Levy ORABS program. [e] All calculations were carried out on a DEC VAX 11/780 computer by using SHELX-76.[21] [f] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$.

vapor diffusion of diethyl ether into a concentrated methylene chloride solution of **3** at −30 °C was used for the diffraction study. The crystal was a parallelepiped of approximate dimensions 0.12 mm × 0.47 mm × 0.20 mm, bound by the faces $(11\bar{1})$, $(\bar{1}\bar{1}1)$, {100}, (011), and $(0\bar{1}\bar{1})$. Study on the diffractometer revealed only triclinic ($\bar{1}$) symmetry consistent with space group $P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)[19b] and acceptable ω-scans. Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structures. $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)(H_2PO_4)\cdot 0.5CH_2Cl_2$ (2). The structure was solved in the centrosymmetric space group *Pnnm* by standard Patterson and difference Fourier methods. Anisotropic temperature factors were assigned to all non-hydrogen atoms. A dichloromethane solvent molecule was identified on a twofold symmetry axis and refined at half-occupancy. Hydrogen atoms of the 2,2′-bipyridine and (*N,N*′-di-*tert*-butyldiamino)acetylene ligands were placed at calculated positions [d(C–H) = 0.95 Å] and constrained to "ride" on the carbon atoms to which they are attached. These hydrogen atoms were refined with a common isotropic thermal parameter. The hydrogen atoms of the five *tert*-butyl groups and of the dichloromethane solvent molecule were also placed at calculated positions and refined isotropically with a separate, but common, thermal parameter. Calculations were performed by using SHELX-76, with neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms obtained from ref 22 and hydrogen atom scattering factors from ref 23. Least-squares refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ where weights were set at $w = 3.9841[\sigma^2(F_o) + 0.000832(F_o)^2]^{-1}$ after analysis of the data as a function of F_o, 2θ, and the Miller indices in the final stages of refinement. This refinement converged to the R-factors reported in Table I. A final difference electron density map showed a peak of 1.21 e Å^{-3} at 0.1 Å from the dihydrogen phosphate phosphorus atom. The large anisotropic thermal parameters of the oxygen atoms of this group suggest some possibly unresolved disorder. Final non-hydrogen positional and thermal parameters are given in Tables II and S1 (supplementary material), respectively, final hydrogen positional and thermal parameters in Table S2, and a listing of observed and calculated structure factors in Table S3.

$[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)](PF_6)_2\cdot[N(CH_3)_4(PF_6)]\cdot 0.5CH_2Cl_2$ (3). This structure was solved and refined in space group $P\bar{1}$ by methods analogous to those reported above for **2**. The tetramethylammonium hexafluorophosphate salt was severely disordered, as reflected by its thermal parameters. Hydrogen atom positions, excluding those of the tetramethylammonium cation, were calculated as in **2** and included in the refinement. Weights were set at $w = 2.5554[\sigma^2(F_o) + 0.000625(F_o)^2]^{-1}$ and least-squares refinement converged to the R-factors reported in Table I. The final difference Fourier showed no residual peak greater than 0.8 e Å^{-3}. Final non-hydrogen atom positional parameters, thermal parameters, and a listing of observed and calculated structure factors are reported in Tables III, S4, and S5, respectively. Hydrogen positional and thermal parameters are reported in Table S6.

Results and Discussion

Reductive coupling of coordinated isocyanides has been successfully extended in this work to complexes containing the chelating ligand 2,2′-bipyridine. Electrochemical[16,17] and X-ray structural[13] studies of the $[Mo(CNR)_5(bpy)]^{2+}$ and $[Mo(CNR)_4(bpy)Cl]^+$ cations revealed that these seven-coordinate complexes have the requisite electronic and steric properties to undergo reductive coupling. The

---

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(23) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table II. Final Non-Hydrogen Positional Parameters for 2[a]

atom	*x*	*y*	*z*
Mo	0.20066(10)	0.18921(7)	0.0000
C1	0.2639(8)	0.1107(5)	-0.0418(7)
C1′	0.2639(8)	0.1107(5)	0.0418(7)
N1	0.3004(8)	0.0683(4)	-0.0906(6)
N1′	0.3004(8)	0.0683(4)	0.0906(6)
C11	0.3025(6)	0.0697(4)	-0.1811(4)
C11′	0.3025(6)	0.0697(4)	0.1811(4)
C12	0.3478(6)	0.0075(4)	-0.2049(4)
C12′	0.3478(6)	0.0075(4)	0.2049(4)
C13	0.2033(6)	0.0685(4)	-0.2128(4)
C13′	0.2033(6)	0.0685(4)	0.2128(4)
C14	0.3520(6)	0.1305(4)	-0.2087(4)
C14′	0.3520(6)	0.1305(4)	0.2087(4)
C3	0.1822(8)	0.2118(5)	-0.1224(7)
C3′	0.1822(8)	0.2118(5)	0.1224(7)
N3	0.1651(9)	0.2350(6)	-0.1837(8)
N3′	0.1651(9)	0.2350(6)	0.1837(8)
C31	0.1443(14)	0.2650(6)	-0.2621(9)
C31′	0.1443(14)	0.2650(6)	0.2621(9)
C32	0.1339(8)	0.3346(5)	-0.2418(7)
C32′	0.1339(8)	0.3346(5)	0.2418(7)
C33	0.2102(14)	0.2487(6)	-0.3235(9)
C33′	0.2102(14)	0.2487(6)	0.3235(9)
C34	0.0513(14)	0.2371(6)	-0.2884(9)
C34′	0.0513(14)	0.2371(6)	0.2884(9)
C5	0.0733(10)	0.1461(7)	0.0000
N5	0.0033(12)	0.1256(9)	0.0000
C51	-0.0915(18)	0.1072(16)	0.0000
C52	-0.1448(10)	0.1633(7)	0.0000
C53	-0.1186(10)	0.0792(7)	0.0728
C53′	-0.1186(10)	0.0792(7)	-0.0728
N6	0.1443(12)	0.2883(8)	0.0000
C61	0.2052(18)	0.3365(10)	0.0000
C62	0.1766(18)	0.3986(13)	0.0000
C63	0.087(2)	0.4111(15)	0.0000
C64	0.024(2)	0.3635(16)	0.0000
C65	0.0566(16)	0.3023(11)	0.0000
N7	0.3169(9)	0.2553(7)	0.0000
C71	0.3028(16)	0.3185(10)	0.0000
C72	0.373(2)	0.3617(13)	0.0000
C73	0.457(2)	0.3435(13)	0.0000
C74	0.4754(16)	0.2825(15)	0.0000
C75	0.4055(14)	0.2376(9)	0.0000
C8	0.5000	0.5000	0.153(4)
Cl	0.4569(10)	0.4411(7)	0.1986(8)
Cl′	0.5431(10)	0.5589(7)	0.1986(8)
P1	0.7405(5)	0.4141(4)	0.0000
F1	0.7995(15)	0.4424(11)	0.0592(11)
F1′	0.7995(15)	0.4424(11)	-0.0592(11)
F2	0.6712(10)	0.3872(9)	-0.0631(10)
F2′	0.6712(10)	0.3872(9)	0.0631(10)
F3	0.7900(16)	0.3550(11)	0.0000
F4	0.6826(15)	0.4719(10)	0.0000
P2	0.4090(15)	-0.0993(11)	0.0000
O1	-0.3647(14)	0.0445(7)	0.0000
O2	-0.3763(19)	0.1589(12)	0.0000
O3	-0.4724(13)	0.1045(9)	0.0650(10)
O3′	-0.4724(13)	0.1045(9)	-0.0650(10)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 2 for atom labeling scheme.

reactions are less straightforward than eq 1, however, with the distribution of products being influenced by the specific composition of the starting materials.

Reaction of [Mo(CN-*t*-Bu)$_4$(bpy)Cl](PF$_6$) with Zinc. This reaction proceeds as shown in eq 4 to give a mixture

$$[\mathrm{Mo(CN}\text{-}t\text{-}\mathrm{Bu})_4(\mathrm{bpy})\mathrm{Cl}]^+ + \mathrm{Zn(s)} \xrightarrow[\mathrm{ZnCl_2,\ reflux\ 69\ h}]{\mathrm{THF,\ H^+}} \underset{\text{red}}{[\mathrm{Mo(CN}\text{-}t\text{-}\mathrm{Bu})_4(t\text{-}\mathrm{BuHNCCNH}\text{-}t\text{-}\mathrm{Bu})\mathrm{Cl}]^+} + \underset{\text{purple}}{[\mathrm{Mo(CN}\text{-}t\text{-}\mathrm{Bu})_3(t\text{-}\mathrm{BuHNCCNH}\text{-}t\text{-}\mathrm{Bu})(\mathrm{bpy})]^{2+}} \quad (4)$$

of red and purple products. The red complex, isolated as its PF$_6^-$ salt 1, was identified as the previously known [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNH-*t*-Bu)Cl]$^+$ cation based on its ^{1}H NMR and infrared spectroscopic properties. X-ray structural studies of two salts of the purple species, 2 and 3, as well as infrared and ^{1}H NMR spectral data revealed the presence of the [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNH-*t*-Bu)(bpy)]$^{2+}$ cation. Both products contain the (*N,N′*-dialkyldiamino)acetylene ligand formed by reductive coupling of two alkyl isocyanide ligands and addition of two protons. The formation of these two complexes, rather than the expected [Mo(CN-*t*-Bu)$_2$(*t*-BuHNCCNH-*t*-Bu)(bpy)Cl]$^+$ cation, reveals eq 4 to be mechanistically complicated. Although we have not investigated the reaction mechanism, it is reasonable that [Mo(CN-*t*-Bu)$_6$Cl]$^+$ and [Mo(CN-*t*-Bu)$_5$(bpy)]$^{2+}$ are the immediate precursors of the red and purple products, respectively. By analogy with our studies of the reductive coupling of [Mo(CNR)$_5$(bpy)]$^{2+}$ (vide infra), it is likely that Zn^{2+} formed in the reaction abstracts Cl$^-$ or bpy from the starting molybdenum complex, which then releases isocyanide to displace further Cl$^-$ and bpy, leading to the putative reductive coupling precursors.

Table III. Final Positional Parameters for 3[a]

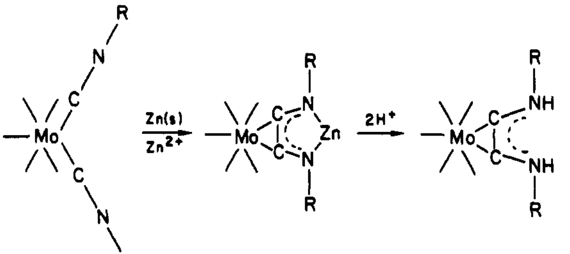
atom	*x*	*y*	*z*
Mo	0.03480(5)	0.24197(4)	0.33047(4)
C1	0.9204(6)	0.2595(5)	0.2277(5)
N1	0.8429(6)	0.2472(4)	0.1612(5)
C11	0.7958(4)	0.1775(3)	0.1209(4)
C12	0.8968(4)	0.1090(3)	0.0763(4)
C13	0.7081(4)	0.1954(3)	0.0454(4)
C14	0.7272(4)	0.1670(3)	0.2025(4)
C2	0.9712(7)	0.3205(5)	0.2618(5)
N2	0.9543(6)	0.3819(4)	0.2353(5)
C21	1.0117(5)	0.4466(3)	0.2668(3)
C22	0.9475(5)	0.5060(3)	0.2190(3)
C23	1.1430(5)	0.4133(3)	0.2316(3)
C24	1.0000(5)	0.4819(3)	0.3739(3)
C3	0.9936(7)	0.1340(6)	0.3039(5)
N3	0.9907(7)	0.0712(5)	0.2928(5)
C31	1.0141(8)	-0.0135(4)	0.2749(5)
C32	0.9047(8)	-0.0393(4)	0.2171(5)
C33	1.1260(8)	-0.0519(4)	0.2062(5)
C34	1.0202(8)	-0.0256(4)	0.3697(5)
C4	1.1550(7)	0.3100(5)	0.3889(5)
N4	1.2345(6)	0.3331(4)	0.4213(5)
C41	1.3497(5)	0.3474(4)	0.4573(5)
C42	1.3382(5)	0.4356(4)	0.4697(5)
C43	1.4404(5)	0.2937(4)	0.3737(5)
C44	1.3665(5)	0.3298(4)	0.5513(5)
C5	1.1642(7)	0.1824(5)	0.2223(6)
N5	1.2307(6)	0.1532(4)	0.1578(5)
C51	1.3003(4)	0.1230(3)	0.0685(3)
C52	1.4185(4)	0.1451(3)	0.0910(3)
C53	1.2296(4)	0.1628(3)	0.0005(3)
C54	1.3116(4)	0.0373(3)	0.0294(3)
N6	1.1179(5)	0.1987(4)	0.4478(4)
C61	1.0600(7)	0.2303(5)	0.5351(5)
C62	1.1125(9)	0.2079(6)	0.6129(7)
C63	1.2175(11)	0.1561(7)	0.6004(8)
C64	1.2728(8)	0.1241(6)	0.5119(8)
C65	1.2234(8)	0.1457(5)	0.4374(7)
N7	0.9132(5)	0.2971(4)	0.4574(4)
C71	0.9480(7)	0.2824(5)	0.5400(6)
C72	0.8787(9)	0.3184(6)	0.6241(6)
C73	0.7708(10)	0.3650(6)	0.6226(7)
C74	0.7339(8)	0.3793(5)	0.5408(8)
C75	0.8065(7)	0.3442(5)	0.4573(6)
N8	0.397(3)	0.3523(16)	0.9011(20)
C81	0.3327(19)	0.3295(12)	0.8057(16)
C82	0.380(2)	0.2991(14)	0.9671(17)
C83	0.505(3)	0.3831(18)	0.921(2)
C84	0.333(3)	0.4359(18)	0.9554(19)
C9	0.653(2)	0.1303(14)	0.532(2)
Cl1	0.7529(11)	0.1498(6)	0.4667(7)
Cl2	0.6429(17)	0.2014(8)	0.6390(12)
P1	0.5517(3)	0.45400(19)	0.2268(2)
F11	0.4932(12)	0.5028(10)	0.3198(10)
F12	0.616(2)	0.5128(11)	0.2394(10)
F13	0.465(2)	0.4122(15)	0.2136(11)
F14	0.4867(17)	0.4897(11)	0.1543(14)
F15	0.6248(15)	0.4142(12)	0.2874(13)
F16	0.6227(20)	0.4050(11)	0.1429(11)
P2	0.4895(4)	0.0315(3)	0.7301(3)
F21	0.4815(19)	0.0175(10)	0.6280(10)
F22	0.5696(18)	-0.0432(10)	0.7236(12)
F23	0.5910(19)	0.0444(17)	0.747(3)
F24	0.429(2)	0.1116(8)	0.7458(12)
F25	0.479(3)	0.038(2)	0.8285(13)
F26	0.3716(16)	0.0166(16)	0.732(3)
P3	0.9202(6)	0.3209(4)	-0.0812(3)
F31	0.8440(14)	0.3555(9)	0.0081(9)
F32	0.9573(16)	0.2487(14)	-0.0453(14)
F33	0.864(2)	0.3772(11)	-0.1201(16)
F34	1.0177(19)	0.3499(15)	-0.0156(10)
F35	0.867(2)	0.2738(12)	-0.1530(14)
F36	1.0100(20)	0.3010(19)	-0.1562(9)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 3 for atom labeling scheme.

Reductive Coupling of Alkyl Isocyanides in [Mo(CNR)$_5$(bpy)]$^{2+}$ Cations. Identification of the purple cation [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNH-*t*-Bu)(bpy)]$^{2+}$ in 2 and 3 suggested that [Mo(CNR)$_5$(bpy)]$^{2+}$ complexes might undergo reductive coupling under the conditions of eq 1 and 4. Indeed, such a reaction does occur for R = CH_3, C_2H_5, *i*-C_3H_6, *t*-C_4H_9, c-C_6H_{11}, and CH_2Ph. The red starting solutions in these reactions turn purple over 5–36 h of reflux. With use of thin-layer chromatography, we monitored the disappearance of the red [Mo(CNR)$_5$(bpy)]$^{2+}$ cations followed by the appearance of purple and yellow products (eq 5). The purple complexes were isolated as their PF_6^- salts 4–9 in 8–27% yields and characterized by elemental analysis, cyclic voltammetry, and spectroscopy as described below. The yellow products were identified as the homoleptic [Mo(CNR)$_7$]$^{2+}$ cations on the basis of their well-known[24] spectroscopic properties. As in eq 4, the reaction products of eq 5 suggest that bipyridine is displaced by free isocyanide, possibly generated by decomposition of the starting material, to form [Mo(CNR)$_7$]$^{2+}$. As shown previously,[25] this homoleptic complex will not undergo reductive coupling under the conditions of reaction 5. Instead, more prolonged reflux leads, at least in the case where R = *tert*-butyl, to dealkylation followed by reductive coupling of the resulting cyanohexakis(*tert*-butyl isocyanide)molybdenum(II) complex (eq 6).

$$\underset{\text{red}}{[\mathrm{Mo(CNR)_5(bpy)}]^{2+}} + \mathrm{Zn(s)} \xrightarrow[\mathrm{ZnCl_2,\ reflux\ 5\text{–}36\ h}]{\mathrm{THF,\ H^+}} \underset{\text{purple}}{[\mathrm{Mo(CNR)_3(RHNCCNHR)(bpy)}]^{2+}} + \underset{\text{yellow}}{[\mathrm{Mo(CNR)_7}]^{2+}} \tag{5}$$

$$[\mathrm{Mo(CNR)_7}]^{2+} \xrightarrow[\mathrm{reflux}]{\mathrm{THF}} [\mathrm{Mo(CNR)_6(CN)}]^{+} \xrightarrow[\mathrm{THF,\ reflux}]{\mathrm{Zn,\ H^+}} [\mathrm{Mo(CNR)_4(RHNCCNHR)(CN)}]^{+} \tag{6}$$



(7)

Trace amounts of zinc chloride added to reactions 4 and 5 accelerate the rate of reductive coupling, presumably because their Lewis acidity stabilizes the coupled ligand prior to protonation (eq 7).[3,6] More divalent zinc is generated as the reaction proceeds. Since Zn^{2+} ion forms stable complexes with bipyridine, we considered the possibility that the low yields of reaction 5 might be due to decomposition of the starting material promoted by divalent zinc. When eq 5 was carried out in the presence of 3 equiv of bipyridine, the isolated yield of [Mo(CNR)$_3$(RHNCCNHR)(bpy)]$^{2+}$ increased to 44% for R = *tert*-butyl but only to 10% for R = methyl. The low yield in the latter case may be due to high volatility of methyl isocyanide. A control reaction showed that excess bipyridine does not react with [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNH-*t*-Bu)(bpy)]$^{2+}$ in refluxing THF. Furthermore, when $ZnSO_4$ was added to a 1:1 mixture of [Mo(CNCy)$_5$(bpy)](PF$_6$)$_2$ and [Mo(CNCy)$_3$(CyHNCCNHCy)(bpy)](PF$_6$)$_2$ in THF and refluxed, it was shown that some [Mo(CNCy)$_7$](PF$_6$)$_2$ was produced. This result again indicates a role for Zn^{2+} in the formation of the homoleptic complexes produced (eq 5).

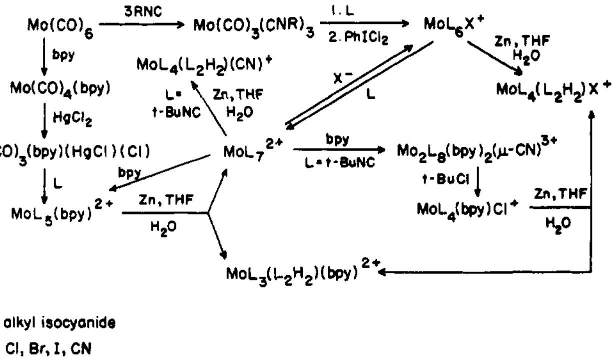


Figure 1. Scheme depicting reductive coupling and related reactions of seven-coordinate molybdenum(II) alkyl isocyanide complexes (see ref 3, 16, 17, and 18).

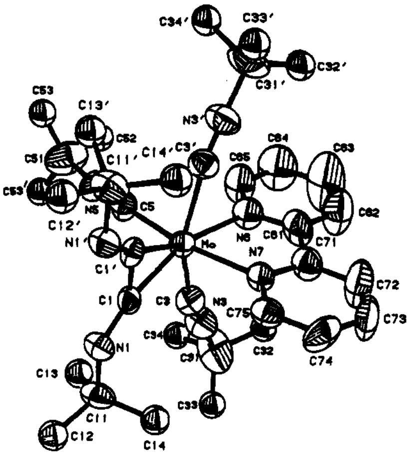


Figure 2. Structure of the cation in 2 showing the atom-labeling scheme and 40% probability thermal ellipsoids. For clarity, all *tert*-butyl group methyl carbon atoms are assigned as spheres with $B = 5.0$ Å^2. Primed and unprimed atoms are related by a crystallographic mirror plane.

As with [Mo(CNR)$_6$X]$^+$ complexes,[3] aryl isocyanides do not reductively couple in the [Mo(CNR)$_5$(bpy)]$^{2+}$ cations. After 48 h of reflux with zinc or aluminum in wet THF, the only detectable reaction of [Mo(CNR)$_5$(Me$_2$bpy)](PF$_6$)$_2$, R = *m*-xylyl, was hydrolysis of the hexafluorophosphate anion.[18] The relationship between the new reactions studied here and those of related seven-coordinate molybdenum(II) isocyanide complexes is given in Figure 1.

Crystal Structures of 2 and 3. Geometry of the [Mo(CN-*t*-Bu)$_3$(*t*-BuHNCCNH-*t*-Bu)(bpy)]$^{2+}$ Cation. As shown in Figures 2 and 3, the structure of this complex in both 2 and 3 consists of a seven-coordinate molybdenum atom with 2,2′-bipyridine, bis(*tert*-butylamino)acetylene, and three *tert*-butyl isocyanides as its ligand set. The geometry at the molybdenum center is distorted pentagonal bipyramidal, with a bipyridine nitrogen atom, N(7), and an isocyanide carbon atom, C(5), occupying the axial sites and the five equatorial sites being filled by two acetylene carbon atoms, C(1) and C(2), two isocyanide carbon atoms, C(3) and C(4), and the other bipyridine nitrogen atom, N(6). In 2, a crystallographically required mirror plane passes through the Mo atom, bipyridine ligand, and axial isocyanide group, requiring the (*N*,*N*′-dialkyldiamino)acetylene and 2,2′-bipyridine planes to be mutually perpendicular (Figure 4). In 3 the complex has no crystallographically imposed symmetry.

---

(24) Lippard, S. J. *Prog. Inorg. Chem.* **1976**, *21*, 91.

(25) Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069.

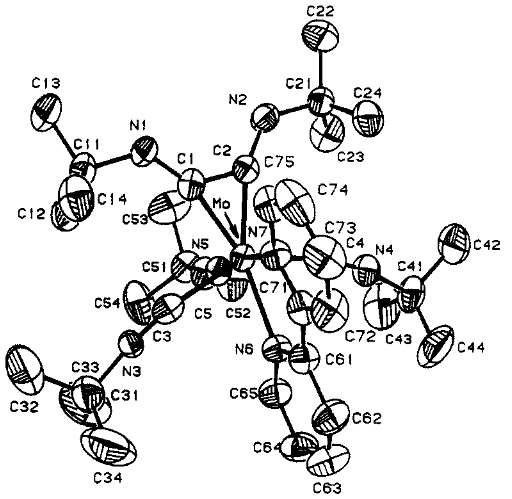


Figure 3. Structure of the cation in **3** showing the atom-labeling scheme and 40% probability thermal ellipsoids.

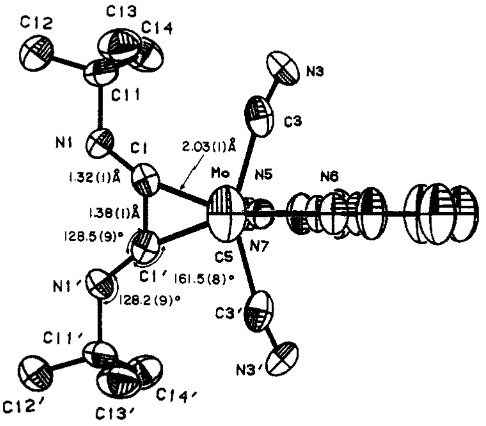


Figure 4. View of the coordination and coupled ligand geometry in **2**. A mirror plane passing through Mo and bisecting the C(1)–C(1)′ bond is perpendicular to the plane of the diagram.

Selected features of the molecular geometry of the $[Mo(CN\text{-}t\text{-}Bu)_3(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(bpy)]^{2+}$ cations in **2** and **3** are summarized in Table IV. Comparison of the 21 L–Mo–L bond angles with published tables for idealized seven-coordinate geometries[26,27] confirms the D_{5h} pentagonal bipyramid as the best reference polyhedron. Distortions from this idealized geometry arise mainly from the chelating nature of the bpy and acetylene ligands. Only one other seven-coordinate Mo(II) complex having a pentagonal-bipyramidal structure and a bis(alkylamino)acetylene ligand has been structurally characterized, namely, $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)]^+$, in which the acetylene ligand also occupies two positions in the pentagonal plane.[25] This stereochemistry arises naturally from the small "normalized bite" of the μ_2-acetylene group.[28] Although no examples of $[M(unidentate)_3(bidentate)(bidentate)']$structures have been theoretically analyzed, the respective normalized bite values of 0.68 and 1.19 for *t*-BuHNCCNH-*t*-Bu and bpy would appear to be reasonable for a structure with the former spanning a pair of equatorial sites and the latter an equatorial/axial pair of sites in the pentagonal bipyramid.[28]

The geometry of the coupled ligand reported in Table IV for **2** and **3** is fully consistent with several structural studies of complexes containing a coordinated (*N*,*N*′-dialkyldiamino)acetylene.[25,29] The average acetylenic C–C and C–N bond lengths of 1.38 (1) and 1.32 (1) Å, respectively, and the Mo–C–N and C–C–N bond angles of 161.5 (8) and 128.5 (9)° imply extensive multiple-bond delocalization in the coupled ligand system, consistent with sp^2 hybridization of nitrogen. The fact that the acetylenic Mo–C(1) and Mo–C(2) bonds are shorter than the Mo–CNR bonds (Table IV) is consistent with the acetylene ligand being a four-electron donor, a point discussed in more detail elsewhere.[3,29] The d^4 Mo(II) center thus achieves a stable 18-electron configuration.

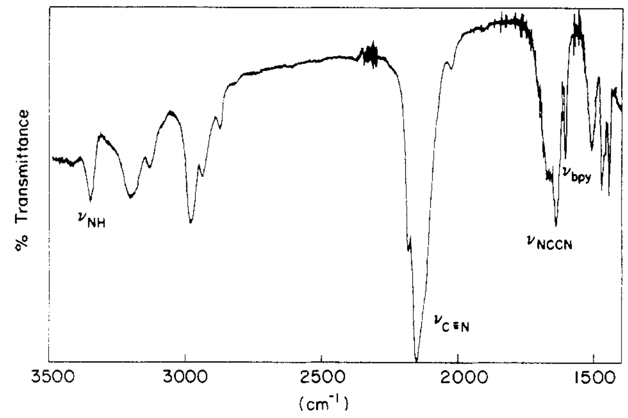


Figure 5. FTIR spectrum of **8**.

In **2** there are dihydrogen phosphate and hexafluorophosphate anions situated on mirror planes in the lattice to balance the charge. The former, which arises by hydrolysis of PF_6^- under the reaction conditions,[18] is hydrogen bonded through one of its oxygen atoms to a proton on one of the coupled ligand nitrogen atoms [distance O(1)···N(1) = 2.96 (2) Å; angle O(1)–H(1)–N(1) = 165 (9)°]. Compound **3** is a double salt, crystallizing with $(Me_4N)(PF_6)$ in the lattice. Both **2** and **3** also have methylene chloride in the crystal which, together with a large number of fluorine and *tert*-butyl carbon atoms with high thermal parameters and possibly some unresolved disorder, combine to limit the precision of the structure determinations for both compounds.

Spectroscopic and Electrochemical Properties. (i) Infrared Spectra. Selected IR bands characteristic of the coupled ligand product are collected in Table V and displayed in Figure 5. All the complexes show a strong C≡N stretching band at 2146–2178 cm^{-1}, a less intense higher energy band between 2175 and 2207 cm^{-1}, and a weak shoulder at 2097–2131 cm^{-1} due to the alkyl isocyanide ligands. A solution spectrum of **4** in CH_2Cl_2 was identical, except for a sharpening of some IR absorptions, to that in the solid state, implying similar structures.

Several absorptions arise from the coupled ligand, including N–H stretching (3306–3400 cm^{-1}) and deformation (1497–1522 cm^{-1}) modes assigned previously.[3] In addition, one broad and two sharper bands of medium to strong intensity appear between 1584 and 1687 cm^{-1}. The variation (Table V) in the positions of these bands with the alkyl substituent is consistent with their previous assignment as having considerable C=N character. A sharp band of medium intensity observed between 1596 and 1607 cm^{-1} in both starting material and products is due to a vibrational overtone of the bipyridine ligand system.

(ii) Electronic Spectra. The red to purple color change that accompanies reaction 5 is due largely to a shift

---

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

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

(28) Kepert, D. L. *Inorganic Stereochemistry*; Springer-Verlag: Berlin, 1982; pp 130–151.

(29) Corfield, P. W. R.; Baltusis, L. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 922.

Table IV. Interatomic Distances (Å) and Angles (deg) for 2 and 3[a,b]

2

Coordination Sphere			
Bond Distances			
Mo — C1	2.02(1)	Mo — C1'	2.02(1)
Mo — C3	2.10(1)	Mo — C3'	2.10(1)
Mo — C5	2.08(1)	Mo — N6	2.24(2)
Mo — N7	2.20(1)		
Bond Angles			
C5 — Mo — N7	166.7(5)	C5 — Mo — C3	89.0(3)
C1 — Mo — N6	158.5(4)	C5 — Mo — C3'	89.0(3)
C1' — Mo — N6	158.5(4)	C3 — Mo — N7	87.6(3)
C3 — Mo — C3'	149.8(5)	C3' — Mo — N7	87.6(3)
C1 — Mo — C3'	125.2(5)	C1 — Mo — C3	85.0(4)
C1' — Mo — C3	125.2(5)	C1' — Mo — C3'	85.0(4)
C1 — Mo — N7	99.0(5)	C3 — Mo — N6	75.1(3)
C1' — Mo — N7	99.0(5)	C3' — Mo — N6	75.1(3)
C5 — Mo — N6	94.1(6)	N7 — Mo — N6	72.6(6)
C1 — Mo — C5	93.4(5)	C1 — Mo — C1'	40.2(5)
C1' — Mo — C5	93.4(5)		
Ligand Geometry			
(i) N,N'-Bis(tert-butylamino)acetylene			
Bond Distances			
C1 — C1'	1.39(2)	N1 — C11	1.50(1)
C1 — N1	1.32(1)	C11 — C12	1.52(1)
C11 — C14	1.54(1)	C11 — C13	1.55(1)
Bond angles			
N1 — C1 — Mo	162.2(9)	C1 — C1' — Mo	69.9(6)
C1 — N1 — C11	127.5(9)	N1 — C1 — C1'	128(1)
N1 — C11 — C12	104.5(6)	C12 — C11 — C13	108.2(6)
N1 — C11 — C13	108.5(7)	C12 — C11 — C14	115.4(7)
N1 — C11 — C14	108.8(7)	C13 — C11 — C14	111.0(6)
(ii) tert-Butyl Isocyanide Groups			
Bond Distances			
C3 — N3	1.15(2)	N3 — C31	1.48(2)
C5 — N5	1.12(2)	N5 — C51	1.45(3)
mean C-C(methyl)	1.47(2)	range C-C(methyl)	1.40-1.55
Bond Angles			
N3 — C3 — Mo	167(1)	N5 — C5 — Mo	177(2)
C3 — N3 — C31	179(1)	C5 — N5 — C51	173(2)
mean N-C-C(methyl)	109(1)	range N-C-C(methyl)	104-113
mean C(methyl)-C-(methyl)	110(1)	range C(methyl)-C-C(methyl)	101-119
(iii) N,N'-Bipyridine Ligand			
Bond Distances			
N6 — C61	1.35(3)	N7 — C71	1.34(2)
N6 — C65	1.32(3)	N7 — C75	1.36(2)
C61 — C71	1.49(4)	mean C(ring)-C(ring)	1.36(4)
		range C(ring)-C(ring)	1.30-1.40
Bond Angles			
C61 — N6 — Mo	117(1)	C65 — N6 — C61	119(2)
C65 — N6 — Mo	125(1)	C71 — N7 — C75	115(2)
C71 — N7 — Mo	120(1)	N6 — C61 — C61	121(2)
C75 — N7 — Mo	125(1)	N6 — C61 — C71	117(2)
N6 — C65 — C64	123(2)	mean C(ring)-C(ring)-C(ring)	121(3)
N7 — C71 — C72	122(2)		
N7 — C71 — C61	114(2)	range C(ring)-C(ring)-C(ring)	116-123
N7 — C75 — C74	122(2)		
Anion Geometry			
(i) Hexafluorophosphate			
Bond Distances and Angles			
mean P-F	1.49(2)	mean cis F-P-F	90(1)
range P-F	1.44-1.57	min trans F-P-F	175(1)
min cis F-P-F	83.8(9)	max trans F-P-F	176(1)
max cis F-P-F	95(1)	mean trans F-P-F	176(1)
(ii) Dihydrogenphosphate			
Bond Distances and Angles			
P2 — O1	1.32(3)	P2 — O2	1.34(3)
P2 — O3	1.43(2)	O3 — P2 — O3'	98(2)
O1 — P2 — O2	129(2)	O2 — P2 — O3	99(2)
O1 — P2 — O3	113(1)		
Dichloromethane Molecule			
Bond Distances and Angles			
C8 — Cl	1.58(3)	Cl — C8 — Cl'	123(4)

3

Coordination Sphere			
Bond Distances			
Mo — C1	2.04(1)	Mo — C2	2.04(1)
Mo — C3	2.12(1)	Mo — C4	2.11(1)
Mo — C5	2.08(2)	Mo — N6	2.24(1)
Mo — N7	2.21(2)		
Bond Angles			
C5 — Mo — N7	172.2(3)	C2 — Mo — C5	90.4(6)
C1 — Mo — N6	160.3(4)	C1 — Mo — C5	88.3(4)
C2 — Mo — N6	157.1(4)	C1 — Mo — C3	87.6(6)
C4 — Mo — C3	146.2(4)	C2 — Mo — C4	85.5(5)
C2 — Mo — C3	126.7(4)	C5 — Mo — C3	85.2(7)
C1 — Mo — C4	124.1(5)	C5 — Mo — C4	84.5(5)
C5 — Mo — N6	99.4(5)	C3 — Mo — N6	75.2(6)
C1 — Mo — N7	99.1(4)	C4 — Mo — N6	75.0(5)
C2 — Mo — N7	97.0(5)	N7 — Mo — N6	72.7(4)
C4 — Mo — N7	93.3(5)	C1 — Mo — C1	39.1(5)
C3 — Mo — N7	92.6(6)		
Ligand Geometry			
(i) N,N'-Bis(tert-butylamino)acetylene			
Bond Distances			
C1 — C2	1.37(1)	C2 — N2	1.31(1)
C1 — N1	1.32(1)	N2 — C21	1.47(1)
N1 — C11	1.49(1)	C21 — C22	1.55(1)
C11 — C12	1.51(1)	C21 — C23	1.56(1)
C11 — C13	1.55(1)	C21 — C24	1.50(1)
C11 — C14	1.57(1)		
Bond Angles			
N1 — C1 — Mo	160.0(8)	C1 — C2 — Mo	70.5(6)
C2 — C1 — Mo	70.4(6)	N2 — C2 — Mo	161.5(7)
N1 — C1 — C2	130(1)	N2 — C2 — C1	128.0(8)
C1 — N1 — C11	128.2(9)	C2 — N2 — C21	129.5(7)
N1 — C11 — C12	108.7(6)	N2 — C21 — C22	106.3(6)
N1 — C11 — C13	105.4(7)	N2 — C21 — C23	106.9(7)
N1 — C11 — C14	108.8(7)	N2 — C21 — C24	110.2(8)
C12 — C11 — C13	112.0(6)	C24 — C21 — C22	110.2(6)
C12 — C11 — C14	112.7(7)	C22 — C21 — C23	111.8(7)
C13 — C11 — C14	109.0(4)	C24 — C21 — C23	111.3(8)
(ii) tert-Butyl Isocyanide Groups			
Bond Distances			
C3 — N3	1.15(1)	N3 — C31	1.49(1)
C4 — N4	1.15(2)	N4 — C41	1.49(1)
C5 — N5	1.16(1)	N5 — C51	1.45(1)
mean C-C(methyl)	1.55(1)	range C-C(methyl)	1.49-1.60
Bond Angles			
N3 — C3 — Mo	168.5(7)	mean N-C-C(methyl)	106.2(8)
N4 — C4 — Mo	166.1(7)	range N-C-C(methyl)	104.3-108.3
N5 — C5 — Mo	174.1(8)	mean C(methyl)-C-C(methyl)	112.4(7)
C3 — N3 — C31	168.0(9)		
C4 — N4 — C41	169.1(7)	range C(methyl)-C-C(methyl)	107.8-117.2
C5 — N5 — C51	170.7(8)		
(iii) N,N'-Bipyridine Ligand			
Bond Distances			
N6 — C61	1.36(1)	N7 — C71	1.36(1)
N6 — C65	1.37(1)	N7 — C75	1.35(1)
C61 — C71	1.43(1)	mean C(ring)-C(ring)	1.38(2)
		range C(ring)-C(ring)	1.35-1.42
Bond Angles			
C61 — N6 — Mo	116.5(6)	C61 — N6 — C65	119.4(9)
C65 — N6 — Mo	124.1(7)	C75 — N7 — C71	118.5(9)
C71 — N7 — Mo	117.9(6)	N6 — C61 — C62	118.5(8)
C75 — N7 — Mo	123.5(7)	N6 — C61 — C71	116.5(9)
N6 — C65 — C64	121.9(9)	mean C(ring)-C(ring)-C(ring)	121(1)
N7 — C71 — C72	121.0(8)		
N7 — C75 — C74	121(1)	range C(ring)-C(ring)-C(ring)	119.4-123
N7 — C71 — C61	116.1(9)		
Tetramethylammonium Cation Geometry			
Bond Distances and Angles			
mean N8-C(methyl)	1.56(5)	range N8-C(methyl)	1.50-1.66
mean C(methyl)-N8-C(methyl)	108(2)	range C(methyl)-N8-C(methyl)	84-129
Anion Geometry			
Bond Distances and Angles			
mean P-F	1.45(2)	mean cis F-P-F	90(2)
range P-F	1.27-1.58	min trans F-P-F	160(1)
min cis F-P-F	74(2)	max trans F-P-F	173.3(9)
max cis F-P-F	109(2)	mean trans F-P-F	168(1)
Dichloromethane Molecule			
Bond distances and Angles			
C9 — Cl1	1.72(4)	C9 — Cl2	1.70(3)
Cl2 — C9 — Cl1	103.(2)		

[a] See footnote *a*, Table II. Primed and unprimed atoms are related to one another by mirror symmetry. [b] Distances reported have not been corrected for thermal motion. Standard deviations, quoted for mean values, are the average of the standard deviations for the individual values.

to longer wavelength of the Mo(4d)→bpy(π*) absorption bands at ~505 nm[16,30] in the $[Mo(CNR)_5(bpy)]^{2+}$ starting materials to two bands at ~530–540 and ~600–625 in the coupled ligand products (Table V). These latter bands are tentatively assigned as Mo(4d)→bpy(π*) and Mo(4d)→RHNCCNHR(π*) transitions, respectively, owing to their relatively high intensity. Weaker Mo d→d bands would also be expected to occur in this region of the spectrum, by analogy to the electronic spectral properties

---

[30] McWhinnie, W. R.; Miller, J. D. *Adv. Inorg. Chem. Radiochem.* 1969, *12*, 162–167.

Table V. Spectroscopic Properties of [Mo(CNR)$_3$(RHNCCNHR)(bpy)](PF$_6$)$_2$ Complexes

	IR absorptns,[a] cm^{-1}		
R	ν(C≡N)	ν(C=N, C=C)[b]	electronic absorptn spectra,[c] nm
methyl	2207 (sh), 2178 (s)	1687 (m, br), 1607 (m)	600 (sh), 529 (2276), 349 (8172), 306 (22 170), 297 (25 790)
ethyl	2197 (m), 2163 (s), 2097 (sh)	1681 (s), 1655 (s), 1605 (m)	602 (sh), 532 (3962), 351 (14 150), 307 (36 200), 298 (34 700)
isopropyl	2184 (m), 2153 (s), 2120 (sh)	1672 (m, br), 1639 (m), 1606 (m)	607 (sh), 537 (3440), 354 (13 440), 307 (34 330), 299 (33 300)
tert-butyl	2178 (s), 2146 (s), 2126 (sh)	1610 (m), 1596 (m), 1584 (m)	600 (sh), 536 (3183), 356 (11 850), 306 (28 500), 298 (27 900)
cyclohexyl	2175 (sh), 2152 (s), 2127 (sh)	1651 (m, br), 1604 (m)	625 (sh), 540 (3310), 355 (13 200), 307 (33 350), 298 (32 570)
benzyl	2192 (m), 2159 (s), 2131 (sh)	1676 (s, br), 1605 (m)	608 (sh), 525 (3450), 352 (17 820), 307 (40 760); 299 (41 760)

[a] IR spectra were recorded as KBr pellets. [b] Vibrations associated with the N,N′-dialkyldiaminoacetylene ligand or bipyridine. [c] ϵ_{max} values (M^{-1} cm^{-1}) when recorded are given in parentheses. Spectra were recorded on dichloromethane solutions ranging in concentration from 2.24 × 10^{-5} to 6.25 × 10^{-5} M.

of the [Mo(CNR)$_4$(RHNCCNHR)X]$^+$ cations.[3] These bands may underlie the charge-transfer transitions. Intense bands ~353 nm appearing only in the spectra of complexes containing the coupled ligand are assigned as LMCT transitions, coupled ligand (π^*)→Mo(4d), by analogy to the [Mo(CNR)$_4$(RHNCCNHR)X]$^+$ system.[3]

Free bipyridine has a 280-nm $\pi \rightarrow \pi^*$ absorption that typically red-shifts upon coordination to a metal ion.[30,31] In [Mo(CNR)$_5$(bpy)]$^{2+}$ this band occurs at ~303 nm but is replaced by two bands at 298–307 nm in the [Mo(CNR)$_3$(RHNCCNHR)(bpy)]$^{2+}$ cations (Table V). One of these absorptions is most likely due to a bpy ($\pi \rightarrow \pi^*$) transition while the other could possibly be a coupled ligand ($\pi \rightarrow \pi^*$) transition or possibly, owing to the asymmetry of the complex (Figures 1 and 2), a second bpy ($\pi \rightarrow \pi^*$) excitation. Definitive spectroscopic assignments for the entire class of Mo(II) bis(alkylamino)acetylene complexes must await single-crystal optical spectroscopy as well as theoretical calculations of the energy level dependence upon variations in the donor–acceptor properties of the alkyl groups, other ligands in the coordination sphere, and the orientation[32] of the acetylene ligand with respect to the rest of the ligands.

(iii) ^{1}H NMR Spectra. All the [Mo(CNR)$_5$(bpy)]$^{2+}$ starting materials have spectra in acetonitrile-d_3 consistent with rapid exchange of all five isocyanides on the NMR time scale. After reductive coupling, the *tert*-butyl analogue had two methyl resonances with a relative intensity ratio of 3:2 assigned to the RNC and RHNCCNHR ligands, respectively, also suggestive of fluxional behavior. In methanol, however, the former split into two singlets of 2:1 relative intensity. This result is that expected from the solid-state structures of **2** and **3**. Perhaps the freezing out of the fluxional processes in methanol is the result of hydrogen bonding with the solvent. A detailed study of this behavior was not undertaken. In the case where R = isopropyl, **7**, the proton NMR spectrum in CD$_2$Cl$_2$ is consistent with the solid-state structure illustrated in Figure 2, with the methyl groups on the coupled ligand being magnetically inequivalent. For the R = *tert*-butyl analogue, **4**, the most downfield resonance was confirmed as the NH proton of the coupled ligand by its disappearance upon its exchange with deuterium from D$_2$O in the manner described previously.[3]

(iv) Electrochemical Behavior. Figure 6 illustrates the changes in the cyclic voltammograms that typically accompany reductive coupling. Reported in Table VI are half-wave or peak potentials for the new, coupled ligand complexes in CH$_2$Cl$_2$ vs. ferrocene/ferricinium measured over a 3.5-V range. Both [Mo(CNR)$_5$(bpy)]$^{2+}$, as reported previously,[16] and [Mo(CNR)$_3$(RHNCCNHR)(bpy)]$^{2+}$ complexes undergo a reversible one-electron oxidation, confirmed by controlled potential coulometry for compound **8**. All six coupled ligand products are 210–290 mV easier to oxidize than the starting materials. The (dialkyldiamino)acetylene ligands are therefore less able to remove electron density from the Mo(II) center than are two terminal isocyanides. This result parallels that for [Mo(CNR)$_6$X]$^+$ vs. [Mo(CNR)$_4$(RNHCCNHR)X]$^+$[7] and reveals the poorer π-accepting character of the coupled ligand. The relative ordering of potentials for oxidation of [Mo(CNR)$_3$(RHNCCNHR)(bpy)]$^{2+}$ to [Mo(CNR)$_3$(RHNCCNHR)(bpy)]$^{3+}$ (R = Me < *i*-Pr < Cy < *t*-Bu < CH$_2$Ph) follows the trends found for [Mo(CNR)$_6$I]$^+$ and [Mo(CNR)$_7$]$^{2+}$ alkyl isocyanide complexes,[7] although a good rationale for this ordering is not obvious.

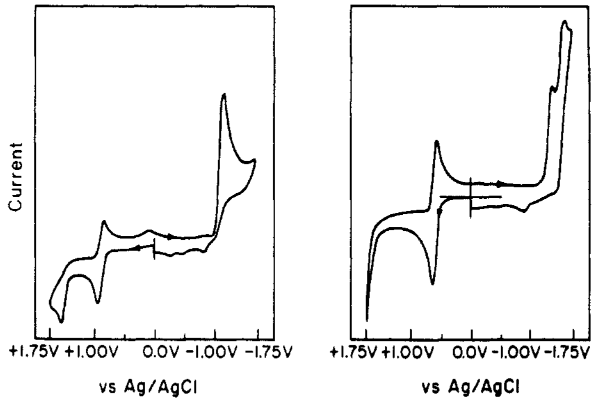


Figure 6. Electrochemical changes upon reductive coupling. On the left is displayed the cyclic voltammogram of [Mo(CNEt)$_5$(bpy)]$^{2+}$ while that of [Mo(CNEt)$_3$(EtHNCCNHEt)(bpy)]$^{2+}$ is shown on the right. The scan speed in these cyclic voltammograms was 200 mV s^{-1}.

Table VI. Voltammetric Half-Wave Potentials for [Mo(CNR)$_3$(RHNCCNHR)(bpy)](PF$_6$)$_2$ Complexes in Dichloromethane[a]

R	$E_{1/2}$ (ox.)	$E_{p,c}$ (1)	$E_{p,c}$ (2)
methyl	+0.084	−1.81	−2.02
ethyl	+0.140	−1.82	−2.03
isopropyl	+0.182	−1.88	−2.05
tert-butyl	+0.247	−1.75	−2.00
cyclohexyl	+0.200	−1.81	−2.08
benzyl	+0.283	−1.74	−1.99

[a] In volts vs. ferrocene/ferricinium with a Pt disk electrode (1 mm in diameter) and 0.2 M TBAH as supporting electrolyte.

The starting [Mo(CNR)$_5$(bpy)]$^{2+}$ complexes also exhibit an irreversible oxidation at +0.59 to +0.90 V which is not observed in the products. An irreversible reduction at −2.04 to −2.12 V clearly splits into two irreversible waves in the reduced purple products, possibly due to addition of electron density separately into the π^* orbitals of the bpy and RHNCCNHR ligand systems.

Summary and Conclusions. The finding that [Mo(CNR)$_5$(bpy)]$^{2+}$ complexes undergo reductive coupling (eq

---

(31) (a) Martin, B.; Waind, G. M. *J. Chem. Soc.* **1958**, 4284. (b) Sone, K.; Krumholz, P.; Stammreich, H. *J. Am. Chem. Soc.* **1955**, *77*, 777. (c) Gil, L.; Moraga, E.; Bunel, S. *Mol. Phys.* **1967**, *12*, 333.

(32) Kamata, M.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Yoshida, T.; Otsuka, S. *Inorg. Chem.* **1983**, *22*, 2416.

5) is significant for several reaons. It illustrates that replacement of two linear ligands by a chelating ligand with a small bite angle in a seven-coordinate complex does not alter the steric factors, especially the close nonbonded C···C contact, previously found to promote reductive coupling of isocyanide[3] or carbon monoxide[12] ligands. Reaction 5 also argues against two possible reasons why the [Mo$(CNR)_7]^{2+}$ dications do not undergo reductive coupling without prior dealkylation (eq 6).[25] One possibility is that the 2+ charge on the complex might promote dealkylation[2] and the other is that a halide, or pseudohalide such as cyanide, might be required to mediate electron transfer from zinc to the molybdenum center. The fact that $[Mo(CNR)_5(bpy)]^{2+}$ complexes do reductively couple their isocyanide ligands argues against both of these postulates and suggests that the important factor is the electron density at the metal center.

Both experimental[7] and theoretical[8] work reveals that increasing the electron density at the metal center will promote the reductive coupling of C_1 substrates such as RNC or CO at a seven-coordinate d^4 metal center. For molybdenum(II) complexes, the ease of reductive coupling correlates with the half-wave potential of the Mo(II)/Mo(III) reversible redox couple.[7] All the relevant redox potentials of $[Mo(CNR)_5(bpy)]^{2+}$ complexes studied in the present work fall within, albeit at the high end, of the range found previously to be required for reductive coupling to take place. Since $[Mo(CNR)_5(bpy)]^{2+}$ alkyl isocyanide complexes undergo reductive coupling whereas [Mo$(CNR)_7]^{2+}$ species do not,[3] we conclude that bpy is more electron releasing than two RNC ligands in this system. This conclusion is supported by the fact that [Mo(CN-*t*-Bu$)_7]^{2+}$ is ~200 mV more difficult to oxidize than [Mo(CN-*t*-Bu$)_5(bpy)]^{2+}$. Equation 8 depicts in simple valence bond terms the interaction of isocyanide with a molybdenum center. As charge accumulates on the metal, the

$$\mathrm{Mo{-}C{\equiv}N{-}R \longleftrightarrow Mo{=}C{=}\ddot{N}{\diagdown}R} \qquad (8)$$

structure on the right becomes more favored. Lewis acids also stabilize this carbenoid-type structure, which is favorable for reductive coupling, as has been explored theoretically.[33] Thus, any modification that favors the valence bond isomer on the right-hand side of eq 8 will activate these complexes for reductive coupling of adjacent isocyanide ligands.

Acknowledgment. This work was supported by National Science Foundation Grant NSF CHE85-42205.

Registry No. 1, 102747-03-5; 2, 102747-06-8; 3, 103000-51-7; 4, 103000-52-8; 5, 102747-08-0; 6, 102747-10-4; 7, 102747-12-6; 8, 102747-14-8; 9, 102747-16-0; [Mo(CN-*t*-Bu$)_4$(bpy)Cl](PF_6), 86954-23-6; [Mo(CN-*t*-Bu$)_5$(bpy)]$(PF_6)_2$, 86954-25-8; [Mo(CN-*t*-Bu$)_7$]$(PF_6)_2$, 41982-05-2; $[Mo(CNMe)_5(bpy)](PF_6)_2$, 86954-21-4; $[Mo(CNEt)_5(bpy)](PF_6)_2$, 102849-99-0; [Mo(CN-*i*-Pr$)_5$(bpy)]$(PF)_2$, 86968-44-7; $[Mo(CNCy)_5(bpy)](PF_6)_2$, 86954-17-8; $[Mo(CNBz)_5(bpy)](PF_6)_2$, 90885-45-3; $[Mo(CNCy)_7](PF_6)_2$, 72155-82-9.

Supplementary Material Available: Tables S1–S6 containing heavy-atom thermal parameters, hydrogen atom positional and thermal parameters, and structure factors for 2 and 3 (55 pages). Ordering information is given on any current masthead page.

---

[33] Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* 1982, *104*, 632.