Organometallics 1991, *10*, 693-702 693

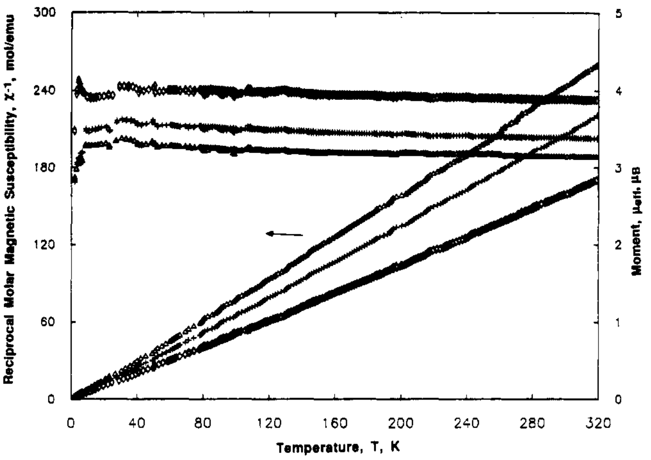

Figure 4. Reciprocal molar magnetic susceptibility, χ_M^{-1} (left), and moment, μ_{eff} (right), as a function of temperature for $[Fe(C_5Et_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ (Δ), $[Fe(C_5Et_5)_2]^{\bullet+}[TCNQ]^{\bullet-}$ (◇), and $[Fe(C_5Et_5)_2]^{\bullet+}[PF_6]^{\bullet-}$ (+).

$(C_5Et_5)_2]^{\bullet+}[A]^{\bullet-}$ (A = TCNQ, TCNE) possesses isolated $S = {}^1/_2$ anions and a $\cdots D^{\bullet+}A^{\bullet-}D^{\bullet+}A^{\bullet-}\cdots$ structural motif analogous to the corresponding $[Fe(C_5Me_5)_2]^{\bullet+}$ salts.[3-5] The $[Fe(C_5Et_5)_2]^{\bullet+}$ salts exhibit ferromagnetic coupling as evidenced from Θ of +6.8 K. Ferromagnetic coupling has been previously attributed to interchain (1-D) interactions; however, due to the substantial increase in the intrachain Fe⋯Fe separation (2.70 Å), the coupling is expected to be significantly reduced. The interchain separations, albeit ≤0.33 Å longer, would appear to be the most important in determining the net magnetic coupling. Most significantly, the ferromagnetic Fe⋯N and the Fe⋯Fe separations are only slightly longer, while the interchain antiferromagnetic N⋯N interactions are substantially longer (~1.2 Å) suggesting that ferromagnetic coupling would dominate. Unlike the $[Fe(C_5Me_5)_2]^{\bullet+}$ salts, however, the $[Fe(C_5Et_5)_2]^{\bullet+}$ salts do not exhibit magnetic ordering and a field dependence of the magnetization characteristic of long-range (bulk) magnetic ordering. Thus, the inter- and intrachain spin separations are longer, and this leads to weaker exchange interactions and a critical temperature reduced below 1.5 K.

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Supplementary Material Available: For $[Fe(C_5Et_5)_2]^{\bullet+}[TCNQ]^{\bullet-}$ tables of anisotropic thermal parameters, bond distances, bond angles, and intermolecular separations (5 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Isocyanide Ligands in Tp′(CO)$_2$IMo(CNR) Complexes as Precursors to Aminocarbyne, η^2-Iminoacyl, and η^2-Vinyl Ligands

A. S. Gamble, P. S. White, and J. L. Templeton*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

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A mixture of molybdenum aminocarbyne, η^2-iminoacyl, and η^2-acyl complexes, $Tp'(CO)_2Mo{\equiv}CN(Me)(Bu^t)$, $Tp'(CO)_2Mo(\eta^2\text{-}C(NBu^t)Me)$, and $Tp'(CO)(Bu^tNC)Mo(\eta^2\text{-}C(O)Me)$, has been prepared via the addition of MeI to the anionic *tert*-butyl isocyanide complex $[Na][Tp'(CO)_2Mo(CNBu^t)]$. Addition of MeI to the analogous anionic methyl or phenyl isocyanide complex yields only aminocarbyne complexes. The η^2-iminoacyl complex can be deprotonated at the C_β methyl site with KH to give an anionic η^2-enamide intermediate, and quenching with MeI yields the ethyl product, $Tp'(CO)_2Mo(\eta^2\text{-}C(NBu^t)Et)$. The η^2-iminoacyl complex undergoes cleavage in air to give *N*-*tert*-butylacetamide. Protonation of $Tp'(CO)_2Mo{\equiv}CN(Me)(Bu^t)$ in the presence of phenylacetylene ultimately yields a cationic η^2-vinyliminium complex, $[Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}C(H)C(H){=}N(Me)(Bu^t))][BF_4]$. This material is fluxional in the ^1H NMR spectrum due to rapid inversion at the vinyl β-carbon. The X-ray structure of this η^2-vinyl cation is reported. A neutral η^2-vinylamine complex, $Tp'(CO)_2Mo(\eta^2\text{-}C(Ph){=}C(H)CH_2N(Me)(Bu^t))$, has been synthesized by addition of $LiEt_3BH$ to the cationic η^2-vinyliminium complex.

Introduction

The chemistry of transition-metal isocyanide complexes complements the chemistry of metal carbonyl complexes.[1] Two modes of reactivity dominate electrophilic addition to metal isocyanides. First, isocyanide complexes, like carbonyl complexes,[2] undergo migratory insertion with alkyl ligands.[3] A common synthetic route to η^2-iminoacyl

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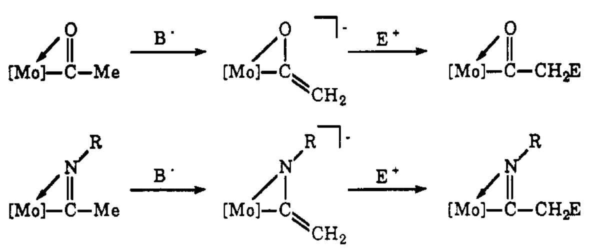
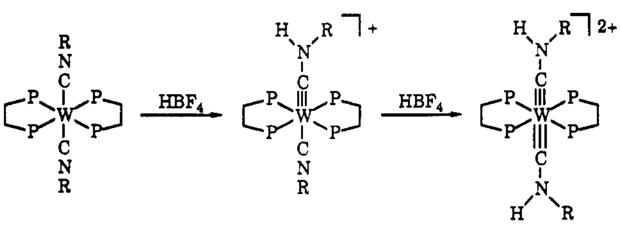
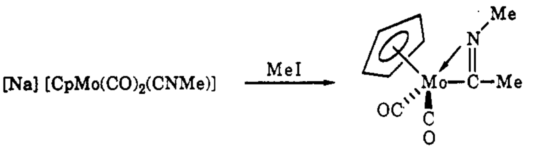
Scheme I



Scheme II



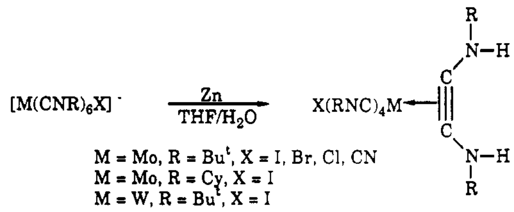
complexes is addition of alkyl halides to anionic isocyanide complexes.[4,5] The synthesis of η^2-iminoacyl complexes of molybdenum via addition of MeI to anionic molybdenum isocyanide complexes is a specific example (eq 1).[4]



(1)

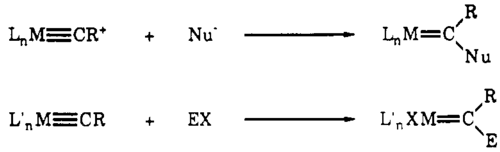
Several reactivity patterns characterize η^2-acyl and η^2-iminoacyl complexes.[3,6] Alkylation at carbon yields the respective η^2-ketone[7] or η^2-imine[8] complex. Coupling of acyls or iminoacyls to form enediolate[9] or enediamide[10] complexes has been reported. Additional insertions of carbon monoxide[11] or isocyanide[12] can occur. Less common is deprotonation at C_β. The synthesis of η^2-enolate complexes of molybdenum, via deprotonation of η^2-acyl complexes, Tp′(CO)$_2$Mo(η^2-C(O)Me), has been reported, with electrophile addition yielding substituted η^2-acyl complexes.[13] We now report analogous chemistry for the η^2-iminoacyl ligand (Scheme I).

A second reactivity mode of metal isocyanide complexes is addition of electrophiles to nitrogen-yielding aminocarbyne complexes.[14,15] Stepwise protonation of the bis(isocyanide) complex, trans-(dppe)$_2$W(CNR)$_2$ (R = Me, Bu^t, Ar) yields mono- and bis(carbyne)complexes[16] (Scheme II). A series of six- and seven-coordinate (aminocarbyne)tungsten complexes have recently been prepared by addition of triethyloxonium salts to [Cp(CO)$_2$W(CNEt)]$^-$ followed by oxidation with iodine and ligand substitution reactions.[17] Bis(isocyanide) complexes have been shown to undergo reductive coupling through an aminocarbyne intermediate[14] when reduced in the presence of a Lewis acid and water (eq 2).[18]

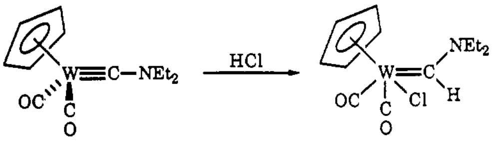


(2)

Frontier-orbital-directed[19] addition of nucleophiles to carbyne carbons has been observed for electron-poor metal centers.[20] In contrast, charge-controlled[21] electrophilic attack at carbon is common for electron-rich metal centers.[22,23]



Protonation of an aminocarbyne carbon has yielded a Fischer-type aminocarbene complex, Cp(CO)$_2$ClW=C(H)(NEt$_2$) (eq 3).[24]



(3)

Reactions of aminocarbene complexes with alkynes have been utilized in organic synthesis.[25] The reaction of an

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aziridinecarbene chromium complex with diphenylacetylene to form an azabicyclized product is proposed to involve an iminium intermediate formed by initial alkyne insertion into the metal–carbene bond.[26]

We have prepared a series of aminocarbyne complexes of molybdenum, Tp'(CO)$_2$Mo≡CN(R)(Me) (R = Bu^t, Me, Ph) via the addition of iodomethane to the corresponding anionic isocyanide complexes, [Na][Tp'(CO)$_2$Mo(CNR)]. For R = Bu^t, additional products, η^2-iminoacyl and η^2-acyl complexes (Tp'(CO)$_2$Mo(η^2-C(NBu^t)Me) and Tp'(CO)(Bu^{t}NC)Mo(η^2-C(O)Me)), were formed. Addition of HCl to [Na][Tp'(CO)$_2$Mo(CNBu^t)] yielded Tp'(CO)$_2$Mo≡CN(Bu^t)(H).

Deprotonation of Tp'(CO)$_2$Mo(η^2-C(NBu^t)Me) at the iminoacyl methyl, followed by addition of iodomethane, yield Tp'(CO)$_2$Mo(η^2-C(NBu^t)Et). Protonation of the aminocarbyne complex, Tp'(CO)$_2$Mo≡CN(Bu^t)(Me), in the presence of phenylacetylene, formed an η^2-vinyl iminium complex, [Tp'(CO)$_2$Mo(η^2-C(Ph)=C(H)C(H)=N(Bu^t)(Me))][BF$_4$]. Addition of LiEt$_3$BH to this cationic complex produced a neutral η^2-vinyl product, Tp'(CO)$_2$Mo(η^2-C(Ph)=C(H)CH$_2$N(Bu^t)(Me)).

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et$_2$O), and hexanes were distilled from sodium benzophenone ketyl; methylene chloride (CH$_2$Cl$_2$) was distilled from P$_2$O$_5$; acetonitrile (CH$_3$CN) was distilled from CaH$_2$; all other solvents were purged with nitrogen and used without further purification. Iodomethane (MeI) was dried over alumina before use. [NEt$_4$][Tp'Mo(CO)$_3$],[27] methyl isocyanide (MeNC),[28] and phenyl isocyanide (PhNC)[29] were prepared according to literature methods. *tert*-Butyl isocyanide (Bu^{t}NC) was obtained from Aldrich and used without further purification.

Infrared spectra were collected on a Mattson Polaris FTIR spectrometer or a Beckman IR 4250 spectrometer and calibrated with a polystyrene standard. ^{1}H and ^{13}C NMR were recorded on a Bruker AC 200 (200 MHz) or a Varian XL 400 (400 MHz) spectrometer. Analyses were by Galbraith Laboratories of Knoxville, TN, or Oneida Research Servies of Whitesboro, NY.

Tp'(CO)$_2$(I)Mo(CNBu^t) (1). A 1-equiv sample of iodine (1.67 g, 6.58 mmol) was added to a slurry of [NEt$_4$][Tp'Mo(CO)$_3$] (4.00 g, 6.58 mmol) in 100 mL of THF, resulting in an immediate color change from yellow to dark brown and an increase in IR CO stretching frequencies from 1885 and 1745 to 2025 and 1937 cm^{-1}. The solution was allowed to stir for 20 h, resulting in a gradual color change to dark red and a decrease in IR CO stretching frequencies to 1998 and 1921 cm^{-1} (Tp'(CO)$_2$MoI). (When iodine oxidation is carried out in CH$_2$Cl$_2$ solution, IR CO stretches are observed at 2030 and 1942 cm^{-1} for the tricarbonyl complex, and 2005 and 1925 cm^{-1} for the dicarbonyl complex.) Attempted isolation at this point in other experiments led to decomposition to form an intractable material. Instead, the solution was filtered and 1 equiv of Bu^{t}NC (0.55 g, 6.6 mmol) was added while the solution was stirred, resulting in an immediate color change to darker red, a shift in IR CO stretching frequencies to lower wavenumber, and the appearance of a CN stretch at 2159 cm^{-1}, above that of free Bu^{t}NC (2133 cm^{-1}). To maximize the yield for the remainder of the reaction sequence, the product was generally not isolated at this point. However, dark red crystals of 1 may be recovered by reducing the volume of the reaction solution to 50 mL, layering 200 mL of hexanes on top, and storing overnight at −25 °C. IR (KBr): ν_{CN} 2158 (m) cm^{-1}, ν_{CO} 1953 (s), 1853 (s) cm^{-1}. The NMR spectrum of Tp'(CO)$_2$(I)Mo(CNBu^t) exhibited fluxionality at room temperature. A series of ^{1}H NMR spectra were collected over a temperature range from −80 to +20 °C. The following data for ^{1}H and ^{13}C NMR are for spectra collected at −60 °C: ^{1}H NMR (CD$_2$Cl$_2$) δ 5.95, 5.89 (each a s, 1:2 H, Tp' C–H), 2.43, 2.42, 2.39, 2.38, 2.22, 2.06 (each a s, 3 H each, Tp' Me's), 1.23 (s, 9 H, CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 251.1 (CO), 237.5 (CO), 159.5 (CNCMe$_3$), 152.8, 150.8, 150.7, 146.4, 145.2, 143.7 (Tp' *C*–Me), 107.0, 105.6, 105.1 (Tp' C–H), 58.4 (*C*Me$_3$), 28.6 (C*Me*$_3$), 18–12 (Tp' C*Me*). Anal. Calcd: C, 40.08; H, 4.74; N, 14.88. Found: C, 40.18; H, 4.79; N, 14.85.

Tp'(CO)$_2$Mo≡CNMe$_2$ (2). A 100-mL THF solution of Tp'(CO)$_2$MoI (3.79 g, 6.58 mmol) was prepared as above. MeNC (0.31 g, 7.6 mmol) was added dropwise with stirring, resulting in an immediate color change to darker red, a shift in IR CO stretching frequencies to 1950 and 1872 cm^{-1}, and appearance of a CN stretch at 2185 cm^{-1}, above that of free MeNC (2161 cm^{-1}). After 30 min, the solution was transferred to a flask containing 10% Na/Hg and stirred for 30 min, resulting in a color change to yellow. The solution was cannulated away from the amalgam, and MeI (3.0 g, 21 mmol) was added with stirring, resulting in a color change to orange over a 5-min period. After 1 h the solution was stripped to a tar, which was taken up in a minimum of benzene (leaving a white precipitate of NaI) and chromatographed on alumina. A single orange band was eluted with 3:1 hexanes/Et$_2$O. Solvent removal gave 2.31 g of an orange powder (70% yield based on [NEt$_4$][Tp'Mo(CO)$_3$]). Recrystallization from Et$_2$O/hexanes gave orange crystals. IR (KBr) ν_{CO} 1939 (s), 1884 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 5.93, 5.87 (each a s, 2:1 H, Tp' C–H), 3.20 (s, 6 H, NMe$_2$), 2.56, 2.51, 2.45, 2.42 (each a s, 6:3:6:3 H, Tp' Me's); ^{13}C NMR (CD$_2$Cl$_2$) δ 253.7 (s, Mo≡C), 228.7 (s, CO), 152.1, 151.2, 145.3, 145.0 (each a m, Tp' *C*-Me), 106.5, 106.3 (each a d, $^1J_{CH}$ = 172 Hz, Tp' C–H), 39.4 (q, $^1J_{CH}$ = 138 Hz, NMe$_2$), 16.0, 15.0, 12.9, 12.8 (each a q, $^1J_{CH}$ = 127 Hz, Tp' C*Me*). Anal. Calcd: C, 47.54; H, 5.59; N, 19.41; Mo, 18.99. Found: C, 47.79; H, 5.35; N, 19.80; Mo, 18.72.

Tp'(OC)$_2$Mo≡CN(Ph)(Me) (3). A solution of Tp'(CO)$_2$MoI (3.79 g, 6.58 mmol) in 100 mL of THF was prepared as above. A 1-equiv sample of PhNC (0.69 g, 6.7 mmol) was added dropwise with stirring, resulting in an immediate color change to darker red, a shift in IR CO stretching frequencies to 1950 and 1882 cm^{-1}, and appearance of a CN stretch at 2125 cm^{-1}, in the vicinity of that for free PhNC (2124 cm^{-1}). After 30 min, the solution was transferred to a flask containing 10% Na/Hg and stirred for 1 h, resulting in a color change to dark yellow. The solution was cannulated away from the amalgam and cooled to −78 °C, and 1 equiv of MeI (1.0 g, 7.0 mmol) was added with stirring. After 20 min, the cooling bath was removed, and the solution was stirred for 7 h, resulting in a color change to dark orange. Solvent removal left an orange tar, which was taken up in a minimum of benzene (leaving a white precipitate of NaI) and chromatographed on alumina. One orange band was eluted with 3:1 hexanes/Et$_2$O. Solvent removal gave 2.66 g of an orange powder (71% yield based on [NEt$_4$][Tp'Mo(CO)$_3$]). Recrystallization from Et$_2$O/hexanes gave orange crystals. IR (KBr) ν_{CO} 1963 (s), 1856 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.40–7.03 (m, 5 H, Ph), 5.89, 5.86 (s, 2:1 H, Tp' C–H), 3.62 (s, 3 H, NMe), 2.45, 2.43, 2.42 (s, 3:6:9 H, Tp' Me's); ^{13}C NMR (CD$_2$Cl$_2$) δ 244.5 (s, Mo≡C), 228.2 (s, CO), 151.8, 151.7, 145.7, 145.2 (each a m, Tp' *C*–Me), 142.8 (m, ipso C of Ph), 129.6, 124.0, 116.9 (each a d, $^1J_{CH}$ = 159 Hz, C–H of Ph), 106.6, 106.5 (each a d, $^1J_{CH}$ = 173 Hz, Tp' C–H), 36.5 (q, $^1J_{CH}$ = 138 Hz, NMe), 15.8, 15.0, 13.0, 12.9 (each a q, $^1J_{CH}$ = 128 Hz, Tp' C*Me*). Anal. Calcd: C, 52.92; H, 5.33; N, 17.29; Mo, 16.91. Found: C, 53.48; H, 5.85; N, 16.97; Mo, 16.41.

Addition of MeI to [Na][Tp'(CO)$_2$Mo(CNBu^t)]. A 100-mL THF solution of 1 (4.34 g, 6.58 mmol) was stirred over 10% Na/Hg for 30 min, resulting in a color change from dark red to yellow. The solution was cannulated away from the amalgam and cooled to −78 °C. A 1-equiv sample of MeI (1.0 g, 7.0 mmol) was added with stirring. After 10 min the cooling bath was removed, and

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the solution was stirred for 4 h. A gradual color change to dark orange-red was observed. The solution was stripped to a tar, taken up in a minimum of benzene (leaving a white precipitate of NaI), and chromatographed on alumina. An orange band was eluted with 9:1 hexanes/Et$_2$O (Tp′(CO)$_2$Mo$\equiv$CN(Bu^t)(Me) (**4**)), a red band was eluted with 1:1 hexanes/Et$_2$O (Tp′(CO)$_2$Mo(η^2-C(NBu^t)Me) (**5**)), and a dark orange band was eluted with 1:3 hexanes/Et$_2$O (Tp′(CO)(Bu^{t}NC)Mo(η^2-C(O)Me) (**6**)). A total of 1.34 g of **4** (2.45 mmol, 37%), 0.65 g of **5** (1.2 mmol, 18%), and 0.34 g of **6** (0.62 mmol, 9%) were recovered, for an overall yield of 64% based on [NEt$_4$][Tp′Mo(CO)$_3$]. Each of the three products can be recrystallized from Et$_2$O/hexanes.

Tp′(CO)$_2$Mo$\equiv$CN(Bu^t)(Me) (**4**): IR (KBr) ν_{CO} 1945 (s), 1848 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 5.84, 5.77 (each a s, 2:1 H, Tp′ C–H), 3.12 (s, 3 H, NMe), 2.55, 2.36, 2.34, 2.33 (each a s, 6:6:3:3 H, Tp′ Me's), 1.37 (s, 9 H, CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 253.5 (s, Mo$\equiv$C), 229.7 (s, CO), 151.6, 151.2, 145.3, 145.0 (each a m, Tp′ *C*–Me), 106.2, 106.1 (each a d, $^1J_{CH}$ = 171 Hz, Tp′ C–H), 58.2 (m, *C*Me$_3$), 32.4 (q, $^1J_{CH}$ = 138 Hz, NMe), 28.6 (q, $^1J_{CH}$ = 127 Hz, C*Me*$_3$), 15.7, 14.9, 13.0, 12.8 (each a q, $^1J_{CH}$ = 128 Hz, Tp′ C*Me*). Anal. Calcd: C, 50.47; H, 6.26; N, 17.92; Mo, 17.53. Found: C, 50.22; H, 6.54; N, 17.64; Mo, 17.27.

Tp′(CO)$_2$Mo(η^2-C(NBu^t)Me) (**5**): IR (KBr) ν_{CO} 1942 (s), 1793 (s) cm^{-1}, $\nu_{C=N}$ 1717 (w) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 5.71, 5.70 (each a s, 2:1 H, Tp′ C–H), 2.98 (s, 3 H, C(NBu^t)*Me*), 2.33, 2.24, 2.23, 2.04 (each a s, 6:3:3:6 H, Tp′ Me's), 1.04 (s, 9 H, CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 240.0 (s, CO), 204.7 (q, $^2J_{CH}$ = 7.6 Hz, *C*(NBu^t)Me), 152.7, 151.8, 146.2, 144.7 (each a m, Tp′ *C*–Me), 106.8, 106.7 (each a d, $^1J_{CH}$ = 172 Hz, Tp′ C–H), 58.1 (m, *C*Me$_3$), 28.8 (q, $^1J_{CH}$ = 126 Hz, C*Me*$_3$), 20.8 (q, $^1J_{CH}$ = 129 Hz, C(NBu^t)Me) 16.1, 15.8, 13.4, 12.9 (each a q, $^1J_{CH}$ = 126 Hz, Tp′ C*Me*). Anal. Calcd: C, 50.47; H, 6.26; N, 17.92. Found: C, 49.55; H, 6.68; N, 17.63.

Tp′(CO)(Bu^{t}NC)Mo(η^2-C(O)Me) (**6**): IR (KBr) ν_{CN} 2119 (m) cm^{-1}, ν_{CO} 1802 (s) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 5.68, 5.64, 5.57 (each a s, 1 H each, Tp′ C–H), 3.01 (s, 3 H, C(O)Me), 2.70, 2.48, 2.23, 2.19, 2.16, 1.93 (each a s, 3 H each, Tp′ Me's), 0.92 (s, 9 H, CMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 268.9 (*C*(O)Me), 234.5 (CO), 159.0 (*C*NCMe$_3$), 152.9, 152.5, 149.6, 145.2, 143.4, 142.9 (Tp′ *C*–Me), 106.9, 106.8, 106.2 (Tp′ C–H), 56.9 (*C*ME$_3$), 30.4 (C*Me*$_3$), 27.8 (C(O)*Me*), 16.1, 14.5, 13.9, 13.1, 12.6, 12.5 (Tp′ C*Me*). Anal. Calcd: C, 50.47; H, 6.26; N, 17.92. Found: C, 50.95; H, 6.56; N, 17.63.

Tp′(CO)$_2$Mo$\equiv$CN(Bu^t)(H) (7). A solution of [Na][Tp′(CO)$_2$Mo(CNBu^t)] (1.0 g, 1.8 mmol) in 50 mL of THF was prepared as before. The solution was cooled to 0 °C and 1 mL of 1.5 M HCl was added. After 10 min, the solution was warmed to room temperature, resulting in a gradual color change from dark yellow to dark brown. After an additional 30 min the solution was stripped to a tar, which was taken up in a minimum of benzene (leaving a white precipitate of NaI) and chromatographed on alumina. One orange band was eluted with Et$_2$O. Solvent removal gave an air-sensitive orange powder in 40% yield. IR (THF) ν_{CO} 1948 (s), 1852 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 5.94 (br s, 1 H, NH), 5.87, 5.82 (each a s, 2:1 H, Tp′ C–H), 2.52, 2.45, 2.40, 2.38 (each a s, 6:3:6:3 H, Tp′ Me's), 1.42 (s, 9 H, CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 251.6 (s, Mo$\equiv$C), 228.2 (s, CO), 152.3, 152.2, 145.7, 145.5 (each a m, Tp′ *C*–Me), 106.8, 106.7 (each a d, $^1J_{CH}$ = 172 Hz, Tp′ C–H), 56.3 (m, *C*Me$_3$), 31.0 (q, $^1J_{CH}$ = 127 Hz, C*Me*$_3$), 16.3, 15.4, 13.3, 13.2 (each a q, $^1J_{CH}$ = 127 Hz, Tp′ C*Me*).

Tp′(CO)$_2$Mo(η^2-C(NBu^t)Et) (8). A solution of the iminoacyl complex **5** (0.20 g, 0.36 mmol) in 20 mL THF was stirred over an excess of KH for 30 min, resulting in a color change from red to yellow-green, and a shift in IR CO stretching frequencies from 1944 and 1798 to 1897 and 1710 cm^{-1}. The solution was filtered into a flask containing 3 mL of MeI, resulting in a color change to red over a 5-min period and a shift in IR CO stretching frequencies to 1943 and 1796 cm^{-1}. The solution was stripped to a tar, which was taken up in a minimum of benzene (leaving a white precipitate of KI) and chromatographed on alumina. One red band was eluted with 3:1 hexanes/Et$_2$O. Spectroscopic data indicated formation of Tp′(CO)$_2$Mo(η^2-C(NBu^t)Et) (**8**) with a small impurity of **5**. ^{1}H NMR (CD$_2$Cl$_2$) δ 5.80 (s, 3 H, Tp′ C–H), 3.57 (q, 2 H, $^3J_{HH}$ = 7.7 Hz, C(NBu^t)C*H*$_2$Me), 2.43, 2.34, 2.32, 2.13 (each a s, 6:3:3:6 H, Tp′ Me's), 1.48 (t, 3 H, $^3J_{HH}$ = 7.7 Hz, C(NBu^t)CH$_2$*Me*), 1.11 (s, 9 H, CMe$_3$).

Air Decomposition of 5. A sample of **5** left exposed to the atmosphere for a period of 2 weeks decomposed to form a light brown solid and a quantity of clear needles. An IR spectrum of the brown material indicated no metal carbonyl stretches. The clear needles were characterized as (Bu^t)(H)NC(=O)Me, *N*-*tert*-butylacetamide. IR (KBr) ν_{NH} 3283 (m) cm^{-1}; $\nu_{C=O}$ 1653 s; ^{1}H NMR (C$_6$D$_6$) δ 1.48 (s, 3 H, C(O)Me), 1.19 (s, 9 H, NCMe$_3$); mp 98°–99°C.[30]

[Tp′(CO)$_2$Mo(η^2-C(Ph)=C(H)C(H)=N(Bu^t)(Me))][BF$_4$] (9). A solution of the aminocarbyne complex **4** (2.53 g, 4.62 mmol) and PhC$\equiv$CH (0.50 g, 4.9 mmol) in 40 mL of CH$_2$Cl$_2$ was cooled to −78 °C, and HBF$_4$·OMe$_2$ (0.65 g, 4.8 mmol) was added dropwise with stirring, resulting in an immediate color change to dark brown. After 5 min, the solution was allowed to warm to room temperature, resulting in a color change to dark green-brown. After an additional 30 min, the solution was placed on an alumina plug. Washing with toluene removed neutral impurities. The product was then washed through the alumina with acetonitrile. Solvent removal and trituration with hexanes gave the product as an olive solid in 62% yield. Recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded dark olive crystals. IR (CH$_2$Cl$_2$) ν_{CO} 2027 (s), 1944 (s) cm^{-1}. The complex exhibited fluxionality in the ^{1}H and ^{13}C NMR spectra at room temperature. The following spectral data were recorded at −22 °C: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.85 (d, 2 H, $^3J_{HH}$ = 7 Hz, Ph ortho H), 7.68 (t, 2 H, $^3J_{HH}$ = 7 Hz, Ph meta H), 7.56 (t, 1 H, $^3J_{HH}$ = 7 Hz, Ph para H), 7.49 (d, 1 H, $^3J_{HH}$ = 10.8 Hz, C(H)C(*H*)=N), 6.04, 6.01, 5.95 (each a s, 1 H each, Tp′ C–H), 4.12 (d, 1 H, $^3J_{HH}$ = 10.8 Hz, C(Ph)=C(*H*)C(H)), 2.88 (s, 3 H, NMe), 2.58, 2.48, 2.36, 2.20, 1.97 (s, 3:6:3:3:3 H, Tp′ Me's), 1.03 (s, 9 H, CMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 242.6 (s, Mo–*C*(Ph)), 224.2, 221.4 (each a s, CO), 170.2 (dd, $^1J_{CH}$ = 169 Hz, $^2J_{CH}$ = 3 Hz, =C(H)*C*(H)=N), 152.8, 152.6, 151.3, 147.3, 147.2, 147.0 (each a m, Tp′ *C*–Me), 141.3 (m, ipso C of Ph), 133.7, 131.9, 129.7 (each a d, $^1J_{CH}$ = 162 Hz, meta, para, ortho C–H of Ph), 108.4, 107.8, 107.7 (each a d, $^1J_{CH}$ = 175 Hz, Tp′ C–H), 63.4 (s, *C*Me$_3$), 40.7 (dd, $^1J_{CH}$ = 162 Hz, $^2J_{CH}$ = 3 Hz, C(Ph)=*C*(H)C(H)), 33.0 (qd, $^1J_{CH}$ = 138 Hz, $^3J_{CH}$ = 6 Hz, C(H)=N*Me*), 26.7 (q, $^1J_{CH}$ = 127 Hz, NC*Me*$_3$), 15.8, 15.4, 15.0, 13.2, 12.7, 12.6 (each a q, $^1J_{CH}$ = 126 Hz, Tp′ C*Me*). Anal. Calcd: C, 46.74; H, 5.27; N, 11.93. Found: C, 46.96; H, 5.30; N, 11.96. Percentages are based on MoF$_4$O$_2$N$_7$C$_{31}$B$_2$H$_{41}$·CH$_2$Cl$_2$.

Variable-Temperature ^{1}H NMR Spectroscopy of 9. A series of ^{1}H NMR spectra were collected in 10-deg increments over a temperature range from 30 to 70 °C. ^{1}H NMR at 22 °C: (CD$_3$CN) δ 7.97–7.50 (m, 6 H, Ph, C(H)C(*H*)=N), 6.04, 6.00, 5.96 (each a s, 1 H each, Tp′ C–H), 4.14 (d, 1 H, $^3J_{HH}$ = 10.8 Hz, C(Ph)=C(*H*)C(H)), 2.80 (s, 3 H, NMe), 2.54, 2.45, 2.33, 2.08, 1.90 (s, 3:6:3:3:3 H, Tp′ Me's), 1.00 (s, 9 H, CMe$_3$). At 70 °C, the two lower field proton signals for the Tp′ ring protons had coalesced to a singlet at 6.02 ppm, and the two highest field Tp′ Me signals had coalesced to form a broad singlet at 2.00 ppm.

Collection of Diffraction Data. A dark olive octahedron of dimensions 0.40 × 0.30 × 0.30 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer. Twenty-five centered reflections found in the region 30.0 < 2θ < 35.0° and refined by least-squares calculations indicated a monoclinic cell. The cell parameters are listed in Table I.

Diffraction data were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table I. Three reflections chosen as intensity standards were monitored every hour and showed no significant (<1.5%) decay. The crystal was checked for orientation every 200 reflections and was recentered if necessary. Only data with $I > 2.5\sigma(I)$ were used in structure solution and refinement.[31]

Solution and Refinement of the Structure. Space group $P2_1/c$ was confirmed, and the position of the molybdenum atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. One molecule of CH$_2$Cl$_2$ per asymmetric unit was located and refined with one of the chlorine atoms disordered in two positions.

The 50 non-hydrogen atoms were refined anisotropically.[32]

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[30] Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045.

[31] Programs used during solution and refinement were from the NRCVAX structure determination package. Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* **1989**, *22*, 384.

[32] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is based on counter statistics.

Table I. Crystallographic Data Collection Parameters for 9

	Crystal Data
mol formula	$MoF_4O_2N_7C_{31}B_2H_{41}\cdot CH_2Cl_2$
fw	822.19
cryst dimens, mm	0.40 × 0.30 × 0.30
space group	$P2_1/c$
cell params	
a, Å	11.170 (2)
b, Å	19.923 (7)
c, Å	17.553 (5)
β, deg	98.59 (2)
V, Å^3	3862.7 (19)
Z	4
d(calcd), g/cm^3	1.410
	Collection and Refinement Parameters
Mo Kα radiation (wavelength, Å)	0.710 73
monochromator	graphite
linear abs coeff, mm^{-1}	0.53
scan mode	$\omega/2\theta$
background	25% of full scan width on both sides
θ limits, deg	$2 < 2\theta < 45$
quadrant collcd	$\pm h,+k,+l$
total no. reflections	5009
data with $I \geq 2.5\sigma(I)$	3539
R (including unobserveds)	0.050 (0.076)
R_w (including unobserveds)	0.056 (0.059)
GOF	2.22
no. of params	456
largest param shift	0.32

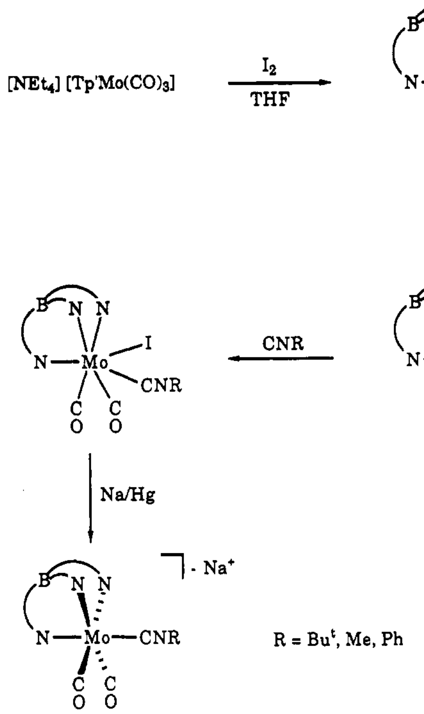
Hydrogen atom positions were calculated by using a C–H distance of 1.08 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. Final least-squares refinement resulted in residuals of $R = 5.0\%$ and $R_w = 5.6\%$.[33] The final difference Fourier map had no peak greater than 0.95 e/Å^3.[34]

Tp′(CO)$_2$Mo(η^2-C(Ph)═C(H)CH$_2$N(Bu^t)(Me)) (10). A solution of the η^2-vinyliminium complex **9** (0.50 g, 0.68 mmol) in 20 mL of THF was cooled to 0 °C, and LiEt$_3$BH (0.65 mL, 1.0 M THF) was added slowly with stirring, resulting in a color change to dark orange-red. The solution was warmed to room temperature and stirred for an additional 5 min. Solvent removal left a dark red-brown tar. The product was extracted with 20 mL of Et$_2$O, passed through an alumina plug, and then washed with an additional 20 mL of Et$_2$O. Solvent removal gave **10** as an air-sensitive dark rust solid in 68% yield. IR (THF) ν_{CO} 1951 (s), 1869 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.45–6.90 (m, 5 H, Ph), 5.88, 5.87, 5.58 (each a s, 1 H each, Tp′ C–H), 3.73 (dd, 1 H, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 2 Hz, C(Ph)═C(H)C(*H*)(H)–), 3.40 (dd, 1 H, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 2 Hz, C(Ph)═C(*H*)CH$_2$–), 2.81 (dd, 1 H, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 9 Hz, C(Ph)═C(H)C(H)(*H*)–), 2.62, 2.56, 2.52, 2.44, 2.40, 1.70, 1.44 (each a s, 3 H each, NMe and Tp′ Me's), 1.15 (s, 9 H, CMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 285.3 (s, Mo–*C*(Ph)), 240.5, 230.6 (each a s, CO), 152.4, 152.2, 152.1, 144.6, 144.1, 143.7 (each a m, Tp′ *C*–Me), 141.8 (m, ipso C of Ph), 130.8, 129.3, 128.5 (each a d, $^1J_{CH}$ = 160 Hz, meta, para, ortho, C–H of Ph), 107.8, 107.3, 107.1 (each a d, $^1J_{CH}$ = 172 Hz, Tp′ C–H), 66.8 (t, $^1J_{CH}$ = 133 Hz, –CH$_2$N(Bu^t)Me), 55.1 (s, *C*Me$_3$), 44.3 (d, $^1J_{CH}$ = 156 Hz, C(Ph)═C(H)CH$_2$–), 36.8 (q, $^1J_{CH}$ = 132 Hz, –CH$_2$N*Me*), 26.6 (q, $^1J_{CH}$ = 124 Hz, –CH$_2$NC*Me*$_3$), 15.4, 15.2, 14.5, 12.9 (double intensity), 12.5 (each a q, $^1J_{CH}$ = 128 Hz, Tp′ C*Me*). Due to thermal instability, a satisfactory elemental analysis was not obtained.

Results

Syntheses. Oxidation of [NEt$_4$][Tp′Mo(CO)$_3$] with iodine forms a d^4 metal complex, Tp′(CO)$_3$MoI, as evidenced by an increase in CO stretching frequencies (2025 (s) and 1937 (s) cm^{-1}). These frequencies are between those of Cp(CO)$_3$MoCl (CCl$_4$; 2040 (vs), 1968 (vs), and 1955 (sh) cm^{-1})[35] and Tp′(CO)$_3$WI (THF; 2015 (s) and 1911 (s) cm^{-1}).[36] Stirring a THF solution of this complex for 20 h resulted in a gradual conversion to a complex proposed to be Tp′(CO)$_2$MoI. The reaction was monitored by the appearance of lower frequency carbonyl stretches. The rate of conversion was inhibited by a carbon monoxide atmosphere. Similar stretching frequencies were observed when the oxidation was performed in CH$_2$Cl$_2$ solution. Neither the tricarbonyl nor the dicarbonyl complex was isolable (Scheme III).

Scheme III



A series of molybdenum isocyanide complexes, Tp′(CO)$_2$IMo(CNR) (R = Me, Ph, Bu^t), was synthesized by addition of isocyanide to a THF solution of Tp′(CO)$_2$MoI. An immediate decrease in the CO stretching frequencies and the appearance of a CN stretch above that of free isocyanide indicated rapid isocyanide coordination. The *tert*-butyl isocyanide derivative, Tp′(CO)$_2$IMo(CNBu^t) (**1**), was isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectra collected at room temperature had broad Tp′ ring proton and methyl signals. At −60 °C six sharp singlets corresponding to the Tp′ methyl groups appear in the region 2.43–2.06 ppm. The ^{13}C NMR spectrum at this temperature revealed carbonyl carbon signals at 251.1 and 237.5 ppm, with the isocyanide carbon signal at 159.5 ppm.

Stirring a dark red THF solution of Tp′(CO)$_2$IMo(CNR) over sodium amalgam resulted in reduction to form a gold anionic isocyanide complex, [Na][Tp′(CO)$_2$Mo(CNR)]. Addition of MeI to the methyl or phenyl isocyanide complexes, [Na][Tp′(CO)$_2$Mo(CNR)], resulted in good yields of aminocarbyne products, Tp′(CO)$_2$Mo≡CN(R)(Me) (R = Me, **2**; R = Ph, **3**) (eq 4). The Tp′ ring protons appear in a 2:1 ratio in both complexes (indicating that each molecule possesses a plane of symmetry). The carbyne carbon signals resonate at 253.7 ppm for **2** and 244.5 ppm

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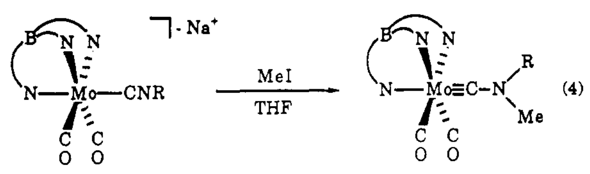
[33] $R_{unweighted} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{weighted} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

[34] Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.

[35] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

[36] Feng, S. G.; Templeton, J. L. Unpublished results.

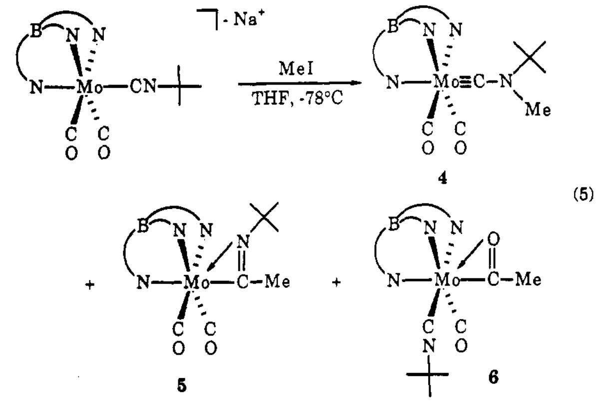


(4)

R = Me, **2**
R = Ph, **3**

for **3**, similar to values for other aminocarbyne complexes.[23,37]

Low-temperature addition of MeI to a THF solution of the *tert*-butyl isocyanide complex, [Na][Tp'(CO)$_2$Mo(CNBu^t)], resulted in a mixture of three isomers, Tp'(CO)$_2$Mo≡CN(Bu^t)(Me) (**4**), Tp'(CO)$_2$Mo(η^2-C(NBu^t)Me) (**5**) and Tp'(CO)(Bu^{t}NC)Mo(η^2-C(O)Me) (**6**) (eq 5). These three isomers, each soluble in Et$_2$O, can be separated from one another by chromatography on alumina. Each compound has been characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of **4** exhibits a 2:1 ratio of Tp' ring proton signals, and the carbyne carbon resonance is located at 253.5 ppm, close to the values observed for **2** and **3**.

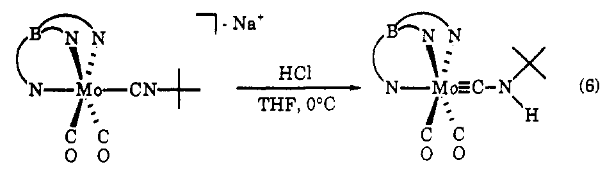


4 (5) **5** **6**

The η^2-iminoacyl complex (**5**) also has a plane of symmetry on the NMR time scale. The iminoacyl carbon resonates at 204.7 ppm in the ^{13}C NMR spectrum, near shifts reported for Cp(CO)$_2$Mo(η^2-C(NMe)Me) and Cp*(CO)$_2$Mo(η^2-C(NMe)Me) (195.15 and 196.99 ppm, respectively).[5] In the gated decoupled spectrum this iminoacyl carbon resonance appears as a quartet ($^2J_{CH}$ = 7.6 Hz) due to coupling to the adjacent methyl protons. Similar coupling ($^2J_{CH}$ = 6 Hz) was observed in the analogous η^2-acyl complex, Tp'(CO)$_2$Mo(η^2-C(O)Me).[13] An iminoacyl CN stretch appears at 1717 cm^{-1}, similar to the value of 1720 cm^{-1} reported for Co(CO)$_2$Mo(η^2-C(NMe)Me).[4]

The IR spectrum of the η^2-acyl complex (**6**) has a single CO stretch at 1802 cm^{-1}, with a CN stretch located at 2119 cm^{-1}. The ^{1}H NMR spectrum contains three separate Tp' ring proton signals, so there is no plane of symmetry. The acyl carbon resonance appears at 268.9 ppm in the ^{13}C NMR spectrum (cf. 261.4 ppm for Tp'(CO)(P(OMe)$_3$)Mo(η^2-C(O)Me[13]), and the isocyanide carbon signal resonates at 159.0 ppm.

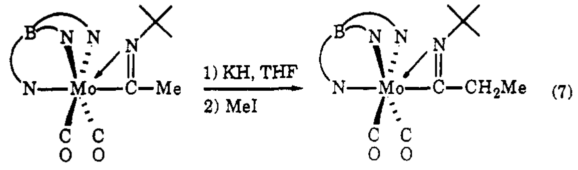
Addition of HCl to [Na][Tp'(CO)$_2$Mo(CNBu^t)] forms an air-sensitive carbyne complex, Tp'(CO)$_2$Mo≡CN(Bu^t)(H) (**7**, eq 6). Metal carbonyl stretches are observed at 1948 and 1852 cm^{-1}. NMR data resemble those for **4** with an additional broad resonance at 5.94 ppm tentatively assigned as the amine proton. The carbyne carbon signal resonates at 251.6 ppm.



(6)

7

Reactions of Tp'(CO)$_2$Mo(η^2-C(NBu^t)Me) (5). Deprotonation of **5** by KH results in a gradual color change to green-gold and a shift to lower CO stretching frequencies. The reaction was judged to be complete when evolution of H$_2$ ceased. Addition of MeI formed the substituted product Tp'(CO)$_2$Mo(η^2-C(NBu^t)Et (**8**, eq 7). The methyl and methylene resonances of the ethyl group appear at 1.48 and 3.57 ppm, respectively, with a $^3J_{HH}$ coupling constant of 7.7 Hz.

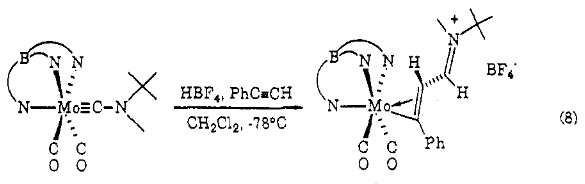


(7)

5 **8**

Complex **5** is air and moisture sensitive and also susceptible to decomposition by thermolysis. Upon prolonged exposure to humid air, the color of solid **5** changed to light brown, and clear needles appeared. The needles were identified as *N-tert*-butylacetamide, a cleavage product of the iminoacyl ligand.

Low-temperature addition of HBF$_4$ to a CH$_2$Cl$_2$ solution of **4** in the presence of PhC≡CH results in formation of a dark olive green η^2-vinyliminium complex, [Tp'(CO)$_2$Mo(η^2-C(Ph)=C(H)C(H)=N(Bu^t)(Me))][BF$_4$] (**9**, eq 8). Due to line broadening at room temperature, NMR spectra were collected at −22 °C. Only one isomer is observed by NMR spectroscopy. The Tp' ring protons appear as three singlets, and the vinyl proton signal appears as a doublet at 4.12 ppm, coupled to the iminium proton doublet resonating at 7.49 ppm, with a coupling constant of 10.8 Hz. The α-carbon of the vinyl ligand resonates at 242.6 ppm, with the β-carbon appearing as a doublet of doublets ($^1J_{CH}$ = 162 Hz, $^2J_{CH}$ = 3 Hz) at 40.7 ppm. These shift values are comparable to values of 237.4 and 35.7 ppm reported for the η^2-vinyl ligand in Cp((MeO)$_3$P)$_2$Mo(η^2-C(Me)=CPh$_2$),[38] and also with values of 264.5 and 38.0 ppm found for Tp(CO)$_2$W(η^2-C(Ph)=CHMe).[36] The iminium carbon signal appears as a double-doublet ($^1J_{CH}$ = 169 Hz, $^2J_{CH}$ = 3 Hz) at 170.2 ppm, as is typical for an iminium carbon.[39] The iminium methyl carbon signal appears as a quartet of doublets ($^1J_{CH}$ = 138 Hz, $^4J_{CH}$ = 6 Hz) at 33.0 ppm, presumably coupling to the proton on the iminium carbon. This suggests that the methyl group is trans to the proton across the C–N double bond, as confirmed by an X-ray structure. A series of ^{1}H NMR spectra of **9** were collected over the range 30–70 °C in 10-deg increments.



(8)

4 **9**

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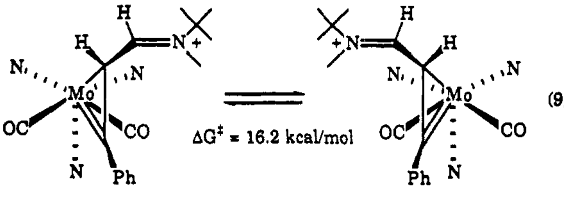
[39] Rabiller, C.; Renou, J. P.; Martin, G. J. *J. Chem. Soc., Perkin Trans. 2* 1977, 536.

Table II. Atomic Positions for 9

atom	*x*	*y*	*z*
Mo	0.30032 (5)	0.57551 (3)	0.18644 (3)
C(1)	0.2179 (6)	0.5783 (4)	0.0770 (4)
O(1)	0.1715 (5)	0.5757 (3)	0.0147 (3)
C(2)	0.4177 (6)	0.5074 (3)	0.1596 (4)
O(2)	0.4871 (4)	0.4689 (3)	0.1462 (3)
C(3)	0.2122 (5)	0.4896 (3)	0.1817 (3)
C(4)	0.1660 (5)	0.5181 (3)	0.2475 (3)
C(5)	0.0415 (5)	0.5338 (3)	0.2402 (4)
N(6)	−0.0145 (5)	0.5534 (3)	0.2958 (3)
C(7)	0.0558 (7)	0.5667 (4)	0.3714 (4)
C(8)	−0.1507 (6)	0.5592 (4)	0.2890 (5)
C(9)	−0.2108 (7)	0.5432 (5)	0.2072 (6)
C(10)	−0.1936 (8)	0.5090 (5)	0.3444 (7)
C(11)	−0.1823 (8)	0.6311 (4)	0.3089 (6)
C(21)	0.1809 (5)	0.4269 (3)	0.1419 (3)
C(22)	0.2224 (6)	0.4111 (3)	0.0721 (4)
C(23)	0.1916 (6)	0.3507 (4)	0.0359 (4)
C(24)	0.1210 (7)	0.3046 (3)	0.0667 (4)
C(25)	0.0798 (7)	0.3198 (4)	0.1362 (4)
C(26)	0.1113 (6)	0.3800 (3)	0.1737 (4)
B(1)	0.4241 (7)	0.7028 (4)	0.2866 (4)
N(31)	0.2891 (5)	0.7164 (3)	0.2627 (3)
N(32)	0.2187 (4)	0.6723 (3)	0.2156 (3)
C(33)	0.1137 (6)	0.7047 (3)	0.1920 (4)
C(34)	0.1159 (7)	0.7670 (4)	0.2250 (4)
C(35)	0.2272 (7)	0.7745 (4)	0.2682 (4)
C(36)	0.0143 (7)	0.6766 (4)	0.1347 (5)
C(37)	0.2776 (8)	0.8342 (4)	0.3134 (5)
N(41)	0.4465 (4)	0.6403 (2)	0.3349 (3)
N(42)	0.4087 (4)	0.5794 (3)	0.3040 (3)
C(43)	0.4556 (6)	0.5321 (3)	0.3550 (4)
C(44)	0.5230 (6)	0.5626 (3)	0.4184 (4)
C(45)	0.5164 (6)	0.6303 (3)	0.4036 (4)
C(46)	0.4380 (6)	0.4585 (3)	0.3430 (4)
C(47)	0.5725 (7)	0.6869 (4)	0.4524 (4)
N(51)	0.4823 (5)	0.6940 (3)	0.2118 (3)
N(52)	0.4424 (5)	0.6456 (3)	0.1577 (3)
C(53)	0.5093 (6)	0.6538 (3)	0.1002 (4)
C(54)	0.5908 (6)	0.7050 (3)	0.1173 (4)
C(55)	0.5716 (6)	0.7303 (3)	0.1867 (4)
C(56)	0.4905 (7)	0.6108 (4)	0.0295 (4)
C(57)	0.6343 (7)	0.7870 (4)	0.2312 (4)
B(2)	0.8776 (8)	0.8736 (5)	0.0762 (6)
F(1)	0.9372 (6)	0.8585 (4)	0.0195 (4)
F(2)	0.7931 (5)	0.9186 (3)	0.0552 (4)
F(3)	0.8292 (5)	0.8146 (3)	0.0953 (4)
F(4)	0.9571 (5)	0.8958 (3)	0.1382 (3)

The two lower field Tp′ ring protons coalesced at ~40 °C, and the two highest field Tp′ methyl signals had become a single broad signal by 70 °C. From line-broadening measurements, a $\Delta G^{\ddagger}$ value of 16.2 kcal/mol was calculated. We believe this reflects the barrier to interconversion of enantiomers of 9 (eq 9).



(9)

A single-crystal X-ray study provided the molecular structure of the vinyliminium complex cation. Considering the η^2-vinyl ligand as occupying a single coordination site, the molybdenum center in 9 adopts a roughly octahedral geometry. Molybdenum and the η^2-vinyl carbons define a plane that approximately bisects the C–Mo–C angle of the carbonyls (Figure 1). Complete atomic positions and bond distances and angles are listed in Tables II–IV. The bond distances for Mo–C(3) (1.970 (6) Å), Mo–C(4) (2.277 (6) Å), and C(3)–C(4) (1.450 (8) Å) are within the normal ranges for an η^2-vinyl moiety. The C(5)–N(6) bond distance of 1.295 (8) Å as well as the bond angle summation about N(6) of ~360° suggests sp^2 hybridization of the nitrogen.

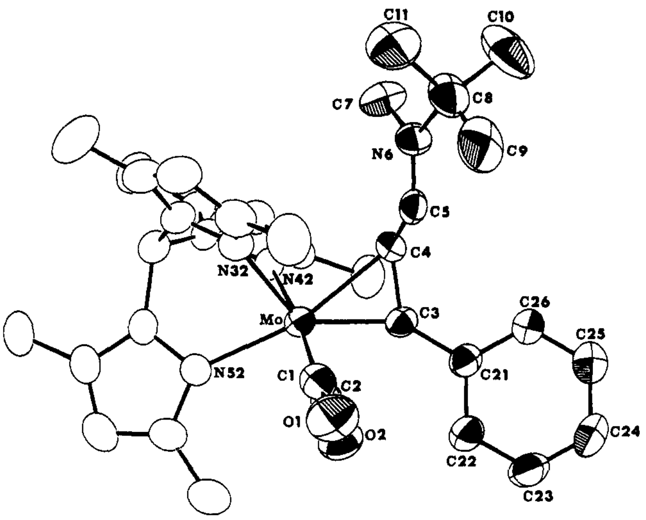
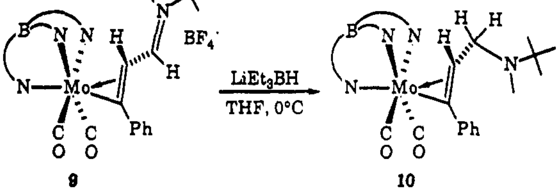


Figure 1. ORTEP representation of the cationic η^2-vinyl iminium complex, 9.

Table III. Complete Bond Distances (Å) for 9

Mo–C(1)	2.004 (7)	N(31)–C(35)	1.358 (8)
Mo–C(2)	1.992 (7)	C(33)–C(36)	1.49 (1)
Mo–C(3)	1.970 (6)	C(34)–C(35)	1.36 (1)
Mo–C(4)	2.277 (6)	C(35)–C(37)	1.49 (1)
Mo–N(32)	2.226 (5)	N(41)–N(42)	1.370 (7)
Mo–N(42)	2.232 (5)	N(41)–C(45)	1.349 (8)
Mo–N(52)	2.228 (5)	N(42)–C(43)	1.350 (8)
C(1)–O(1)	1.139 (8)	C(43)–C(44)	1.387 (9)
C(2)–O(2)	1.139 (8)	C(43)–C(46)	1.490 (9)
C(3)–C(4)	1.450 (8)	C(44)–C(45)	1.374 (9)
C(3)–C(21)	1.448 (9)	C(45)–C(47)	1.497 (9)
C(4)–C(5)	1.412 (8)	N(51)–N(52)	1.380 (7)
C(5)–N(6)	1.295 (8)	N(51)–C(55)	1.358 (8)
N(6)–C(7)	1.462 (9)	N(52)–C(53)	1.352 (8)
N(6)–C(8)	1.514 (9)	C(53)–C(54)	1.37 (1)
C(8)–C(9)	1.53 (1)	C(53)–C(56)	1.50 (1)
C(8)–C(10)	1.52 (1)	C(54)–C(55)	1.37 (1)
C(8)–C(11)	1.53 (1)	C(55)–C(57)	1.49 (1)
C(21)–C(22)	1.409 (9)	B(2)–F(1)	1.31 (1)
C(21)–C(26)	1.385 (9)	B(2)–F(2)	1.31 (1)
C(22)–C(23)	1.38 (1)	B(2)–F(3)	1.36 (1)
C(23)–C(24)	1.37 (1)	B(2)–F(4)	1.37 (1)
C(24)–C(25)	1.40 (1)	Cl(1)–C(61)	1.71 (1)
C(25)–C(26)	1.39 (1)	Cl(2A)–C(61)	1.66 (1)
B(1)–N(31)	1.528 (9)	Cl(2B)–C(61)	1.46 (1)
B(1)–N(41)	1.507 (9)		
B(1)–N(51)	1.559 (9)		
N(31)–N(32)	1.371 (7)		

Complex 9 reacted readily with LiEt$_3$BH to form a neutral η^2-vinyl complex, Tp′(CO)$_2$Mo(η^2-C(Ph)=C(H)-CH$_2$N(Bu^t)(Me)) (10, eq 10). The structure of 10 was deduced from ^{1}H and ^{13}C NMR data. The Tp′ ring protons appear as three singlets. The vinyl proton, at 3.40 ppm, is coupled to both the diastereotopic methylene protons ($^3J_{HH}$ = 9, 2 Hz) on the carbon bound to the amine group. The methylene protons resonate at 3.73 and 2.81 ppm, and exhibit additional geminal coupling of 13 Hz.



(10)

Table IV. Complete Bond Angles (deg) for 9

C(1)–Mo–C(2)	90.9 (3)	N(41)–B(1)–N(51)	109.0 (5)
C(1)–Mo–C(3)	80.1 (3)	B(1)–N(31)–N(32)	120.4 (5)
C(1)–Mo–C(4)	103.0 (2)	B(1)–N(31)–C(35)	128.5 (6)
C(1)–Mo–N(32)	92.9 (2)	N(32)–N(31)–C(35)	109.7 (5)
C(1)–Mo–N(42)	173.5 (2)	Mo–N(32)–N(31)	118.4 (4)
C(1)–Mo–N(52)	90.4 (2)	Mo–N(32)–C(33)	135.3 (4)
C(2)–Mo–C(3)	74.9 (2)	N(31)–N(32)–C(33)	105.9 (5)
C(2)–Mo–C(4)	105.8 (2)	N(32)–C(33)–C(34)	110.1 (6)
C(2)–Mo–N(32)	162.1 (2)	N(32)–C(33)–C(36)	123.6 (6)
C(2)–Mo–N(42)	87.5 (2)	C(34)–C(33)–C(36)	126.2 (6)
C(2)–Mo–N(52)	81.8 (2)	C(33)–C(34)–C(35)	107.0 (6)
C(3)–Mo–C(4)	39.1 (2)	N(31)–C(35)–C(34)	107.4 (6)
C(3)–Mo–N(32)	122.9 (2)	N(31)–C(35)–C(37)	124.2 (7)
C(3)–Mo–N(42)	105.6 (2)	C(34)–C(35)–C(37)	128.5 (7)
C(3)–Mo–N(52)	154.6 (2)	B(1)–N(41)–N(42)	119.6 (5)
C(4)–Mo–N(32)	90.3 (2)	B(1)–N(41)–C(45)	130.5 (5)
C(4)–Mo–N(42)	83.5 (2)	N(42)–N(41)–C(45)	109.1 (5)
C(4)–Mo–N(52)	164.3 (2)	Mo–N(42)–N(41)	119.3 (4)
N(32)–Mo–N(42)	86.7 (2)	Mo–N(42)–C(43)	133.8 (4)
N(32)–Mo–N(52)	80.7 (2)	N(41)–N(42)–C(43)	106.8 (5)
N(42)–Mo–N(52)	83.2 (2)	N(42)–C(43)–C(44)	109.7 (5)
Mo–C(1)–O(1)	175.7 (7)	N(42)–C(43)–C(46)	124.3 (6)
Mo–C(2)–O(2)	177.9 (6)	C(43)–C(44)–C(45)	105.7 (5)
Mo–C(3)–C(4)	82.0 (4)	N(41)–C(45)–C(44)	108.8 (5)
Mo–C(3)–C(21)	148.6 (5)	N(41)–C(45)–C(47)	122.5 (6)
C(4)–C(3)–C(21)	129.3 (5)	C(44)–C(45)–C(47)	128.7 (6)
Mo–C(4)–C(3)	58.9 (3)	B(1)–N(51)–N(52)	121.7 (5)
Mo–C(4)–C(5)	123.7 (4)	B(1)–N(51)–C(55)	129.2 (5)
C(3)–C(4)–C(5)	118.5 (5)	N(52)–N(51)–C(55)	109.0 (5)
C(4)–C(5)–N(6)	125.3 (6)	Mo–N(52)–N(51)	116.8 (4)
C(5)–N(6)–C(7)	119.0 (5)	Mo–N(52)–C(53)	137.4 (4)
C(5)–N(6)–C(8)	123.9 (6)	N(51)–N(52)–C(53)	105.8 (5)
C(7)–N(6)–C(8)	117.0 (5)	N(52)–C(53)–C(54)	110.5 (6)
N(6)–C(8)–C(9)	110.7 (6)	N(52)–C(53)–C(56)	121.7 (6)
N(6)–C(8)–C(10)	108.0 (6)	C(54)–C(53)–C(56)	127.8 (6)
N(6)–C(8)–C(11)	108.6 (6)	C(53)–C(54)–C(55)	106.4 (6)
C(9)–C(8)–C(10)	109.1 (7)	N(51)–C(55)–C(54)	108.3 (6)
C(9)–C(8)–C(11)	109.1 (7)	N(51)–C(55)–C(57)	123.0 (6)
C(10)–C(8)–C(11)	111.4 (7)	C(54)–C(55)–C(57)	128.7 (6)
C(3)–C(21)–C(22)	121.6 (6)	F(1)–B(2)–F(2)	111.7 (8)
C(3)–C(21)–C(26)	119.6 (6)	F(1)–B(2)–F(3)	104.7 (8)
C(22)–C(21)–C(26)	118.5 (6)	F(1)–B(2)–F(4)	109.5 (7)
C(21)–C(22)–C(23)	120.2 (6)	F(2)–B(2)–F(3)	111.3 (7)
C(22)–C(23)–C(24)	121.4 (6)	F(2)–B(2)–F(4)	110.8 (7)
C(23)–C(24)–C(25)	118.7 (6)	F(3)–B(2)–F(4)	108.5 (7)
C(24)–C(25)–C(26)	120.6 (6)	Cl(1)–C(61)–Cl(2A)	105.9 (7)
C(21)–C(26)–C(25)	120.6 (6)	Cl(1)–C(61)–Cl(2B)	119.6 (9)
N(31)–B(1)–N(41)	112.0 (6)	Cl(2A)–C(61)–Cl(2B)	61.8 (6)
N(31)–B(1)–N(51)	107.9 (5)		

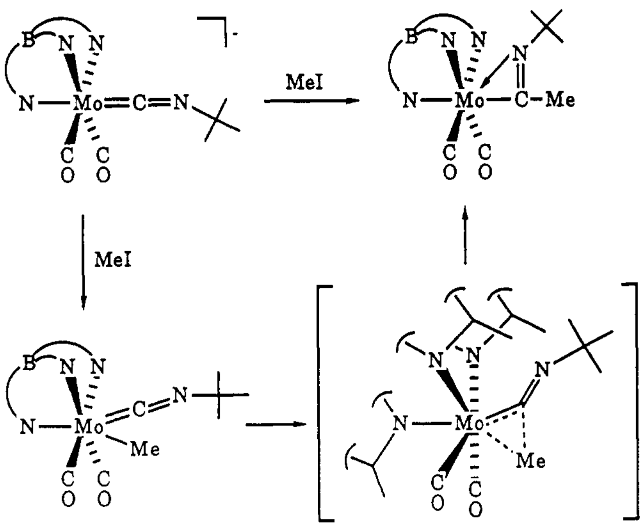
The vinyl ligand α-carbon signal appears at 285.3 ppm, and the vinyl β-carbon resonates as a doublet at 44.3 ppm with a $^1J_{CH}$ coupling constant of 156 Hz. The methylene carbon signal appears as a triplet at 66.8 ppm, with a proton coupling constant of 133 Hz.

Discussion

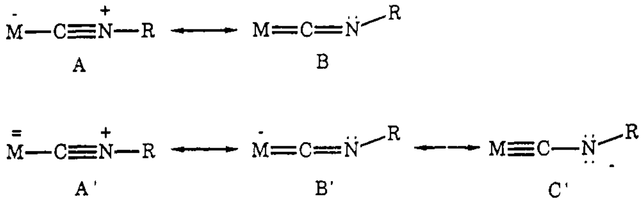
Infrared data indicate that the reaction of iodine with $[NEt_4][Tp'Mo(CO)_3]$ in THF solution initially forms a tricarbonyl iodide intermediate, which then loses carbon monoxide to form a putative 16e dicarbonyl complex, $Tp'(CO)_2MoI$. Although THF coordination may occur, similar carbonyl stretching frequencies are observed for this reaction in CH_2Cl_2 solution. This CO lability is not observed in either the $Cp(CO)_3MoX$ (X = Cl, I)[35] or $Tp'(CO)_3WI$[36] analogues. The greater steric congestion with the Tp′ ligand relative to Cp no doubt destabilizes the seven-coordinate species, and molybdenum carbonyls are more labile than tungsten. Both effects contribute to the facility of CO loss here.

Addition of MeI to $[Na][Tp'(CO)_2Mo(CNR)]$, where R is methyl or phenyl, yields the respective aminocarbyne complexes. The formation of a mixture of carbyne, η^2-iminoacyl, and η^2-acyl complexes from addition of MeI to $[Na][Tp'(CO)_2Mo(CNBu^t)]$ reflects a more complicated reaction coordinate. It has been postulated that syntheses of η^2-acyl and η^2-iminoacyl complexes proceed through initial methylation of the metal center, followed by migratory insertion (Scheme IV).[6] In contrast, formation of the aminocarbyne complex is believed to result from direct attack at nitrogen, consistent with the resonance forms of metal isocyanides shown in Scheme V. The large *tert*-butyl substituent on nitrogen evidently promotes some methylation at molybdenum. Greater electron density at the metal favors resonance form B through greater d → π* donation.[1] This effect is evident in the structure of *trans*-$(dppe)_2Mo(CNMe)_2$, where the C–N–Me bond angle is 156°, suggesting some sp^2 hybridization at nitrogen.[16] For anionic metal complexes, the carbyne-like resonance form C′ may contribute. It appears that increased nucleophilicity at nitrogen and a sterically hindered metal center promote formation of the aminocarbyne complex.

Scheme IV



Scheme V



The formation of a small amount of η^2-acyl (6) may reflect steric effects. Addition of MeI to the isoelectronic cyclopentadienylmolybdenum complex $[Cp(CO)_2Mo(CNMe)][Na]$ forms only the η^2-iminoacyl product.[4] Literature precedents suggest that migratory insertion of isocyanides is more facile than that of carbonyl ligands.[6] Perhaps steric interaction between the *tert*-butyl group of the isocyanide and the methyls of the Tp′ pyrazolyl rings during migratory insertion increases the barrier to η^2-iminoacyl formation here and allows competitive formation of the η^2-acyl complex.

The secondary aminocarbyne complex, 7, formed through addition of acid to the $Tp'(CO)_2Mo(CNBu^t)$ anion, decomposes rapidly in air. A series of similar unsubstituted tris(pyrazolyl)borate complexes, $Tp'(CO)_2W{\equiv}CNRH$ (R = Me, Et, Pr^i, Bu^t, CH_2CH_2OH) (Tp = hydridotris(pyrazolyl)borate), tautomerize to isocyanide hydride complexes in solution.[40] We have been unable to detect

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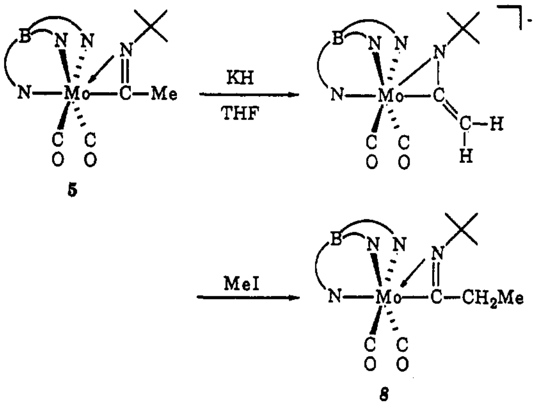
(40) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489.

the hydride form of 7, so if there exists an equilibrium for tautomerization it greatly favors the aminocarbyne form, presumably due to steric congestion at the metal center.

Reactivity of Tp'(CO)$_2$Mo(η^2-C(NBu^t)Me). As with the corresponding η^2-acyl complex,[13] deprotonation of 5 at C_β to form the η^2-enamide complex followed by addition of MeI yields a C_β-substituted product (8, eq 11).



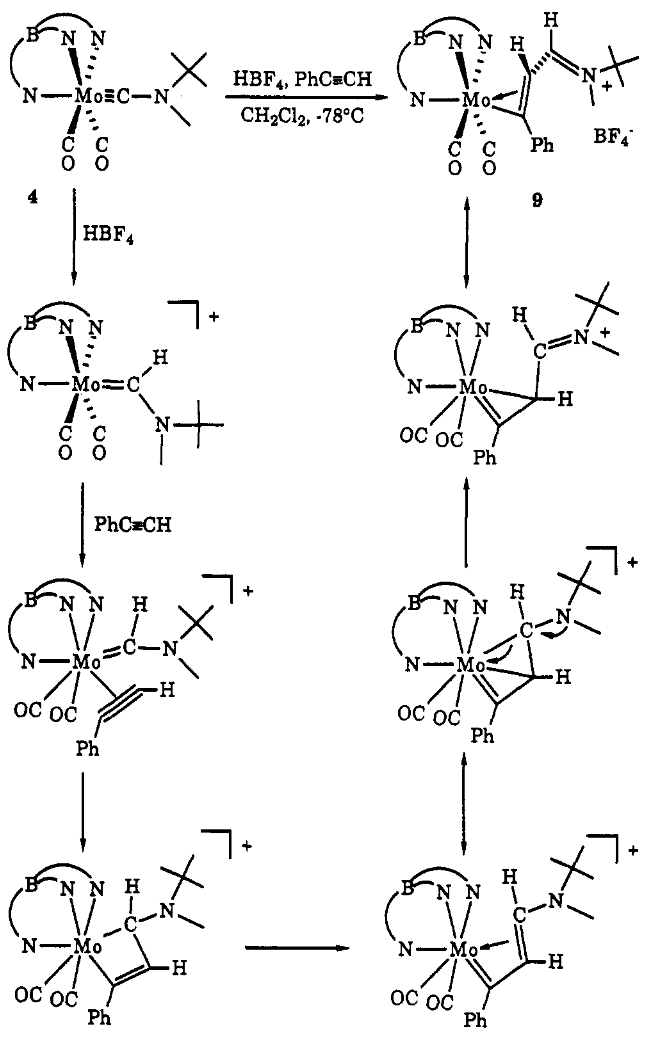
(11)

Protonation of Tp'(CO)$_2$Mo≡CN(Bu^t)(Me) (4) in the presence of phenylacetylene presumably forms a highly reactive 16e carbene intermediate initially. Rapid coordination of alkyne is postulated, possibly followed by insertion to give a metallacyclobutene or, more likely, a vinylcarbene.[41] Similar mechanisms have been postulated for a variety of alkyne/carbene insertion reactions.[42] Most notably, Geoffroy et al.[43] have synthesized the vinylcarbene complex [Cp(CO)$_2$W(η^3-C(Ph)C(Ph)=C(H)(Tol))][BF$_4$] via low-temperature addition of HBF$_4$ to Cp(CO)$_2$W≡CTol in the presence of diphenylacetylene. The vinylcarbene product in Geoffroy's system is unstable, decomposing upon warming to room temperature. For the analogous reaction with 4, the availability of the nitrogen lone pair results in conversion to an η^2-vinyliminium product, 9, with positive charge localized at the nitrogen. The presence of greater electron density at the metal in our product is apparent from the CO stretches at 2027 and 1944 cm^{-1}, which are significantly lower than those reported for Geoffroy's vinylcarbene complex (2054 and 1975 cm^{-1}).[43] A plausible mechanism for the formation of 9 is presented in Scheme VI.

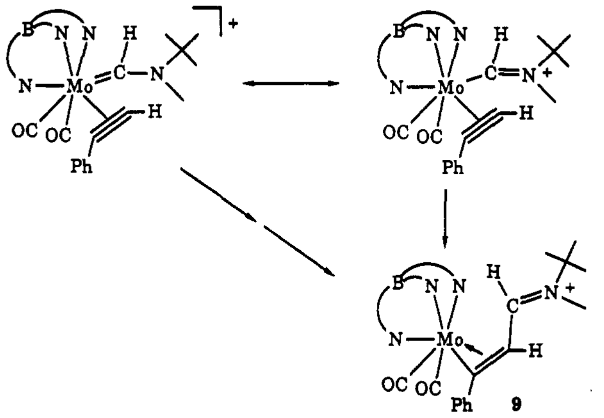
Though formation of a metallacyclobutene intermediate is the classical result for an alkyne/carbene insertion, a simpler mechanism may apply for alkyne insertion into an amino-substituted carbene. An important resonance form for the heteroatom carbene is shown in Scheme VII where nitrogen lone-pair donation generates a metal iminium moiety. Alkyne insertion into the metal–carbon bond could then lead directly to the observed η^2-vinyliminium product. No intermediates have been isolated, and both mechanisms are viable alternatives.

Four isomers of the η^2-vinyliminium complex are possible due to inequivalent alkyne substituents and *E*/*Z* stereochemistry about the C–N double bond, but only one isomer is detected. The carbene intermediate would presumably minimize interaction between the *tert*-butyl group and the Tp' methyls. If the carbene proton is cis to the *tert*-butyl group then either mechanism will yield the *E* isomer from alkyne insertion. Furthermore, formation of a carbene type bond to molybdenum will thermodynamically favor a phenyl substituent on the carbene carbon rather than a proton.

Scheme VI



Scheme VII



Complex 9 exhibits fluxionality in the NMR spectrum, which we believe reflects rapid interconversion of the two mirror isomers shown in Scheme VIII. One can postulate a putative 16e carbene transition state with a plane of symmetry, so the stereochemistry of collapse back to the η^2-vinyliminium complex would be arbitrary. This mechanism would afford inversion at the β-carbon of the η^2-vinyl complex.

Bond distances along the η^2-vinyliminium backbone (C(3)–C(4), 1.450 (8) Å; C(4)–C(5), 1.412 (8) Å; C(5)–N(6),

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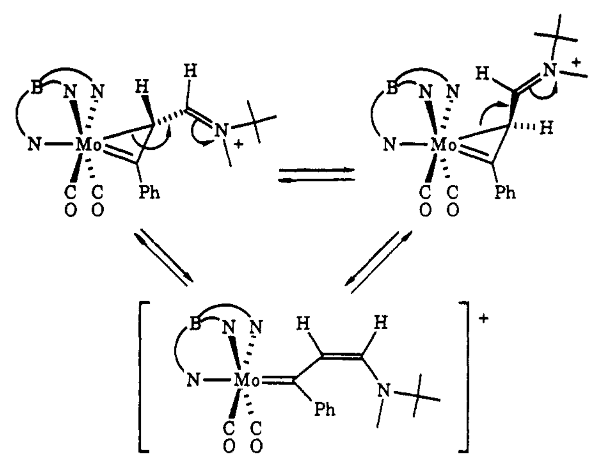
[41] Hofmann, P.; Hammerle, M. *Angew. Chem., Int. Ed. Engl.* 1989, *28*, 908.

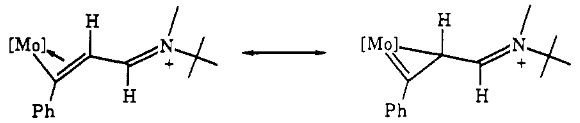
[42] Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 587.

[43] Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. G.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* 1989, *111*, 8383.

Scheme VIII



1.295 (8) Å) lie between values expected for single and double bonds, and suggest extensive π-delocalization in this fragment. The C(3)–C(4)–C(5)–N(6) torsion angle of 173.0 (8)° supports this view. The C(3)–C(4) bond distance of the vinyl is actually longer than that of C(4)–C(5), which is formally a single bond. Bond lengthening in the vinyl group can be understood by examining resonance structures of the compound.



The addition of hydride to 9 to give the neutral η^2-vinyl complex 10 is typical chemistry for iminium salts.[44] Compound 10 is generated as a racemic mixture of enantiomers, which show no fluxionality on the NMR time scale. The electronic ambiguity present in 9 due to potential positive charge localization at either metal or nitrogen is absent in 10.

Conclusion

Electrophilic addition to anionic molybdenum isocyanide derivatives is dominated by direct attack at nitrogen to form carbyne products, but alkylation at the metal followed by insertion can form η^2-iminoacyl complexes in some cases. The aminocarbyne products, formed in high yield for methyl and phenyl isocyanide reagents, can be protonated in the presence of phenylacetylene to form η^2-vinyl complexes via alkyne insertion into the transient metal–carbene bond. Hydride addition to the free iminium carbon generates a neutral η^2-vinylamine complex. The η^2-iminoacyl complex accessible from the *tert*-butyl isocyanide reagent has been elaborated at the iminoacyl C_β position by a deprotonation/alkylation sequence.

Acknowledgment. We gratefully acknowledge the Department of Energy, Division of Chemical Sciences, for support of this research (Grant 85ER13430).

Supplementary Material Available: For 9, tables of anisotropic temperature factors, bond distances and angles, and calculated hydrogen positions as well as an ORTEP diagram of 9 with the complete atomic numbering scheme (5 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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[44] March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 875.

Reaction Pathways of Telluroxide Equivalents. Reductive Elimination of Hydrogen Peroxide from Dihydroxytelluranes and Oxidation of Carbon via Intramolecular Transfer of Oxygen

Michael R. Detty

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2110

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Dihydroxytelluranes 2 undergo a thermal reductive elimination of hydrogen peroxide to generate tellurapyrylium dyes 1 in 99% methanol, 90% methanol, 50% methanol, water, and phosphate-buffered saline (PBS). Temperature-dependent first-order rates of reaction were measured for the disappearance of **2d** in 99% methanol and 90% methanol. The reductive elimination was found to proceed in >95% yield in these solvents. The first-order rate constant for reductive elimination decreased with increasing water concentration, while $\Delta G^\ddagger$ increased from 13.9 kcal mol^{-1} in 99% methanol to 14.8 kcal mol^{-1} in 90% methanol. In PBS, temperature-dependent first-order rate constants were measured for **2b–d** at 310.0, 323.0, and 333.0 K. Values of $\Delta H^\ddagger$ of 21.3 ± 0.6, 20.5 ± 0.9, and 20.9 ± 0.1 kcal mol^{-1} were calculated for **2b–d**, respectively. Corresponding values for $\Delta S^\ddagger$ of 12 ± 2, 11 ± 3, and 10.9 ± 0.5 cal mol^{-1} K^{-1} were calculated for **2b–d**, respectively. The positive charge on species 2 leads to increased acidity of the hydroxyl protons with first pK_a's of −1.9 and −2.1 measured spectrophotometrically for **2c,d**, respectively, and second pK_a's of 7.8 and 7.7 for **2c,d**, respectively. The rate of disappearance of 2 was a function of pH. Over the pH range 4.24–7.37, where compounds 2 would be zwitterionic, fairly constant rates of disappearance were measured ($(2.3 \pm 0.2) \times 10^{-5}$ s^{-1}). At lower pH values, where 2 would be more fully protonated, the rate of disappearance of 2 increases as does the rate of appearance of 1. At a pH of 9.19, where the second acidic proton would be ionized, the rate constant for the disappearance of 2 is much larger. In PBS, a second reaction pathway is observed for **2b–d**. Tellurophene 7 is produced as the product of intramolecular oxidation of carbon with the oxygen of the tellurium(IV) species.

Many synthetic transformations have been devised that incorporate the higher oxidation states of the selenium atom (the selenoxide and selenone states) in organoselenium compounds. Perhaps the best studied of these transformations are elimination reactions of selenoxides to give olefins.[1] In other transformations, the selenoxide

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