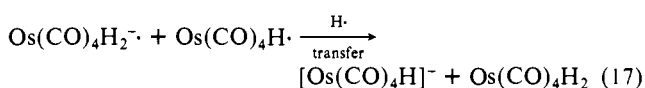
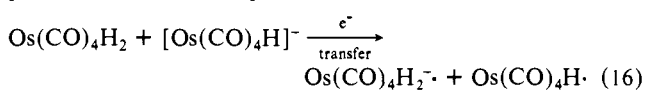


plausible alternative to proton transfer.



Conclusions

On the basis of the systems thus far examined, three generalizations may be proposed: (1) Both thermodynamic and kinetic acidity decrease down a column in the periodic table. (2) The rate of deprotonation of a hydrido transition-metal complex is slow compared with that of an oxygen or nitrogen acid and comparable with that of a carbon acid. (3) The rate of proton transfer from a hydrido transition-metal complex to its conjugate anion is much slower than that to a nitrogen base of comparable thermodynamic base strength.

Future work will test the validity of these generalizations for other types of hydrido transition-metal complexes.

Acknowledgment. This work was supported by NSF Grant CHE79-20373 and by the Colorado State University Regional NMR Center, funded by NSF Grant CHE78-18581. We are grateful to Professor J. W. Faller and to Professor J. I. Brauman for helpful discussions of statistical factors in saturation transfer rate measurements.

Registry No. ($\eta^5\text{-C}_5\text{H}_5$)W(CO)₃H, 12128-26-6; K[[$\eta^5\text{-C}_5\text{H}_5$)W(CO)₃], 62866-03-9; [Et₃NH][($\eta^5\text{-C}_5\text{H}_5$)W(CO)₃], 80462-63-1; ($\eta^5\text{-C}_5\text{H}_5$)Mo(CO)₃H, 12176-06-6; K[($\eta^5\text{-C}_5\text{H}_5$)Mo(CO)₃], 62866-01-7; [morH][($\eta^5\text{-C}_5\text{H}_5$)Mo(CO)₃], 80462-65-3; ($\eta^5\text{-C}_5\text{H}_5$)Cr(CO)₃H, 36495-37-1; K[($\eta^5\text{-C}_5\text{H}_5$)Cr(CO)₃], 69661-90-1; [morH][($\eta^5\text{-C}_5\text{H}_5$)Cr(CO)₃], 80462-67-5; Os(CO)₄H₂, 18972-42-4; K[Os(CO)₄H], 80462-68-6; [Et₃NH][Os(CO)₄H], 80462-70-0; Os(CO)₄(CH₃)(H), 22639-03-8; [TMGH][Os(CO)₄CH₃], 80462-42-6; Os₂(CO)₈H₂, 2565-05-6; [TMGH][Os₂(CO)₈H], 80462-44-8; morpholine, 110-91-8; Et₃N, 121-44-8.

Reductive Coupling of Coordinated Alkyl Isocyanides in Seven-Coordinate Molybdenum(II) and Tungsten(II) Complexes. Removal of the Coupled Ligand as an Oxamide^{1,2}

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Abstract: The synthesis of a variety of [M(CNR)₄(CNHR)₂]X⁺ complexes (M = Mo, R = *t*-C₄H₉, X = Cl, Br, I, CN; M = Mo, R = *c*-C₆H₁₁, X = I; M = W, R = *t*-C₄H₉, X = I) is described. The bright red complexes contain the coordinated RHNCCNHR ligand, formally regarded as an (*N,N*-dialkyldiamino)acetylene, derived by reductive coupling of two isocyanide ligands in the seven-coordinate [M(CNR)₆X]⁺ cations. When zinc is used as the reducing agent in a refluxing protic solvent such as wet THF or ethanol, the products were isolated in good to excellent (>90%) yields. Small amounts (~7%) of [Mo(CN-*t*-C₄H₉)₄(CNH-*t*-C₄H₉)₂]I⁺ were also obtained in homogeneous reactions of the trityl radical or of the photochemically generated benzophenone diradical with [Mo(CN-*t*-C₄H₉)₆I]⁺ in ethanol at room temperature. Although [Mo(CN-*t*-C₄H₉)₇]²⁺ yields mainly [Mo(CN-*t*-C₄H₉)₄(CNH-*t*-C₄H₉)₂(CN)]⁺ when subjected to the reductive coupling reaction conditions, the desired blue cation [Mo(CN-*t*-C₄H₉)₅(CNH-*t*-C₄H₉)₂]²⁺ was prepared by addition of *tert*-butyl isocyanide to [Mo(CN-*t*-C₄H₉)₄(CNH-*t*-C₄H₉)₂]I⁺. Proton and ¹³C NMR studies of the blue complex showed that, although the four *tert*-butyl isocyanide ligands *cis* to the acetylene are equivalent at room temperature, the fifth (*trans*) ligand is not in rapid exchange with the others. The mixed ligand [Mo(CNCH₃)₄(CNH-*t*-C₄H₉)₂]I⁺ complex was prepared by addition of methyl isocyanide to [Mo(CN-*t*-C₄H₉)₄(CNH-*t*-C₄H₉)₂]I⁺ under mild conditions. The coupled acetylene ligand could be removed with its C-C bond intact by oxidation, which produced the corresponding *N,N*-dialkyl oxamide. The best yields (~40%) were achieved by using hydrogen peroxide as the oxidant. Bonding interactions between the metal and coupled ligand are qualitatively discussed and used to rationalize trends in the structural and spectroscopic properties of the [Mo(CN-*t*-C₄H₉)₄(CNH-*t*-C₄H₉)₂]X⁺, X = Cl, Br, I, CN, and [Mo(CN-*t*-C₄H₉)₅(CNH-*t*-C₄H₉)₂]²⁺ cations. Mechanistic aspects of the coupling reaction are briefly considered.

Compounds of the group 6 transition metals of the general formula [M(CNR)₇]²⁺, [M(CNR)₆X]⁺ (R = alkyl, X = Cl, Br, I, CN, SnCl₃; R = aryl, X = I), and M(CNR)₅X₂ comprise a well-studied²⁻¹² class. These complexes have close interligand

contacts which could give rise to ligand migration or coupling reactions. Reductive coupling of two isocyanide ligands was found to occur in the reaction of [Mo(CN-*t*-C₄H₉)₆I]⁺ with zinc.¹³ In particular, a brilliant red crystalline material was obtained, the nature of which was revealed by X-ray crystallography. The complex turned out to be [Mo(CN-*t*-C₄H₉)₄(CNH-*t*-C₄H₉)₂]I,

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containing what is formally (*N,N'*-di-*tert*-butyldiamino)acetylene coordinated to molybdenum(II). This reductive coupling of isocyanides and the resulting coupled ligand product were both unprecedented in the literature. Subsequently, the chemistry was extended to the complexes $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{X}]^+$, $\text{X} = \text{Cl}, \text{Br}$.¹⁴ These gave the same type of product although the chloride and bromide complexes were obtained in lower yields and isolated as their tetrahalozincate(II) salts. The complex $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{I}]^+$ could be regenerated from $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}]^+$ photochemically in the presence of free *tert*-butyl isocyanide.^{14a} No organic products were isolated, however. An attempt to couple reductively the *tert*-butyl isocyanide ligands in the parent cation $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_7]^{2+}$ gave rise to $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2(\text{CN})\}]^+$, in which both reductive coupling¹³ and dealkylation² of the *tert*-butyl isocyanide ligands occurred.¹⁵

At the outset of the present study there were two broad objectives. First, we wished to determine the parameters (choice of metal, ligand, reducing agent, solvent, and redox properties¹⁶ of the complex) that influence the reductive coupling reaction. Second, we wanted to remove the coupled ligand with its newly formed carbon-carbon bond intact. Both of these objectives have been achieved, as described in the present article.

Experimental Section

All reactions were carried out by using the highest purity reagents commercially available. The $[\text{M}(\text{CNR})_6\text{X}]^+$ cations and $[\text{M}(\text{CNR})_7]^{2+}$ dications ($\text{M} = \text{Mo}, \text{W}$) were prepared by the methods described previously.² Isocyanides were prepared by standard literature procedures¹⁷ from the appropriate amine or *N*-alkylformamide. Microchemical analyses were performed by Galbraith Laboratories, Knoxville, TN, except for zinc which was determined by flame ionization using a Varian AA-375 atomic absorption spectrometer. Nuclear magnetic resonance spectra were taken on a Perkin-Elmer R-32, a Bruker WP-80, or a Bruker WM-300 spectrometer. A Perkin-Elmer 621 or a Jasco infrared spectrometer was used to record infrared spectra. Electronic spectra were recorded on a Cary 118 C spectrophotometer. All chromatographic separations were carried out by using "flash" chromatography as described by Still et al.¹⁸

The Coupling Reaction. Synthesis of Coupled Ligand Complexes. Bromotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Tetrabromozincate(II), $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Br}\}_2\text{ZnBr}_4]$. About 0.65 g (9.9 mmol) of zinc dust was added to a suspension of 2.2 g (2.9 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{Br}]$ in 150 mL of tetrahydrofuran (THF) containing 1 mL of water and refluxed for 6 h. The final deep red solution was filtered, and the solvent was removed in vacuo. The resulting red powder was dissolved in a minimal amount of 1:1 (v/v) of $\text{CH}_2\text{Cl}_2/\text{THF}$. A 70–300 mesh silica gel column (50 × 3 cm) was charged with this solution and eluted with THF. The deep red effluent was collected and the volume reduced. Deep red crystals (55% yield) were formed by slow diffusion of diethyl ether vapor into the concentrated THF solution: IR (Nujol mull) 3234 (m), 3104 (w), 2176 (s), 2125 (vs, br), 1594 (vs), 1504 (s), 1244 (w), 1224 (s), 1198 (vs) cm^{-1} ; ¹H NMR (CDCl_3) δ 1.49 (s), 1.64 (s), 9.20 (br), 20:10:1. Anal. Calcd for $\text{C}_{60}\text{H}_{112}\text{N}_{12}\text{Br}_6\text{Mo}_2\text{Zn}$: C, 41.46; H, 6.49; N, 9.64; Br, 27.58; Zn, 3.76. Found: C, 41.91, 41.54; H, 6.34, 6.70; N, 9.74, 9.89; Br, 26.85; Zn, 3.90, 3.57.

Chlorotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Tetrachlorozincate(II), $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Cl}\}_2\text{ZnCl}_4]$. A 2.0-g portion of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{Cl}]$ was used in a procedure analogous to that reported above for the bromide analogue. A 40% yield of product was obtained: IR (Nujol mull) 3232 (m), 3107 (w), 2177 (s), 2127 (vs, br), 1592 (vs), 1515 (s), 1242 (w), 1227 (s), 1202 (vs) cm^{-1} ; ¹H NMR (CDCl_3) δ 1.49 (s), 1.62 (s), 9.10 (br), 20:10:1. Anal. Calcd for $\text{C}_{60}\text{H}_{112}\text{N}_{12}\text{Cl}_6\text{Mo}_2\text{Zn}$: C, 48.97; H, 7.67; N, 11.42; Cl, 14.45; Zn, 4.44. Found: C, 48.29; H, 7.78; N, 11.48; Cl, 14.58, 14.62; Zn, 4.52.

Chlorotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Chloride, $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Cl}\}]$. A mixture containing 6.75 g (10 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{Cl}]$, 2 g (31 mmol) of Zn, 25 mL of H_2O , and 100 mL of tetrahydrofuran was refluxed for 12 h. The resulting red solution was filtered and the solvent removed under reduced pressure, giving 6.11 g of red $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Cl}\}]$ (91% yield). Analysis for Zn by AA (flame ionization) indicated the compound contained less than 0.35% Zn by weight. Therefore it is not the tetrachlorozincate salt: mp 183–188 °C; IR (KBr pellet) 3253 (m), 2980 (m), 2182 (m), 2133 (s), 2060 (sh), 1580 (m), 1515 (w), 1505 (w), 1460 (w), 1413 (m), 1400 (m), 1373 (m), 1230 (m), 1205 (m), 940 (s), 552 (m), 520 (w) cm^{-1} ; ¹H NMR (CDCl_3) δ 1.5 (s), 1.57 (s), 8.0 (br), 36:20:1; NMR ($\text{C}_6\text{D}_6/\text{CDCl}_3$) δ 1.15 (s), 1.75 (s), 6.4 (br), 47:23:1. Anal. Calcd for $\text{C}_{30}\text{H}_{56}\text{N}_6\text{Cl}_2\text{Mo}$: C, 53.97; H, 8.45; N, 12.59; Cl, 10.62. Found: C, 53.82; H, 8.48; N, 12.46; Cl, 10.80.

Iodotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Iodide, $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}]$. **Method A. A suspension containing 2.5 g (2.9 mmol) of orange $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{I}]$ and about 0.65 g (~10 mmol) of zinc dust in 150 mL of THF containing 1 mL of water was refluxed for at least 2 h. The final deep red solution was filtered, and the solvent was removed in vacuo. The red powder was recrystallized from acetone or benzene and diethyl ether (yield 90%): IR (Nujol mull) 2175 (s), 2125 (vs, br), 1593 (vs), 1533 (s), 1250 (w), 1222 (s), 1197 (vs) cm^{-1} ; ¹H NMR (CDCl_3) δ 1.48 (s), 1.66 (s), 9.68 (br), 25:10:1. Anal. Calcd for $\text{C}_{30}\text{H}_{56}\text{N}_6\text{I}_2\text{Mo}$: C, 42.36; H, 6.64; N, 9.88; I, 29.84. Found: C, 42.16, 42.64; H, 6.68, 6.27; N, 9.80, 9.83; I, 29.97, 28.91.**

Method B. This compound was prepared in 90% yield according to the method described for $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Cl}\}]$. A 4–6-h reflux period was required.

Method C. A solution of 0.103 g (0.12 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{I}]$ and 0.307 g (1.1 mmol) of triphenylmethyl chloride dissolved in 50 mL of 95% ethanol was purged with N_2 for 30 min. Then 0.8 g (12 mmol) of Zn dust was added while the solution was stirred. Gas evolution was observed. The mixture was allowed to stir for 24 h at room temperature, conditions under which no reductive coupling is observed in the reaction with zinc alone. Then 0.1 g (0.67 mmol) of NaI was added to the solution. The residue was chromatographed on a 1 × 15 cm silica gel column eluted with 3% EtOH/ CHCl_3 . A red band was collected and the solvent removed under reduced pressure leaving a red powder. Deep red crystals, 6 mg (6% yield), having a PMR spectrum identical with that of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CHN}-t\text{-C}_4\text{H}_9)_2\text{I}\}]$ were obtained by vapor diffusion of ether into an absolute ethanol solution of the red powder.

Method D. A nitrogen purged solution of 112 mg (0.13 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{I}]$ and 1.5 g of benzophenone (8.2 mmol) in 60 mL of absolute alcohol was photolyzed for 24 h. The solvent was removed and the residue chromatographed on silica gel eluted with 3% EtOH/ CHCl_3 . The red band (8 mg) was collected and shown by ¹H NMR spectroscopy to be identical with that of authentic $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}]$. The yield was 7%.

Iodotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Hexafluorophosphate, $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}(\text{PF}_6)_2]$. To a solution of 0.85 g (1 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{I}]$ in 25 mL of methanol was added a solution of 1.2 g (7 mmol) of NaPF_6 in 25 mL of warm methanol. The mixture was allowed to stand at 0 °C overnight after which time 0.4 g of yellow crystals was isolated. These crystals were refluxed in the presence of 0.6 g (9 mmol) of zinc dust in 150 mL of THF for 3 days in the presence of 5 mL of an aqueous solution containing 0.6 g (3.5 mmol) of NaPF_6 . The final deep red solution was filtered, and the solvent was removed completely in vacuo. The residual red powder was extracted with 20 mL of a 1:1 THF/ CH_2Cl_2 solution. A silica gel (70–300 mesh) 50 × 3 cm column packed with THF was charged with the red solution and eluted with THF. The deep red effluent was collected and its volume was reduced. Slow addition of diethyl ether gave the product in ~10% yield: IR (Nujol mull) 3327 (s), 2179 (s), 2173 (vs, br), 1587 (vs), 1502 (s), 1249 (w), 1244 (s), 1199 (vs), 839 (vs) cm^{-1} ; ¹H NMR (CDCl_3) δ 1.51 (s), 1.58 (s), 7.95 (br), 25:10:1. Anal. Calcd for $\text{C}_{30}\text{H}_{56}\text{N}_6\text{IMoPF}_6$: C, 41.48; H, 6.50; N, 9.68. Found: C, 41.69, 41.54; H, 6.57, 6.66; N, 9.71, 9.57.

Iodotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Tetrafluoroborate, $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}(\text{BF}_4)]$. A solution of 1.46 g (1.7 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6\text{I}]$ dissolved in 50 mL of methanol was passed through a 2-cm diameter column containing 25 mL of Dowex 2-X8 anion exchange resin (BF_4^- form) at a rate of 1 mL/min. The solvent was removed under reduced pressure leaving a red powder. Crystals were obtained by vapor diffusion of Et_2O into an acetone solution of the powder: ¹H NMR (CDCl_3) δ 1.49 (s), 1.60 (s), 8.19 (br), 20:10:1; IR

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(KBr pellet) 3299 (m), 3170 (m), 2980 (m), 2170 (m), 2122 (s), 2060 (sh), 1593 (m), 1530 (w), 1475 (m), 1460 (m), 1395 (m), 1370 (m), 1230 (m), 1205 (s), 1100 (s), 520 (m) cm^{-1} . Anal. Calcd for $\text{C}_{30}\text{H}_{56}\text{N}_6\text{MoBF}_4$: C, 44.46; H, 6.97; N, 10.37; I, 15.66. Found: C, 45.30; H, 7.16; N, 10.55; I, 17.51.

Iodotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)tungsten(II) Iodide, $[\text{W}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$. A 1:3 (by volume) $\text{H}_2\text{O}/\text{MeOH}$ solution containing 105 mg (0.11 mmol) of $[\text{W}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ and 100 mg (1.5 mmol) of Zn was refluxed for 40 h. The final orange-red solution was filtered, and the solvent was removed under reduced pressure. The crude product was "flash" chromatographed on a 1.25×30 cm silica gel column eluted with 2% $\text{EtOH}/\text{CH}_2\text{Cl}_2$. The first band eluted was red-orange and contained 45 mg (43% yield) of solid $[\text{W}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$. A smaller orange band, which has the same retention time as starting material, followed but was not collected. Crystalline $[\text{W}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$ was obtained by vapor diffusion of Et_2O into a methanolic solution of the compound: IR (KBr pellet) 3185 (m), 2980 (m), 2933 (m), 2175 (m), 2120 (s), 2065 (sh), 1590 (m), 1520 (m), 1475 (m), 1460 (m), 1396 (m), 1370 (m), 1232 (m), 1205 (m), 520 (m), 410 (w) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.5 (s), 1.63 (s), 9.47, 20:10:1. Anal. Calcd for $\text{C}_{30}\text{H}_{56}\text{N}_6\text{WI}_2$: C, 38.40; H, 6.01; N, 8.95; W, 19.59. Found: C, 38.41; H, 6.02; N, 8.86; W, 19.84.

Iodotetrakis(cyclohexyl isocyanide)((*N,N'*-dicyclohexyldiamino)-acetylene)molybdenum(II) Iodide, $[\text{Mo}(\text{CN}-c\text{-C}_6\text{H}_{11})_4(\text{CNH}-c\text{-C}_6\text{H}_{11})_2]\text{I}$. This complex was prepared in a manner analogous to that of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$ (method B). The red product was chromatographed on silica eluted with 3% $\text{EtOH}/\text{CHCl}_3$ and recrystallized from hot acetone. The overall yield was 28%: ^1H NMR (CDCl_3) δ 1.4 (br), 1.8 (br), 3.95 (br), 9.8 (d, $J = 8$ Hz); IR (KBr pellet) 3160 (m), 3115 (m), 2930 (s), 2850 (m), 2175 (sh), 2127 (s), 1660 (m, br), 1510 (m), 1495 (w), 1453 (m), 1365 (m), 1355 (w), 1325 (m), 1260 (w), 1245 (w), 1157 (w), 1130 (m), 700 (m), 652 (w), 532 (w) cm^{-1} . Anal. Calcd for $\text{C}_{42}\text{H}_{88}\text{N}_6\text{MoI}_2$: C, 50.11; H, 6.81; N, 8.35; I, 25.25. Found: C, 49.91; H, 6.84; N, 8.24; I, 25.07.

Cyanotetrakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Hexafluorophosphate, $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2(\text{CN})](\text{PF}_6)$. **Method A.** A solution containing 1.1 g (1.4 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6(\text{CN})](\text{PF}_6)$ and 1.5 g (23 mmol) of Zn in 125 mL of 1:4 (by volume) $\text{H}_2\text{O}/\text{EtOH}$ was refluxed for 10 days. During this time, the initial yellow solution turned brown then purple. The solution was allowed to cool and was filtered, and the solvent was removed under reduced pressure. The resulting solid was chromatographed on a 2.5×20 cm silica gel column eluted with 3% $\text{EtOH}/\text{CHCl}_3$. A purple band containing 0.36 g (33% yield) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2(\text{CN})](\text{PF}_6)$ came off first: mp 180–183 °C; IR (KBr pellet) 3250 (w), 2930 (m), 2900 (m), 2185 (m), 2147 (s), 1583 (m), 1378 (m), 1240 (m), 1210 (m), 845 (s), 700 (w), 555 (w), cm^{-1} ; ^1H NMR (CDCl_3) δ 1.51 (s), 1.55 (s), 8.29 (s) 20:10:1. Anal. Calcd for $\text{C}_{31}\text{H}_{56}\text{N}_7\text{MoPF}_6$: C, 48.50; H, 7.35; N, 12.77; P, 4.03. Found: C, 49.21; H, 7.44; N, 12.68; P, 3.95.

Method B. This compound was also obtained by refluxing $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_7](\text{PF}_6)_2$ with Zn in 95% ethanol as described elsewhere. The preparation and crystal structure determination of the tetraphenylborate salt have also been reported.¹⁵

Pentakis(*tert*-butyl isocyanide)((*N,N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) Salts, $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_5(\text{CNH}-t\text{-C}_4\text{H}_9)_2](\text{NO}_3)_2$. To a stirred solution of 0.50 g (0.59 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$ and 0.43 g (5.2 mmol) of *tert*-butyl isocyanide in 25 mL of methanol was added 0.42 g (1.6 mmol) of $\text{Ti}(\text{NO}_3)_3$. An immediate precipitate (TII) formed. After being stirred for 12 h at room temperature, the solution turned from red to deep purple. The TII was removed by filtration, and the solvent was removed under reduced pressure. The deep purple residue was redissolved in CH_2Cl_2 and filtered to remove the excess $\text{Ti}(\text{NO}_3)_3$. The solvent was removed under reduced pressure to yield 0.43 g (91% yield) of blue $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_5(\text{CNH}-t\text{-C}_4\text{H}_9)_2](\text{NO}_3)_2$: IR (KBr pellet) 3132 (m), 3090 (m), 2972 (m), 2930 (m), 2207 (m), 2178 (m), 2123 (s), 2050 (sh), 1599 (m), 1529 (m), 1460 (m), 1370 (s), 1228 (m), 1190 (s), 1030 (w), 827 (w), 699 (w), 690 (w), 635 (w), 550 (w), 520 (w) cm^{-1} ; ^1H NMR acetone- d_6 , δ 1.62 (s), 1.74 (s), 10.8 (br), 62:10:1; NMR ($\text{C}_6\text{D}_6/\text{CD}_3\text{OD}$) δ 1.28 (s), 1.50 (s), 1.54 (s), 4.2:2.2:1.

To a solution of 1 g (1.2 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_5(\text{CNH}-t\text{-C}_4\text{H}_9)_2](\text{NO}_3)_2$ in 50 mL of methanol was added a solution of 2 g (5.9 mmol) of NaBPh_4 dissolved in 50 mL of methanol. Blue crystals of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_5(\text{CNH}-t\text{-C}_4\text{H}_9)_2](\text{BPh}_4)_2 \cdot \text{CH}_3\text{OH}$ precipitated from the solution over a period of 4 h and were collected by vacuum filtration (1.4 g, 86% yield): IR (KBr pellet) 3275 (w), 3052 (m), 3030 (m), 2980 (m), 2925 (w), 2208 (m), 2180 (w), 2135 (s), 1632 (w), 1579 (m), 1475 (m), 1452 (m), 1425 (w), 1370 (m), 1230 (w), 1185 (m), 1030 (w), 725

(m), 697 (s), 600 (m) cm^{-1} ; IR (MeOH, CaF_2 cells) 2208 (m), 2179 (m), 2145 (s) cm^{-1} ; ^1H NMR (CD_3OD): 1.53 (s), 1.58 (s), 1.62 (s) δ , 4.2:1. Anal. Calcd for $\text{C}_{84}\text{H}_{108}\text{N}_7\text{MoB}_2\text{O}$: C, 74.77; H, 8.07; N, 7.27; B, 1.60; Mo, 7.11. Found: C, 74.68, 74.75; H, 7.94, 8.11, N, 7.23, 7.23; B, 1.64; Mo, 7.75. The methanol of crystallization was detected in a single-crystal X-ray diffraction study.¹⁹

The Coupling Reaction. Control Experiments. Reaction of Zinc with *tert*-Butyl Isocyanide. Two grams of *tert*-butyl isocyanide was refluxed in 150 mL of THF containing 1 mL of H_2O in the presence of 0.65 g of Zn powder for 2 days under a nitrogen atmosphere. A 2-mL aliquot was withdrawn before and after reflux, cooled to room temperature, and examined by optical, infrared, and NMR spectroscopy in THF, hexane, and CDCl_3 , respectively. No changes were noted.

Studies of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ in Refluxing THF. A 2.5-g portion of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ was refluxed in 150 mL of wet THF under nitrogen for 2 days. No color change was observed. Isolation of the yellow-orange complex and spectroscopic analysis showed it to be unreacted starting material.

Reaction of Zinc with $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ in Dry THF. A 2.5-g portion of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ was refluxed in 150 mL of dry THF in the presence of 0.65 g of Zn powder under a dry nitrogen atmosphere for 2 days. A deep orange color was observed during the course of the reaction. The solution was filtered under nitrogen and pumped to dryness. Spectroscopic analysis of the brownish orange powder did not indicate the presence of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$. The product was not further characterized.

Preparation of a Deuterated Sample of Coupled Ligand Complex. A 2.5-g portion of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ was refluxed with 0.65 g of Zn powder in 150 mL of dry THF containing 1.5 mL of D_2O under nitrogen for 4 h. The deep red solution was filtered and the solvent volume reduced. Dry Et_2O was added to precipitate red microcrystals. Spectroscopic data of the red product showed it to be identical with that obtained by direct deuterium exchange as reported previously.¹³

Solvent Dependence. Method A for preparing $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$ was followed except that wet methanol or acetone was substituted for wet THF. Spectroscopic analysis showed the same product to be formed; the yields were ~90%.

Reactions of the Coupled Ligand Product Including Its Isolation as an Oxamide. Exchange of *tert*-Butyl for Methyl Isocyanide Ligands in $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$. A 30-mL benzene solution containing 0.5 g (0.6 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$ and 1 mL of methyl isocyanide was refluxed for 6 h. After the solution cooled, the solvent was removed under reduced pressure. A ^1H NMR spectrum of the resultant red oil indicated the presence of several products. The oil was redissolved in benzene containing 1 mL of methyl isocyanide and refluxed for an additional 6 h. The solution was allowed to cool and stand at room temperature for 2 days, during which time a red precipitate formed. The precipitate, 165 mg of $[\text{Mo}(\text{CNCH}_3)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{I}$ (pure by a ^1H NMR spectroscopic criterion), was collected by vacuum filtration (41% yield). The solvent was removed from the deep red solution and a ^1H NMR spectrum of the residue dissolved in CDCl_3 indicated that it contained a mixture of ligand displacement products. A thin-layer chromatogram of the product mixture on silica eluted with 3% $\text{EtOH}/\text{CHCl}_3$ showed only traces of orange or yellow products. These colors would indicate the presence of $[\text{Mo}(\text{CNR})_6\text{X}]^+$ and $[\text{Mo}(\text{CNR})_7]^+$ which are the expected organometallic products resulting from the displacement of the bis(*tert*-butylamino)-acetylene ligand: IR (KBr pellet) 3155 (m), 2197 (m), 2150 (s), 1581 (m), 1407 (m), 1350 (w), 1205 (m), 715 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.66 (s), 3.52 (s), 10.06 (br), 3:2:0.14.

***N,N'*-Di-*tert*-butyl Oxamide.** A mixture of 30 mL (0.29 mol) of *tert*-butylamine and 10 mL (0.074 mmol) of diethyl oxalate was refluxed for 2 days under nitrogen. The reaction mixture was allowed to cool, and the precipitate was collected and recrystallized from 100 mL of isopropyl alcohol: IR (CHCl_3) 3375 (m), 3015 (s), 2970 (m), 1680 (s), 1510 (s), 1480 (m), 1457 (m), 1422 (m), 1395 (w), 1370 (m) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.38 (s), 7.33 (br).

Oxidative Removal of the Bis(*tert*-butylamino)acetylene Ligand. Method A. To a solution of 0.175 g (0.26 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4(\text{CNH}-t\text{-C}_4\text{H}_9)_2]\text{Cl}$ in 10 mL of ethanol was added 100 mL of H_2O followed by 0.3 mL of 3% H_2O_2 (0.26 mmol). The red solution decolorized over a 1-h period, and a white precipitate formed. The solution was extracted three times with a total of 100 mL of hexanes. The organic layer was dried over Na_2SO_4 , and the solvent was removed under reduced pressure. A yield of 20 mg (38%) of white crystals, having a PMR spectrum identical with that of authentic *N,N'*-di-*tert*-butyl oxamide, was obtained: mass spectrum (CI, methane), m/e (relative

(19) Bianconi, P. A.; Hollis, L. S.; Dewan, J. C.; Lippard, S. J., to be submitted for publication.

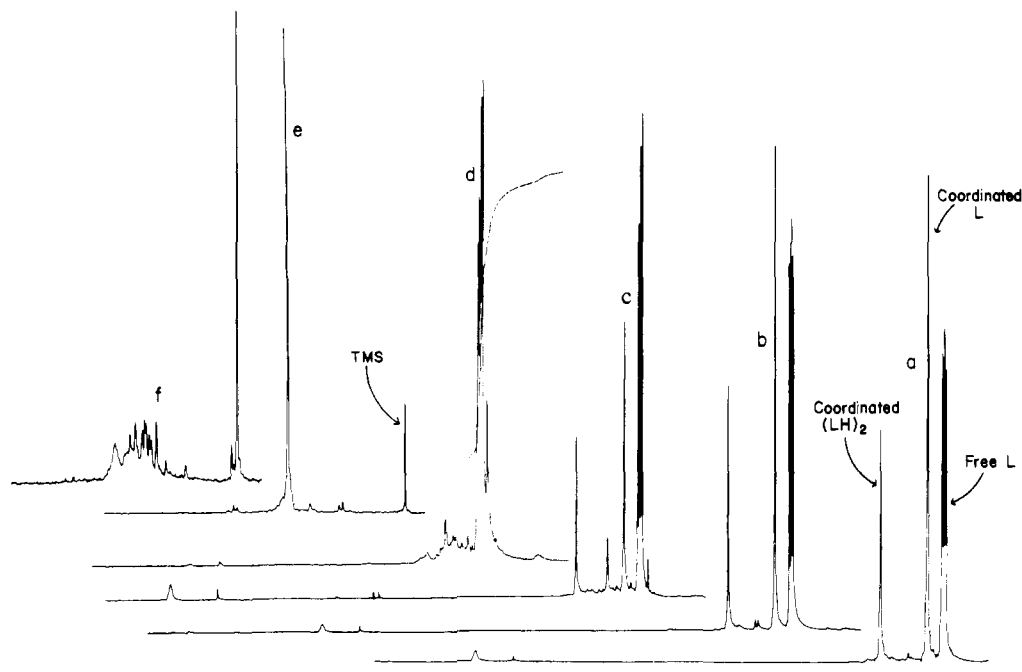


Figure 1. Proton NMR spectroscopic study of the photolysis of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4]_2^+$ in C_6D_6 in the presence of *tert*-butyl isocyanide. The solution was irradiated with a 200-W high-pressure Hg arc lamp. (a) $t = 0$; (b) $t = 24$ h; $\lambda > 500$ nm; (c) $t = 48$ h; 366-nm band-pass filter; (d) $t = 72$ h; Pyrex glass filter; (e) spectrum of the crystalline precipitate dissolved in CDCl_3 ; (f) spectrum in CDCl_3 of the hexane soluble photolysis products. For more details, see text.

intensity) 201 (18%), 145 (80%), 89 (100%).

Method B. To a solution of 1 g (1.5 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4]_2^+$ $\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Cl}\}\text{Cl}$ was added 0.82 g (3.0 mmol) of PhICl_2 (see ref 2). The solution was stirred at room temperature for 5 min. The solvent was removed and the residue chromatographed on a 0.5×7 cm silica gel column eluted with 25% hexanes/ CH_2Cl_2 . The first UV active band contained iodobenzene and aliphatic products which had six sharp ^1H NMR resonances in the range of δ 1.2–1.7. The second UV active band contained 14.7 mg (5% yield) of a compound whose ^1H NMR spectrum was identical with that of authentic *N,N'*-di-*tert*-butyl oxamide.

Method C. To a solution of 0.92 g (1.1 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4]_2^+$ $\{(\text{CN}-t\text{-C}_4\text{H}_9)_2\text{I}\}\text{I}$ dissolved in 50 mL of isopropyl alcohol and wrapped in aluminum foil was added 0.6 g (3.5 mmol) of AgNO_3 . The solution was stirred overnight at room temperature before adding 0.18 g (1.2 mmol) of NaI . The resulting precipitate was removed by filtration, the solvent was removed under reduced pressure, and the residue was washed with a total of 50 mL of hexanes. The organic layer was filtered and removed under reduced pressure, giving 95 mg of a yellow oil whose most abundant component (by ^1H NMR spectroscopy) was *N,N'*-di-*tert*-butyl oxamide. The ^1H NMR spectrum also contained sharp resonances at δ 1.05, 1.22, 1.33, 1.36, 1.41 and 1.43 which ranged from 0.1 to 0.5 times the intensity of the peak at δ 1.38. Very weak but sharp peaks at δ 6.55 and broad peaks at δ 6.8, 7.4, 7.6, and 8.2 were probably N-H protons.

Photochemical Displacement of the Bis(alkylamino)acetylene Ligand.

Method A. A degassed and sealed NMR tube containing a solution of 10.6 mg (0.016 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4]_2^+$ $\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{Cl}\}\text{Cl}$ and 7.5 mg (0.10 mmol) of *tert*-butyl isocyanide dissolved in C_6D_6 (the integrated intensity of free isocyanide to coordinated ligand *tert*-butyl resonances was 1.08:1.0) was photolyzed by a 200-W high-pressure mercury arc lamp filtered with a Corning glass CS-69 filter (cutoff ~ 500 nm). After 24 h the integrated ratio of free isocyanide to coordinated ligand resonances was largely unchanged (1.01:1), no additional signals had appeared, and no visible change occurred in the sample. The photolysis was continued, replacing the filter with a Corning glass 366-nm band-pass filter. After 24 h more, the solution had turned light brown and deposited a yellow-orange precipitate, which was subsequently shown to be $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{Cl}$ (vide infra). The integrated ratio of free isocyanide to coordinated ligand resonances had increased to 1.71:1 ($\sim 45\%$ conversion). Two new small singlets also appeared, one at δ 0.79, a value identical with the chemical shift of commercial *tert*-butyl cyanide from Aldrich dissolved in C_6D_6 with a drop of *tert*-butyl isocyanide, and the other at δ 1.34 (unidentified); a number of very small peaks also appeared from δ 1.0 to 1.7. The photolysis was continued with a Pyrex glass filter until the solution was pale yellow (~ 24 more hours), after which time more yellow-orange crystalline precipitate had formed. The

^1H NMR spectrum showed that all of the initial metal complex was gone while the peak at δ 0.79 had grown substantially with respect to the *tert*-butyl isocyanide peak. The additional peaks ranging from δ 1.0 to 1.7 also grew, nearly obscuring the peak at δ 1.34.

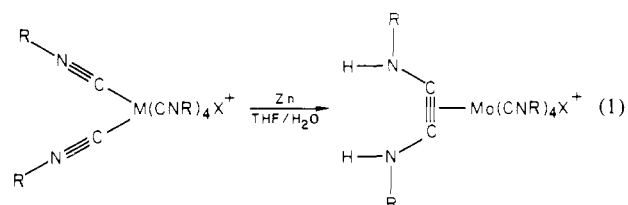
The NMR tube was opened, the yellow-orange crystals were collected, and the C_6D_6 was removed under reduced pressure. The ^1H NMR spectrum of the yellow-orange crystals (δ 1.55 in CDCl_3) was identical with that of an authentic sample of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{Cl}$. The ^1H NMR of the hexane soluble portion of the residue from the C_6D_6 solution shows a mixture of products with chemical shifts ranging from δ 0.9 to 1.7. The NMR spectra corresponding to the course of the photolysis reaction are displayed in Figure 1.

Method B. A deoxygenated solution containing 1.03 g (1.2 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4]_2^+$ $\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}\text{I}$ dissolved in 300 mL of EtOH was photolyzed for 40 h by a Pyrex-jacketed 450-W medium-pressure Hanovia mercury lamp. The solution turned from red to yellow over the course of the reaction. The solvent was removed under reduced pressure and chromatographed on silica eluted with 3% EtOH/ CHCl_3 . A bright orange band that contained 700 mg of a compound having a ^1H NMR spectrum identical with that of authentic $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ (100% yield based on isocyanide) was the only product detected.

Method C. To a suspension of 0.5 g (0.58 mmol) of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4]_2^+$ $\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\text{I}\}\text{I}$ in 30 mL of degassed benzene was added 1 g (12 mmol) of *tert*-butyl isocyanide. The solution was irradiated for 3 days with a 550-W Hanovia high-pressure quartz Hg vapor lamp. About 0.45 g of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6]\text{I}$ (90% yield) precipitated.

Results and Discussion

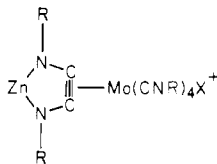
Synthesis. The Coupling Reaction. The complexes $[\text{M}(\text{CNR})_6\text{X}]^+$ ($\text{M} = \text{Mo}$, $\text{R} = t\text{-C}_4\text{H}_9$, $\text{X} = \text{I}$, Br , Cl , CN ; $\text{M} = \text{Mo}$, $\text{R} = c\text{-C}_6\text{H}_{11}$, $\text{X} = \text{I}$; $\text{M} = \text{W}$, $\text{R} = t\text{-C}_4\text{H}_9$, $\text{X} = \text{I}$) are reduced by zinc in a protic solvent to produce complexes containing a coordinated bis(alkylamino)acetylene, eq 1, in good to very high



yield ($>90\%$). By contrast, the complexes $[\text{Mo}(\text{CNAr})_6]\text{I}^+$ ($\text{Aryl} = p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$) and $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_6(\text{SnCl}_3)]^+$

cannot be reductively coupled. The aryl isocyanide molybdenum(II) complexes are not stable under the reaction conditions. Instead they decompose even in the absence of a reducing agent, resulting in complex mixtures of unidentified products. Attempts to couple the trichlorostannyl derivative gave the $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_7]^{2+}$ cation.²⁰

The reducing agent of choice is zinc metal. Stronger reducing agents such as sodium amalgam or magnesium preferentially reduce the protic solvent generating hydrogen gas, while more weakly reducing metals such as mercury are unreactive. The complex $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{I}]^+$ is not produced by electrochemical reduction of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{I}]\text{I}$ in THF/ H_2O at room temperature.¹⁶ This result is not unexpected because the LUMO is σ antibonding with respect to the ligands. Instead, electrochemical reduction may result in ligand dissociation and generation of a hexacoordinate Mo(0) species.¹⁶ Although it is uncertain whether the high yields obtained with zinc and unique, coordination of Zn^{2+} with the deprotonated nitrogen atoms of the coordinated bis(alkylamino)acetylene ligand might occur along the reaction pathway

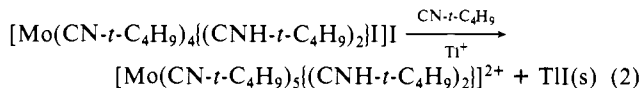


Small yields of the complex $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{I}]^+$ are obtained when a homogeneous reducing agent, the trityl radical, produced by reduction of chlorotriphenylmethane with zinc, is allowed to react with $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{I}]\text{I}$ in ethanol at room temperature. Benzophenone diradical, produced photochemically, also reduces $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{I}]\text{I}$, but in low yield. In contrast, the homogeneous reducing agent SnCl_2 reacts with $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{Cl}]\text{Cl}$ to produce the complex $[\text{Mo}(\text{SnCl}_3)(\text{CN-}t\text{-C}_4\text{H}_9)_6]^+$ containing the trichlorostannate ligand.²⁰

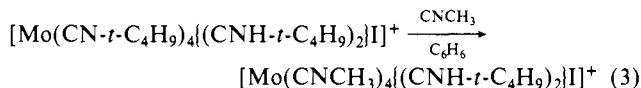
Control experiments show that free alkyl isocyanides react neither with zinc nor with each other in the presence of zinc under reflux in wet THF, demonstrating that coordination with the group 6 metal is required for the coupling reaction to occur. Both zinc and a source of protons are needed since eq 1 yields only starting material if either the metal or water, respectively, are omitted.

One example of the reductive coupling of coordinated isocyanides was found in which W(II) rather than Mo(II) is the central metal. The lower yield of this reaction compared to that of its Mo analogue may be due to insufficient reaction time since some unreduced starting material was recovered. The reduction of $[\text{W}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{I}]\text{I}$ requires a significantly longer reaction time than its Mo analogue.

The reaction times and overall yields of the reductive coupling of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{X}]^+$ complexes are a function of the unique ligand X. When X = I, the reduction takes only 4 h and proceeds in at least 90% yield. To produce the same yield when X = Cl requires a 12-h reaction time. Shorter reaction times result in a lower yield (~40%) of the coupled product, which was isolated as the tetrachlorozincate salt. The cyanohexakis(*tert*-butyl isocyanide)molybdenum(II) cation and heptakis(alkyl isocyanide)molybdenum(II) dication require a 5–10-day reaction time to obtain a maximum (30%) yield. The product of both reactions is $[\text{Mo}(\text{CN})(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}]^{2+}$. It is not known whether the dealkylation of alkyl isocyanide,² which is observed during the reduction of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_7]^{2+}$, occurs before, after, or concurrently with the reductive coupling reaction. The originally anticipated product of this reaction, $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_5\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}]^{2+}$, has been prepared indirectly by displacement of the coordinated iodide in $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{I}]^+$ with *tert*-butyl isocyanide. The equilibrium (eq 2) is driven by precipitation of thallos iodide. Thallium is preferred to silver since Ag(I) oxidizes the Mo(II) complex.

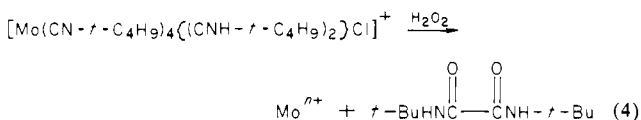


Removal of the Coupled Ligand. Under mild thermal conditions in the presence of a different alkyl isocyanide such as CNCH_3 the coordinated *tert*-butyl isocyanide ligands of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{I}]\text{I}$ are replaced (eq 3), and the fully

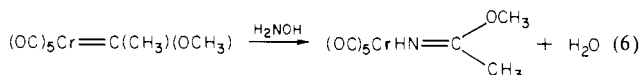
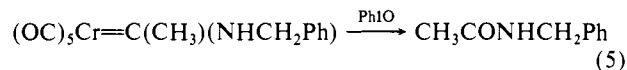


substituted complex $[\text{Mo}(\text{CNCH}_3)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{I}]\text{I}$ may be isolated as the major product in moderate yields. Very little if any of the $[\text{Mo}(\text{CNR})_7]^{2+}$ or $[\text{Mo}(\text{CNR})_6\text{I}]^+$ cations are formed; these would be the expected organometallic products if displacement of the bis(alkylamino)acetylene ligand had occurred.

Oxidation of the complex $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{Cl}]\text{Cl}$ with a variety of reagents (Ag^+ , PhICl_2 , and H_2O_2) proceeds smoothly to produce *N,N*'-di-*tert*-butyl oxamide in moderate yield (up to 40%) (eq 4). Oxidations using 1 mol of



H_2O_2 /mol of metal complex produce the highest yields (~40%). Lower yields are obtained with more oxidant and may be the result of oxidative cleavage of either the oxamide C–C bond or of the coordinated bis(alkylamino)acetylene C≡C bond. Using less oxidant results in incomplete oxidation of the metal complex. This type of oxidation product, an amide, is characteristic of oxidation of carbene complexes,²¹ examples of which are depicted in eq 5^{21b} and 6.^{21c} Presumably, the first step is nucleophilic attack of the oxidant at the coordinated carbon atom.



The coordinated bis(alkylamino)acetylene ligand is liberated photochemically in polar solvents such as ethanol or in aromatic solvents in the presence of free alkyl isocyanide. This reaction leads to complex mixtures of organic products, most of which have not been identified. Possibly the bis(alkylamino)acetylene is released in an excited state which undergoes fragmentation or reaction with solvent. Alternatively, the free ligand may undergo secondary photolysis reactions. The organometallic products of this reaction are the $[\text{Mo}(\text{CNR})_6\text{X}]^+$ or $[\text{Mo}(\text{CNR})_7]^{2+}$ cations. The relative amounts of each cation depend on the particular reaction conditions. The photolysis of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{I}]\text{I}$ in ethanol in the absence of free isocyanide produced $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{I}]\text{I}$ in approximately 70% yield based on Mo. A 67% yield is the expected theoretical value if all the available isocyanide recombined with Mo^{2+} in solution after release of the bis(alkylamino)acetylene. When the photolysis was carried out in benzene with added excess isocyanide, the compound $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{Cl}]\text{Cl}$ precipitated out of solution in good yield. The excess isocyanide serves the dual role of solubilizing $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{Cl}]\text{Cl}$ and occupying vacant coordination sites produced by loss of the bis(alkylamino)acetylene ligand. In benzene the photochemically active absorption band occurs ~350 nm. The course of the photolysis of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{Cl}]\text{Cl}$ in benzene as followed by NMR spectroscopy is shown in Figure 1. After 48 h, irradiating at >300

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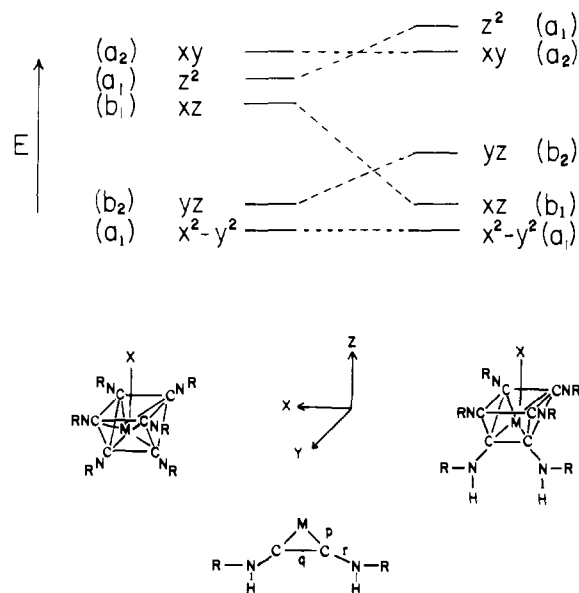


Figure 2. Coordinate system and approximate metal d orbital energies for the $[M(CNR)_6]X^+$ (left) and $[M(CNR)_4(CNHR)_2]X^+$ (right) cations. A C_{2v} -capped trigonal prismatic geometry is assumed with the ligand X on the twofold axis and the bis(alkylamino)acetylene ligand on the unique edge.

nm, the reaction was almost complete. The 1H NMR peak at δ 0.79 matches that of *tert*-butyl cyanide, a known photolysis product of *tert*-butyl isocyanide. The peak at δ 1.34 is not identified but may be $[Mo(CN-t-C_4H_9)_6Cl]Cl$. No clear spectroscopic evidence for free bis(*tert*-butylamino)acetylene or its stable tautomer, *N,N*-di-*tert*-butyl glyoximine, which was prepared by an independent procedure, was observed. There were many organic products however.

Metal-Coupled Ligand Bonding Interactions. In a formal sense the ligand (RHNCCNHR) in the complexes $[Mo(CNR)_4(CNHR)_2]X^+$ may be considered to be a coordinated acetylene. The acetylene must provide four electrons in order for the molybdenum atom to achieve a closed-shell configuration. Bonding schemes²²⁻²⁴ proposed to describe simple acetylene coordinated in a four-electron fashion involve the following: an acetylene-to-metal μ bond, formed from an empty metal d orbital and a filled acetylene π orbital; an acetylene-to-metal π bond, consisting of an empty metal d orbital and the filled acetylene π orbital perpendicular to the first one; and a metal-to-acetylene π bond comprised of filled metal d orbital and an empty ligand π^* orbital. Crystallographic studies^{13-15,19} of a series of complexes $[Mo(CN-t-C_4H_9)_4(CNHR)_2]X^+$ show that the CNCCNC framework of the coordinated bis(alkylamino)acetylene is always planar, indicating that the nitrogen lone-pair electrons are delocalized into the π system. Consequently, the coupled ligand has a more complicated electronic structure than that simply represented by a coordinated acetylene.

Using the coordinate system and orientation of the metal-coupled ligand fragment, taken to have C_{2v} symmetry, defined in Figure 2, the ligand orbitals involved in bonding to the metal may be broken up into two sets. These include a set of horizontal π orbitals, $\pi^h_{a_1}$ and $\pi^h_{b_1}$, and an orthogonal set of π orbitals, π_{b_2} , π_{a_2} , $\pi^*_{b_2}$, $\pi^*_{a_2}$, depicted in Figure 3. The set of orbitals contains eight electrons, two each from the nitrogen lone pairs and four from the acetylene π bonds. In order to determine the relative energies of the two sets of orbitals an extended Hückel calculation was carried out on the ligand using the geometry it adopts in the metal complex. The details of this calculation are reported elsewhere.²⁵ The energy level ordering generated by this cal-

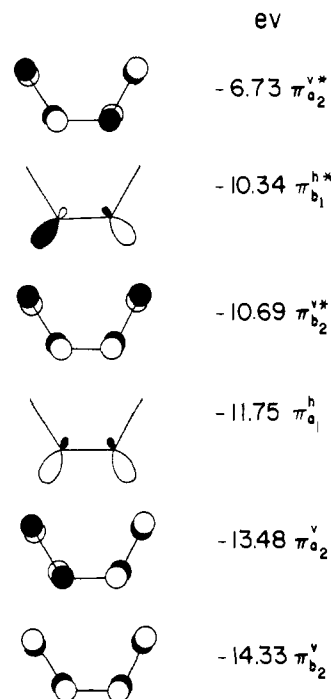


Figure 3. Bis(alkylamino)acetylene ligand orbitals and their relative energies. The vertical (v) superscript is omitted for simplicity in the text and Figure 4.

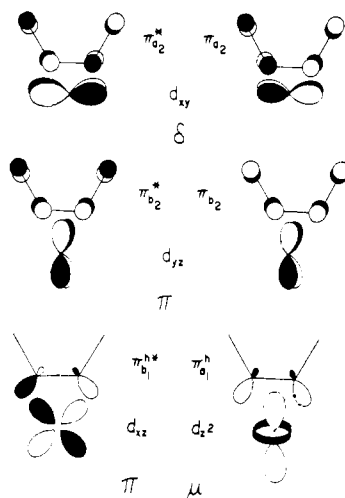


Figure 4. Metal-ligand orbital interactions that occur for bonding of the bis(alkylamino)acetylene to the $M(CNR)_4X^+$ fragment.

ulation is $\pi_{b_2} < \pi_{a_2} < \pi^h_{a_1} < \pi^*_{b_2} < \pi^h_{b_1} < \pi^*_{a_2}$ (Figure 3). The energies of the $\pi^*_{b_2}$ (HOMO) and $\pi^h_{b_1}$ (LUMO) differ by only 0.35 eV, and it is possible that for some ligand geometries these two orbitals may be reversed in energy.

The orbital interactions involved in bonding of the $M(CNR)_4X^+$ fragment to the acetylene ligand are depicted in Figure 4. When these interactions are taken into account, the metal d orbital splitting pattern previously deduced²⁶ for a seven-coordinate complex having a capped trigonal-prismatic stereochemistry would be qualitatively modified as shown in Figure 2. In particular, the $d_{xz}(b_1)$ orbital will be lower in energy while the $d_{yz}(b_2)$ orbital should increase its energy. These results are helpful in discussing the electronic spectral properties of the $[Mo(CNR)_4(CNHR)_2]X^+$ cations (vide infra).

Another useful way of viewing the bonding of the coordinated bis(alkylamino)acetylene is the valence bond representation.¹³ Resonance forms that place a negative charge on the metal center

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Table I. Selected Structural Parameters of the Coordinated Bis(*tert*-butylamino)acetylene Ligand in $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\}_n\text{X}]_n\text{Y}$ Compounds^{a,b}

X	Y	n	p, Å	q, Å	r, Å	∠C-C-N, deg
I	PF ₆	1	2.026 (8) ^c	1.36 (1)	1.331 (9) ^c	129.8 (8) ^c
Br	ZnBr ₄	2	2.03 (2) ^c	1.35 (2)	1.35 (2) ^c	129 (2) ^c
CN	PF ₆	1	2.053 (4)	1.402 (8)	1.312 (5)	127.9 (3)

^a For complete descriptions of the structures see ref 13 and 14. ^b p, q, r, and ∠C-C-N are defined as shown in Figure 2. ^c The distance, angles and standard deviations are averages of the individual values in each structure.

decrease the acetylene C—C bond order and the M—C bond order while at the same time increasing the C=N bond order. Consequently, ligands that are able to delocalize electron density from the metal and stabilize the charged resonance forms will cause a lengthening of the M—C and C—C bonds and a shortening of the C=N bonds. Crystallographically determined bond distances, listed in Table I for capped trigonal prismatic $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\}_n\text{X}]^+$ (X = I, Br, CN) complexes, reflect this predicted behavior. The M—C and C=C bond lengths increase by 0.02 and 0.05 Å, respectively, and the C=N distance decreases by 0.02 Å when the ligands X = I or Br, both π donors, are replaced by CN, a π acceptor. In all of these complexes the ligand X is trans to the coordinated bis(alkylamino)acetylene.

Spectroscopic Properties

Electronic Spectra. The electronic spectral bands for several of the $[\text{M}(\text{CNR})_4\{(\text{CNHR})_2\}_n\text{X}]^{n+}$ complexes are collected in Table II. These complexes all display two bands, one at ~490–560 nm ($\epsilon \sim 600$) and another at 340–360 nm ($\epsilon \sim 15\,000$), that are not present in the corresponding $[\text{M}(\text{CNR})_6\text{X}]^+$ cations.² Both of these bands exhibit a red shift as the ligand X becomes a better π acceptor. Consequently, the excited state must be strongly stabilized by π acceptors trans to the coordinated bis(alkylamino)acetylene. Transitions to the empty $d_{yz}(b_2)$ orbital are the most stabilized by the π acceptor ability of ligand X. Transitions to the antibonding $d_{z^2}(a_1)$ orbital (Figure 2) are less strongly affected.

The lowest energy absorption band is assigned to a transition to the d_{yz} orbital. Transitions from a_1 , a_2 , and b_2 levels are allowed under C_{2v} symmetry, corresponding to LMCT transitions $\pi b_2 \rightarrow yz$ and $\pi a_2 \rightarrow yz$ and the d-d transition $x^2 - y^2 \rightarrow yz$. The low extinction coefficient $\sim 600 \text{ M}^{-1} \text{ cm}^{-1}$ is consistent with assignment

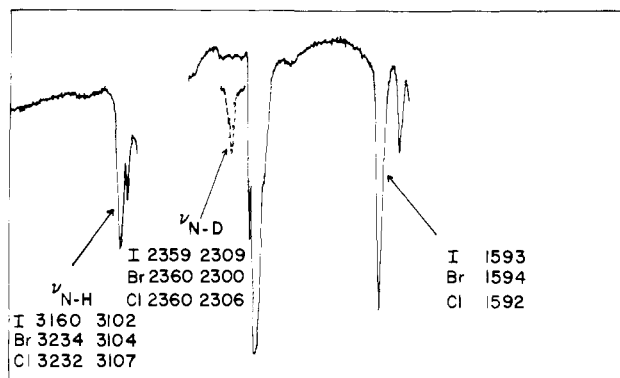


Figure 5. Characteristic infrared spectra of $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\}_n\text{X}]_n\text{Y}$ mullied in Nujol. The dashed line is the deuterated sample. For X = I and Y = I, n = 1. For X = Cl and Br and Y = ZnX₄, n = 2. Frequency values quoted are in cm^{-1} .

to the d-d transition $x^2 - y^2(a_1) \rightarrow yz(b_2)$. The higher energy band $\sim 350 \text{ nm}$ is probably a transition to the $d_{z^2}(a_1)$ orbital. This band exhibits a smaller red shift than the $\sim 500\text{-nm}$ band as a function of the π acceptor ability of the other coordinated ligands. A transition to the $d_{z^2}(a_1)$ level correctly accounts for the observed photochemical displacement of the bis(alkylamino)acetylene ligand when the $\sim 350\text{-nm}$ band is excited. The allowed transitions under C_{2v} symmetry are $d_{x^2-y^2}(a_1) \rightarrow d_{z^2}(a_1)$; $d_{xz}(b_1) \rightarrow d_{z^2}(a_1)$; $\pi^* a_1 \rightarrow d_{z^2}$; and the $\pi^* b_2 \rightarrow d_{z^2}$. The large extinction coefficient ($15\,000\text{--}19\,000 \text{ M}^{-1} \text{ cm}^{-1}$) suggests that this absorbance may be a LMCT band. The lowest energy LMCT band is $\pi^* b_2 \rightarrow d_{z^2}$, to which this transition is tentatively assigned.

Infrared Spectra. The characteristic bands in the infrared spectra of the $[\text{M}(\text{CNR})_4\{(\text{CNHR})_2\}_n\text{X}]^+$ and $[\text{M}(\text{CNR})_5\{(\text{CNHR})_2\}_n\text{X}]^+$ cations are collected in Table II. A typical spectrum is shown in Figure 5. All of the complexes show a strong C≡N stretch around $2120\text{--}2150 \text{ cm}^{-1}$, a less intense, higher energy band around 2180 cm^{-1} , and most have a small shoulder around 2060 cm^{-1} . The complex $[\text{Mo}(\text{CN}-t\text{-C}_4\text{H}_9)_4\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\}_n\text{X}]^+$ has an additional high energy C≡N stretching band at 2205 cm^{-1} which is assigned to the isocyanide ligand trans to the acetylene. This cation has an approximate pentagonal bipyramidal structure with the coupled ligand and three isocyanide ligands comprising the equatorial plane.¹⁹ The π acceptor orbitals of the isocyanide ligand trans to the acetylene will therefore interact with only one filled

Table II. Selected Infrared and Electronic Spectral Bands of $[\text{M}(\text{CNR})_4\{(\text{CNHR})_2\}_n\text{X}]^+$ Cations

compd ^a	IR, ^b cm^{-1}			electronic spectral bands ^c			
	N-H	C≡N	C=N	$\lambda, \text{nm} (\epsilon_{\text{max}}, \text{M}^{-1} \text{ cm}^{-1} \times 10^{-3})$			
$[\text{WL}_4\text{L}'\text{I}] \text{I}$	3185 (m)	2175 (m), 2120 (s), 2065 (sh)	1590 (m)	489 (0.82)	336 (18.9)	278 (21.4)	219 (38.9)
$[\text{MoL}_4\text{L}'\text{I}] \text{I}$	3150 (m)	2170 (m), 2120 (s), 2070 (sh)	1590 (m)	510 (0.58)	347 (15.4)	278 (17.6)	
$[\text{MoL}_4\text{L}'\text{I}] (\text{PF}_6)^d$	3327 (s)	2179 (s), 2137 (vs, br)	1587 (vs)				
$[\text{MoL}_4\text{L}'\text{I}] \text{BF}_4$	3299 (m), 3170 (m)	2170 (m), 2122 (s), 2060 (sh)	1593 (m)				
$[\text{MoL}_4\text{L}'\text{Br}]_2 \text{ZnBr}_4^d$	3234 (m), 3104 (w)	2176 (m), 2125 (s)	1594 (vs)				
$[\text{MoL}_4\text{L}'\text{Cl}] \text{Cl}$	3253 (m)	2182 (m), 2133 (s), 2060 (sh)	1580 (m)	515 (0.54)	344 (14.1)	274 (17.2)	
$[\text{MoL}_4\text{L}'\text{Cl}]_2 \text{ZnCl}_4^d$	3232 (m), 3107 (w)	2177 (m), 2127 (s)	1592 (vs)				
$[\text{MoL}_4\text{L}'(\text{CN})] (\text{PF}_6)^e$	3250 (m)	2185 (m), 2147 (s)	1583 (m)	545 (0.63)	352 (13.8)	280 (18.3)	
$[\text{MoL}_5\text{L}'] (\text{BPh}_4)_2$	3275 (m)	2208 (m), 2108 (m), 2135 (s)	1579 (m)	564 (0.68)	366 (18.5)	288 (14.7)	273 (20.7) 265 (24.9)
$[\text{MoL}_5\text{L}'] (\text{NO}_3)_2$	3132 (m), 3090 (m)	2207 (m), 2178 (m), 2123 (s), 2050 (sh)	1599 (m)				
$[\text{Mo}(\text{Lc})_4\text{L}'\text{I}] \text{I}$	3160 (m), 3115 (m)	2175 (m), 2127 (s)	1660 (m, br)	510 (0.60)	350 (16.8)	282 (22.1)	220 (49.1)
$[\text{Mo}(\text{Lm})_4\text{L}'\text{I}] \text{I}$	3155 (m)	2197 (m), 2150 (s)	1581 (m)				

^a L = CN-*t*-C₄H₉; L' = $\{(\text{CNH}-t\text{-C}_4\text{H}_9)_2\}$; Lc = CN-*c*-C₆H₁₁; Lc' = $\{(\text{CNH}-c\text{-C}_6\text{H}_{11})_2\}$; Lm = CNCH₃. ^b KBr pellet. ^c Methanol solutions at room temperature. ^d Nujol mull. ^e Electronic spectrum in CH₂Cl₂.

Table III. Proton and ^{13}C NMR Spectral Results for $[\text{M}(\text{CNR})_4\{(\text{CNHR})_2\}\text{X}]^+$ Cations

compd ^a	ppm				^{13}C NMR, ^c ppm								
	CH			NH	MC			CR ₃			CR ₃		
	L	X	L'		L	X	L'	L	X	L'	L	X	L'
[W _L L'I]I	1.50		1.63	9.47	152.08		181.52	57.10		54.96	30.41		30.93
[MoL ₄ L'I]I	1.48		1.66	9.68	157.10		192.90	56.89		54.75	29.96		30.29
[MoL ₄ L'I](PF ₆)	1.51		1.58	7.95									
[MoL ₄ L'I]BF ₄	1.49		1.60	8.19									
[MoL ₄ L'Br] ₂ ZnBr ₄	1.49		1.64	9.20	160.40		195.75	56.90		56.65	30.25		30.47
[MoL ₄ L'Cl]Cl	1.50		1.57	8.00	162.90		198.95	56.73		53.90	29.46		29.46
[MoL ₄ L'(CN)](PF ₆)	1.51		1.55	8.29	159.21	143.29	200.19	57.56		54.39	30.36		29.78
[MoL ₄ L'](BPh ₄) ₂ ^d	1.53	1.62	1.58	...	155.38	139.84	202.54	60.04	61.5	55.64	30.60	30.15	30.38
[MoL ₃ L'](NO ₃) ₂ ^e	1.28	1.54	1.50	...									
[Mo(Lm) ₄ L'I]I	3.52		1.66	10.06									
[Mo(Lc) ₄ (L'c)I]I	(1.4(br), 1.8(br), 3.95(br)) ^f				9.80 ^g								

^a L = CN-*t*-C₄H₉; L' = {(CNH-*t*-C₄H₉)₂}; Lc = CN-*c*-C₆H₁₁; Lc' = {(CNH-*c*-C₆H₁₁)₂}; Lm = CNCH₃. ^b In CDCl₃, chemical shifts are relative to Me₄Si. ^c In CDCl₃, with 0.05 M Cr(acac)₃, 30° pulse with 0.5–1-s pulse interval. Chemical shifts are relative to Me₄Si. ^d ¹H NMR in methanol-*d*₄. ^e ¹³C NMR in methanol-*d*₄/Me₂SO-*d*₆. ^f ¹H NMR in benzene-*d*₆/methanol-*d*₄. ^g Resonances assignable to Lc and Lc' are not resolved. ^h Doublet, *J* = 8 Hz.

metal d orbital whereas the remaining four isocyanides overlap with both filled d orbitals. Consequently the trans isocyanide experiences only weak π back-bonding and its stretching frequency occurs at higher energy. In addition, the steric bulk of the bis-(alkylamino)acetylene will force the equatorial girdle toward the trans isocyanide, pushing it away from the metal. The result is loss of overlap of the isocyanide acceptor orbitals with filled d orbitals and an increased C \equiv N stretching frequency. No significant changes in the isocyanide stretching bands of [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}] (BPh₄)₂ are observed (except for a sharpening effect) when the infrared spectrum is taken in MeOH (CaF₂ cells), indicating that this compound most likely has the same structure of both the solid and solution phases.

In addition to the isocyanide stretching bands these complexes all contain N–H stretching modes around 3150–3300 cm⁻¹ and a C \equiv N stretch \sim 1590 cm⁻¹ when R = *t*-C₄H₉ and \sim 1660 cm⁻¹ when R = *c*-C₆H₁₁. The position of the N–H band is quite sensitive to the particular anion associated with the complex, shifting to higher energy with anions less able to form hydrogen bonds. The band at 1590–1660 cm⁻¹ is assigned to a C \equiv N rather than a C=C stretch since complexes which contain simple acetylene acting as four-electron donors bound to d⁴ metal atoms such as Mo(dtc)₂(CO)(C₂H₂) have no assignable C=C stretch²⁶ while complexes such as [Mo(CHNMe₂)(η -C₅H₅)(CO)₃]⁺ exhibit a C \equiv N stretch at 1601 cm⁻¹.²⁷ An N–H deformation band also occurs \sim 1510 cm⁻¹. The assignment of both types N–H vibrational modes has been verified by studies of the deuterated complex (Figure 5 and ref 13). Other bands between 1400 and 1500 cm⁻¹ not present in the infrared spectra of the [M(CNR)₆X]⁺ cations may also be due to the coupled ligand, but these were not further investigated.

NMR Spectra. The ¹H NMR spectral parameters of the [M(CNR)₄{(CNHR)₂}X]⁺ and [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}]²⁺ cations are listed in Table III. In CDCl₃, when the alkyl groups on the bis(alkylamino)acetylene and the isocyanide ligands are *tert*-butyl and X = halide or cyanide, the spectra consist of one or two upfield resonances between δ 1.45 and 1.7 (corresponding to the methyl groups) and a small, broad downfield resonance between δ 8 and 10 (assigned to the N–H protons). The *tert*-butyl resonances associated with the bis(alkylamino)acetylene are 0.0–0.2 ppm upfield of the isocyanide resonances and depend on the nature of the counterion, indicating the presence of ion pairing in solution. The largest downfield shift is produced by anions which form strong hydrogen bonds. The N–H resonance in CDCl₃ solutions is also extremely sensitive to the hydrogen-bonding ability of the anion. For example, the N–H resonance of [Mo(CN-*t*-C₄H₉)₄{(CNH-*t*-C₄H₉)₂}]⁺ shifts from 9.5 to 8.2 ppm when the counterion is changed from iodide to tetrafluoroborate. Hydrogen bonding between the counterion and N–H bonds is a significant feature of the crystal structures of these complexes.^{13–15}

The chemical shifts of the alkyl group proton resonances are solvent dependent. Spectra taken in C₆D₆ with a few drops of CD₃OD added to enhance solubility exhibit isocyanide resonances that are shifted upfield while the bis(alkylamino)acetylene resonance is shifted downfield. In methanol-*d*₄ the complex [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}] (BPh₄)₂ displays three upfield *tert*-butyl resonances (δ 1.62, 1.58, and 1.53) with a relative ratio of 1:2:4, indicating that the isocyanide ligand trans to the bis(alkylamino)acetylene does not exchange with the other four isocyanides. In other solvents such as nitromethane-*d*₃, the ¹H NMR spectrum of [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}] (BPh₄)₂ becomes very complex, possibly due to reaction with solvent.²⁵ The ¹H NMR spectrum of the complex [Mo(CN-*c*-C₆H₁₁)₄{(CNH-*c*-C₆H₁₁)₂}]I is complicated by the large number of aliphatic ring protons obscuring the upfield region from 1 to 2 ppm. Extensive coupling of the α protons of the cyclohexyl groups to the other ring protons, as well as to the N–H (which appears as a doublet) proton of the bis(alkylamino)acetylene, causes them to appear as a single broad resonance. The ¹H NMR spectrum of the mixed alkyl complex [Mo(CNCH₃)₄{(CNH-*t*-C₄H₉)₂}]I shows a single resonance for each of the two different ligands, consistent with those observed for these ligands in other compounds.

The chemical shift of the ¹³C resonance of the alkyne ligand carbon atoms bound to a metal atom has been used as a measure of the electron donor properties of the ligand.²⁸ In complexes in which acetylene is acting as a four-electron donor, the acetylenic ¹³C resonance is nearly 200 ppm downfield of Me₄Si. This position is 40–60 ppm downfield of the ¹³C resonances characteristic of acetylene acting as a two-electron donor.²⁸ For comparison, pure sp²-hybridized metal bound carbon atoms such as those in the metal carbene complexes have chemical shifts ranging from 200 to 400 ppm downfield of Me₄Si.²¹ The ¹³C resonances of the cations [M(CN-*t*-C₄H₉)₄{(CNH-*t*-C₄H₉)₂}X]⁺ (M = Mo, X = I, Br, Cl; M = W, X = I) and [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}]²⁺ are shown in Table III. They range from 181.5 ppm in the case of [W(CN-*t*-C₄H₉)₄{(CNH-*t*-C₄H₉)₂}]I⁺ to 202.5 ppm for [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}]²⁺ and are at the upfield limit of the carbenoid range. The carbene ¹³C resonances of the [W{CH(NMe₂)}(η -C₅H₅)(CO)₃]⁺ and [Mo{CH(NMe₂)}(η -C₅H₅)(CO)₃]⁺ cations are 215.5 and 231.4 ppm relative to Me₄Si.²⁷ This result suggests that the coordinated bis(*tert*-butylamino)acetylene ligand has considerable carbenoid character.

The ¹³C solution NMR spectrum of [Mo(CN-*t*-C₄H₉)₅{(CNH-*t*-C₄H₉)₂}]²⁺ in methanol-*d*₄, like the ¹H NMR spectrum, reveals two distinct isocyanide environments consistent with pseudooctahedral coordination with four equivalent isocyanides and a single isocyanide assigned to a site trans to the bis(alkylamino)acetylene ligand. The latter isocyanide ligand resonance

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is shifted 15.5 ppm upfield from the value of the other four isocyanides. This upfield shift reflects a substantial loss in back-bonding and increase in sp character of the carbon bonded to the Mo center.

Solution Stereochemistry of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_5\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}]^{2+}$. The ^1H NMR, ^{13}C NMR, and solution-phase infrared spectra of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_5\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}](\text{BPh}_4)_2$ indicate that the five isocyanide ligands experience two distinct environments in a ratio of 1:4. This result is consistent with a structure in which four equivalent isocyanides are adjacent to, and a single isocyanide ligand is trans to, the bis(alkylamino)acetylene. The spectral data are unable to distinguish between a completely rigid complex having a capped trigonal prismatic geometry and a partially rigid structure in which the bis(alkylamino)acetylene is freely rotating around its metal acetylene μ bond. A completely rigid stereochemistry is unlikely. In the crystal structure¹⁵ of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}(\text{CN})](\text{BPh}_4)$ the bis(alkylamino)acetylene ligand is partially rotated about the M-C_2 μ -bond axis. The result suggests that the barrier to rotation about the M-C_2 μ bond may be very small. Moreover, calculations of seven-coordinate complexes containing a single bidentate ligand and a small bite indicate that the capped trigonal prism and pentagonal bipyramid become degenerate in energy with essentially no barrier to rotation of the bidentate ligand.²⁹ In the solid state, $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_5\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}](\text{BPh}_4)_2 \cdot \text{CH}_3\text{OH}$ has a pentagonal bipyramidal structure with the coupled ligand lying almost entirely in the pentagonal plane.¹⁹ If this structure were to persist in solution, the NMR spectral results would be explained by rotation about the Mo-C_2 μ bond but with no scrambling of the unique RNC ligand. The lack of complete stereochemical non-rigidity contrasts markedly with the behavior of the cation $[\text{Mo}(\text{CNR})_7]^{2+}$ which is completely fluxional at -70°C .⁷ The complexes $[\text{M}(\text{CNR})_4\{(\text{CNHR})_2\}\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or CN}$) probably have solution structures similar to that of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_5\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}]^{2+}$ with the ligand X occupying the site trans to the bis(alkylamino)acetylene and with rotation about the Mo-C_2 μ -bond axis.

The Coupling Reaction, Mechanistic Aspects. From the control experiments it is reasonably certain that the coupling of the two isocyanide molecules to form a coordinated bis(alkylamino)acetylene occurs within the coordination sphere of the metal atom. We have previously referred to this process as the coupling of

“adjacent” ligands since there seems to be no logical alternative. A prerequisite to carbon-carbon bond formation is close contact of the two ligands which eventually become bonded together. The crowded coordination sphere of seven-coordinate complexes containing linear unidentate ligands promotes this condition. Perusal of the list^{14b} of nonbonded carbon-carbon contacts along the edges of the coordination polyhedra of $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_6\text{X}]^+$ and $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{X}]^+$ cations ($\text{X} = \text{I}, \text{Br}$) reveals that the former contains a nonbonded C-C contact ~ 2.36 Å which is ~ 0.15 Å shorter than any other and is 0.5 Å shorter than the shortest such nonbonded contact in $[\text{Mo}(\text{CN-}t\text{-C}_4\text{H}_9)_4\{(\text{CNH-}t\text{-C}_4\text{H}_9)_2\}\text{X}]^+$. The short contact occurs along the unique edge of the C_{2v} -capped trigonal prism, which coincides with the site of the “incipient bonding interaction” found in molecular orbital calculations of seven coordinate complexes reported by Hoffmann et al.³⁰ Since the product contains no such short nonbonded distances, it is perhaps not surprising that only one pair of isocyanide ligands in the complex is coupled. The failure of the lower coordinate complexes, particularly $[\text{Pt}(\text{CN-}t\text{-C}_4\text{H}_9)_4]^{2+}$ ³¹ and $[\text{Fe}(\text{CN-}t\text{-C}_4\text{H}_9)_5]$,³² to undergo coupling of isocyanide ligands under similar reducing conditions supports the idea that the present reaction may be a manifestation of a higher coordination effect.

Steric factors cannot alone account for the coupling reaction, however, since the yield and rate are strongly influenced by the electronic properties of the remaining ligands in the coordination sphere. In particular, electron-releasing π -donor ligands such as iodide promote the reductive coupling. As seen from Figure 2, the energy of the d_{xz} orbital drops rapidly and the d_{yz} orbital rises in energy as the two isocyanide ligands are reductively coupled. Electron donation into these two orbitals should promote a decrease in the C-M-C bond angle and favor reductive coupling of the adjacent isocyanide ligands. Theoretical investigations of this point are currently in progress.³³

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