Table VIII. Summary of Crystallographic Data

formula	$C_{34}H_{32}NPCl_2Pt$
fw	751.62
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	17.677 (3)
b, Å	15.495 (3)
c, Å	11.371 (2)
β, deg	104.59 (2)
V, Å^3	3014 (2)
D_{exptl}, g cm^{-3}	1.656
Z	4
$F(000)$	1480.0
cryst size, mm^3	0.1 × 0.1 × 0.2
μ(Mo Kα), cm^{-1}	51.50
λ(Mo Kα), Å	0.71069
T, K	298
no. of rflns collected	4733
R	0.045
R_w	0.052

$C_{34}H_{32}Cl_2NPPt$: C, 54.33; H, 4.29; N, 1.86. Found: C, 54.29; H, 4.31; N, 2.10.

[$PtMe_2Br(PPh_3)(C_6H_5CHNCH_2C_6H_4)$] (6h): yield 23 mg (85%); mp 118 °C dec; ν(CH=N) 1615 cm^{-1}. Anal. Calcd for $C_{34}H_{33}BrNPPt$: C, 53.62; H, 4.37; N, 1.84. Found: C, 53.98; H, 4.49; N, 1.69.

X-ray Structure Analysis. Data Collection. Crystals of [$PtMe_2Cl(PPh_3)(C_6H_3ClCHNCH_2C_6H_5)$] (**6c**) were grown from acetone–hexane. A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Phillips PW-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 < \theta < 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation, using ω-scan technique. A total of 4733 reflections were measured in the range $2 \ll \theta \ll 25°$, 3760 of which were assumed as observed by applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz–polarization and absorption corrections were made.

Structure Solution and Refinement. The structure was solved by a Patterson synthesis, using the SHELXS computer program,[20] and refined by the full-matrix least-squares method, with the SHELX76 computer program.[21] The function minimized $\sum w[|F_o| - |F_c|]^2$, where $w = (\sigma^2(F_o) + 0.0095|F_o|^2)^{-1}$. f, f', and f'' were taken from ref 22. The positions of 30 hydrogen atoms were computed and refined with an overall isotropic temperature factor, using a riding model. The final R factor was 0.045 (R_w = 0.052) for all observed reflections. The number of refined parameters was 355. The maximum shift/esd was 0.1; maximum and minimum peaks in the final difference synthesis were 0.4 and −0.4 e Å^{-3}, respectively.

Acknowledgment. We thank Professor R. J. Puddephatt for ideas and for stimulating interest. We thank the DGICYT (Grant No. PB 89-0254) for financial support and Johnson Matthey for a loan of platinum salts.

Supplementary Material Available: Tables of observed rate constants and anisotropic thermal parameters (5 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Stereoselective Stepwise Reduction of Coordinated Acetonitrile with Chiral Tp′(CO)(RC≡CR′)W$^+$ Templates

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Stepwise reduction of the acetonitrile ligand in [Tp′(CO)(RC≡CR′)W(N≡CMe)][BF_4] has been accomplished with sequential addition of nucleophiles and electrophiles to the carbon–nitrogen triple bond. Intermediate metal complexes containing coordinated azavinylidene, imine, amide, and amine nitrogen donor ligands have been isolated and characterized. Nucleophilic addition to the imine complexes is highly stereoselective. Acidification of the amine complex in acetonitrile forms the free ammonium salt, and solvent coordination regenerates the acetonitrile adduct.

Introduction

The work reported here combines the stereochemical control accessible through use of the chiral Tp′W(CO)(PhC≡CMe) fragment (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with the stepwise reduction of coordinated acetonitrile communicated previously.[1] Representative examples of stereoselective reactions of chiral transition-metal reagents, including specific instances utilizing group 6 Tp′ moieties, are referenced first. Reduction reactions of coordinated nitriles are then reviewed briefly before other reactions of coordinated nitriles are catalogued to complete the introduction.

Chiral transition-metal complexes can dictate the stereochemistry of ligand elaboration reactions. The Liebeskind[2] and Davies[3] groups have enantioselectively elaborated η^1-acyl groups in an iron system. Brookhart has used electrophilic carbene complexes, [Cp(CO)(PR_3)Fe=CHR]$^+$, to effect enantioselective formation of cyclo-

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0276-7333/92/2311-1295$03.00/0

Chart I

propanes from olefins.[4] The rhenium chemistry developed by Gladysz illustrates the power of chiral transition-metal centers for controlling the stereochemistry of ligand-based reactions.[5] Diastereoselective transformations of η^2-acyl ligands have been achieved with the Tp'(CO)[P(OPh)$_3$]-Mo[η^2-C(O)CH$_2$R] complex,[6] and recently stereoselective alkyne elaboration in Tp'(CO)IW(PhC$_2$Et) has been achieved.[7]

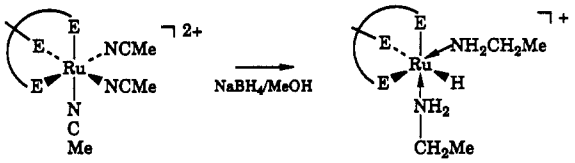
Reduction of nitriles to amines with either hydrogen or hydride reagents is a well-known reaction (eqs 1 and 2).[8]

$$R{-}C{\equiv}N \xrightarrow{H_2,\ cat.} R{-}CH_2{-}NH_2 \qquad (1)$$

$$R{-}C{\equiv}N \xrightarrow{LiAlH_4} R{-}CH_2{-}NH_2 \qquad (2)$$

Conversion of metal-bound nitriles to metal amines with pressurized hydrogen has been reported.[9] Reduction of acetonitrile on metal clusters has yielded isolable intermediates,[10] but characterization of intermediates in nitrile reduction promoted by metal monomers remains rare.

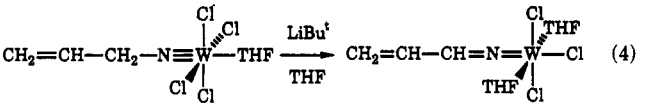
Conversion of acetonitrile to ethylamine results when [(triars)Ru(NCMe)$_3$]$^{2+}$ is treated with NaBH$_4$ in methanol as [(triars)HRu(NH$_2$CH$_2$Me)$_2$]$^+$ forms (eq 3).[11] The ru-



(3)

thenium center polarizes the nitrile and activates the β-carbon toward nucleophilic attack. Repetitive addition of a hydride to the β-carbon and then a proton to the nitrogen would yield the observed amine complex. Mechanistically it is not known whether the hydrides are introduced directly at carbon (A) or indirectly via a 1,3 metal hydride shift from metal to the β-carbon (B) (Chart I). Azavinylidene and imine complexes were postulated as intermediates but were not observed. Azavinylidene ligands are accessible not only via nucleophilic attack at a coordinated nitrile carbon but also by deprotonation of an imido ligand at C$_\beta$, as reported by Maatta and co-workers (eq 4).[12]

Wilkinson and co-workers recently reported that protonation of Cp$_2$Mo(MeCN) with HBF$_4$·Et$_2$O in NCMe



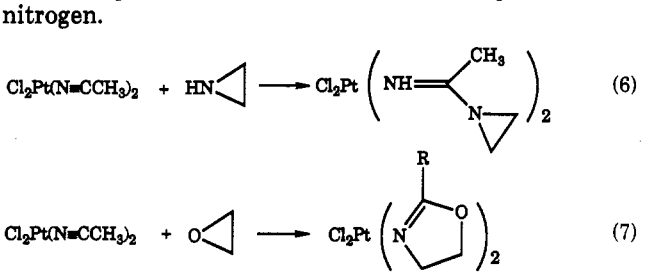
(4)

results in the doubly protonated molybdenum(IV) imine complex [Cp$_2$Mo(NCMe)(NH=CHMe)][BF$_4$]$_2$, which has been structurally characterized (eq 5).[13a] The net result

$$Mo(\eta^5\text{-}C_5H_5)_2(MeCN) + 2HBF_4 \xrightarrow{NCMe} [Mo(\eta^5\text{-}C_5H_5)_2(MeCN)(NH{=}CHMe)][BF_4]_2 \qquad (5)$$

is reduction of the acetonitrile ligand to the imine as molybdenum is oxidized from Mo(II) to Mo(IV). Reduction of acetonitrile ligands in *trans*-[MCl(N≡CMe)-(dmpe)$_2$][BPh$_4$] (M = Cr, Mo) and *trans*-[Cr(N≡CMe)$_2$-(dmpe)$_2$][BPh$_4$]$_2$ with methanol yields *trans*-[MCl-(NCH$_2$Me)(dmpe)$_2$][BPh$_4$][13b,c] and *trans*-[Cr(N=CHMe)$_2$(dmpe)$_2$][BPh$_4$]$_2$,[13b] respectively, while methanol was oxidized to formaldehyde in both cases.

Michelin and co-workers[14] have shown that reaction of platinum nitrile complexes with aziridine or ethylene oxide produces imine and oxazoline complexes, respectively (eqs 6 and 7). These reduction products are compatible with an electrophilic nitrile carbon and a nucleophilic nitrile nitrogen.



(6)

(7)

Stereoselective reduction of nitriles using metal reagents has proven elusive. We have undertaken a study of stepwise reduction of acetonitrile coordinated to the chiral Tp'(CO)(RC$_2$Me)W (R = Me, Ph) moiety. We report here characterization of each of the intermediates in the stepwise reduction of acetonitrile to ethylamine by sequential hydride and proton addition reactions (communicated earlier)[1] and formation of amino nitrile products with high diastereoselectivity when cyanide is used as the second nucleophile.

Experimental Section

General Methods. Manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Solvents were purified as follows: methylene chloride was distilled from P_2O_5; Et_2O, THF, and hexane were distilled from potassium benzophenone ketyl. Acetonitrile was distilled from CaH_2; other solvents were purged with N_2 prior to use. Acetonitrile complexes, [Tp'(CO)(RC≡CMe)W(N≡CMe)][BF$_4$] (R = Ph, Me), were prepared according to literature methods.[1,15] Other reagents were used as obtained from commercial sources.

Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. NMR spectra were recorded on a Varian XL-400 (400-MHz) spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or Oneida Research Services Inc., Whitesboro, NY.

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Syntheses. Tp′(CO)(PhC$_2$Me)W—N=CHCH$_3$ (1). In a representative synthesis, a stoichiometric amount of LiEt$_3$BH (1.0 M in THF, 1.33 mL) was dripped slowly into a cold THF (−78 °C) solution of [Tp′(CO)(PhC$_2$Me)W(NCCH$_3$)][BF$_4$] (1.00 g, 1.33 mmol), resulting in an immediate color change from blue to brown. The solution was warmed to room temperature and stirred for an additional 30 min. The solvent was removed, and the solid residue was chromatographed on alumina with toluene as the eluent. An orange band was collected, and toluene was removed. The solid which remained was recrystallized from toluene/hexane to yield orange crystals (0.62 g, 70%). IR (KBr, cm^{-1}): ν_{CO} = 1885. ^{1}H NMR (CD$_2$Cl$_2$, δ): major isomer (80%), 7.15, 6.52 (m, C$_6H_5$), 6.26 (q, $^3J_{HH}$ = 5.2 Hz, N=C*H*Me), 5.98, 5.83, 5.69 (Tp′ C*H*), 3.24 (PhC$_2$C*H*$_3$), 2.79, 2.58, 2.48, 2.45, 1.72, 1.62 (Tp′ CC*H*$_3$), 1.78 (d, $^3J_{HH}$ = 5.2 Hz, N=CHC*H*$_3$); minor isomer (20%), 7.10, 6.53 (m, C$_6H_5$), 6.45 (q, $^3J_{HH}$ = 5.2 Hz, N=C*H*Me), 5.97, 5.80, 5.67 (Tp′ C*H*), 4.30 (PhC$_2$C*H*$_3$), 2.82, 2.60, 2.49, 2.46, 1.68, 1.65 (Tp′ CC*H*$_3$), 1.78 (d, $^3J_{HH}$ = 5.2 Hz, N=CHC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): major isomer only, 231.9 ($^1J_{WC}$ = 158 Hz, *C*O), 159.7 ($^1J_{WC}$ = 45 Hz, MeC*C*Ph), 158.7 (q, $^2J_{HC}$ = 10 Hz, MeC*C*Ph), 152.4, 152.3, 151.0, 144.5, 144.4, 144.1 (Tp′ *C*CH$_3$), 144.6 (d of q, $^1J_{HC}$ = 167 Hz, $^2J_{HC}$ = 8 Hz, $^1J_{WC}$ = 27 Hz, N=*C*HMe), 137.9, 128.7, 128.3, 126.4 (Ph), 107.6, 107.1, 106.7 (Tp′ *C*H), 19.2 (q of d, $^1J_{HC}$ = 130 Hz, $^2J_{HC}$ = 15 Hz, N=CH*C*H$_3$), 18.0, 17.9, 16.9, 15.9, 15.5, 14.9, 13.0 (Tp′ C*C*H$_3$ and PhC$_2$*C*H$_3$). Anal. Calcd for Tp′(CO)(PhC$_2$Me)W—N=CHCH$_3$·$^1/_2$C$_7$H$_8$, WC$_{30.5}$H$_{38}$N$_7$OB: C, 51.18; H, 5.37; N, 13.80. Found: C, 50.68; H, 5.74; N, 14.13.

Tp′(CO)(MeC$_2$Me)W—N=CHCH$_3$ (2): orange; 70%. IR (KBr, cm^{-1}): ν_{BH} = 2526; ν_{CO} = 1867; ν_{CN} = 1545. ^{1}H NMR (CD$_2$Cl$_2$, δ): major isomer (70%), 6.13 (q, $^3J_{HH}$ = 5.2 Hz, N=C*H*Me), 6.02, 5.89, 5.63 (Tp′ C*H*), 2.95 (CH$_3$C$_2$C*H*$_3$), 2.28 (C*H*$_3$C$_2$CH$_3$), 2.69, 2.50, 2.36, 2.35, 2.14, 1.72 (Tp′ CC*H*$_3$), 1.73 (d, $^3J_{HH}$ = 5.2 Hz, N=CHC*H*$_3$); minor isomer (30%), 6.31 (q, $^3J_{HH}$ = 5.2 Hz, N=C*H*Me), 5.99, 5.88, 5.62 (Tp′ C*H*), 2.92 (CH$_3$C$_2$C*H*$_3$), 2.27 (C*H*$_3$C$_2$CH$_3$), 2.72, 2.51, 2.38, 2.34, 2.16, 1.69 (Tp′ CC*H*$_3$), 1.55 (d, $^3J_{HH}$ = 5.2 Hz, N=CHC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): major isomer only, 232.8 ($^1J_{WC}$ = 161 Hz, *C*O), 157.2 ($^1J_{WC}$ = 43 Hz, $^1J_{WC}$ = 25 Hz, MeC$_2$Me), 152.2, 151.3, 150.7, 149.8, 149.7, 144.3 (Tp′ *C*CH$_3$), 144.2 (d of q, $^1J_{HC}$ = 168 Hz, $^2J_{HC}$ = 7 Hz, $^1J_{WC}$ = 26 Hz, N=*C*HMe), 107.2, 107.0, 106.6 (Tp′ *C*H), 19.3 (q of d, $^1J_{HC}$ = 128 Hz, $^2J_{HC}$ = 15 Hz, N=CH*C*H$_3$), 16.9, 15.9, 15.7, 15.4, 14.1, 12.9, 12.8, 12.7 (Tp′ C*C*H$_3$ and *C*H$_3$C$_2$CH$_3$). Anal. Calcd for WC$_{22}$H$_{32}$N$_7$OB: C, 43.66; H, 5.29; N, 16.21. Found: C, 43.81; H, 5.40; N, 16.14.

Tp′(CO)(PhC$_2$Me)W—N=C(CN)CH$_3$ (3). One equivalent of KCN (0.087 g, 1.33 mmol) was added into a cold MeOH (0 °C; 20 mL) solution of [Tp′(CO)(PhC$_2$Me)W(N≡CCH$_3$)][BF$_4$] (1.0 g, 1.33 mmol), resulting in a color change from blue to orange as an orange powder precipitated. The solid was isolated by filtration after putting the solution in a freezer (−40 °C) for 10 h. The product was redissolved in CH$_2$Cl$_2$, passed through a plug of alumina, and recrystallized from CH$_2$Cl$_2$/hexane to yield orange crystals (0.74 g, 80%). IR (KBr, cm^{-1}): ν_{CO} = 1917. ^{1}H NMR (CDCl$_3$, δ): major isomer (65%), 7.09, 6.40 (m, C$_6H_5$), 5.92, 5.70, 5.57 (Tp′ C*H*), 3.22 (PhC$_2$C*H*$_3$), 2.78, 2.50, 2.39, 2.36, 2.00, 1.59, 1.46 [Tp′ CC*H*$_3$ and N=C(CN)C*H*$_3$]; minor isomer (35%), 7.21, 6.44 (m, C$_6H_5$), 5.88, 5.70, 5.58 (Tp′ C*H*), 3.25 (PhC$_2$C*H*$_3$), 2.67, 2.50, 2.38, 2.36, 1.94, 1.59, 1.58 [Tp′ CC*H*$_3$ and N=C(CN)C*H*$_3$]. ^{13}C NMR (CDCl$_3$, δ): major isomer (65%), 223.5 ($^1J_{WC}$ 151.5 Hz, *C*O), 159.4 ($^1J_{WC}$ = 43 Hz, MeC*C*Ph), 158.7 (q, $^2J_{HC}$ = 7.6 Hz, $^1J_{WC}$ = 10 Hz, MeC*C*Ph), 152.6, 151.9, 150.4, 144.3, 143.7, 143.5 (Tp′ *C*CH$_3$), 136.4, 128.3, 128.0, 126.6 (Ph), 124.1 [q, $^2J_{HC}$ = 7.5 Hz, $^2J_{WC}$ = 29 Hz, N=*C*(CN)Me], 114.4 [N=C(*C*N)Me], 107.4, 107.1, 106.7 (Tp′ *C*H), 18.8, 18.0, 16.5, 15.5, 14.3, 12.8, 12.7, 12.6 [Tp′ C*C*H$_3$, N=C(CN)*Me*, and PhC$_2$*C*H$_3$]; minor isomer (35%), 224.0 ($^1J_{WC}$ = 152 Hz, *C*O), 160.6 ($^1J_{WC}$ = 43 Hz, MeC*C*Ph), 159.7 (q, $^2J_{HC}$ = 7.5 Hz, $^1J_{WC}$ = 10 Hz, MeC*C*Ph), 152.9, 152.1, 150.5, 144.4, 143.7, 143.5 (Tp′ *C*CH$_3$), 136.4, 128.5, 127.9, 126.5 (Ph), 126.4 [N=*C*(CN)Me], 115 [N=C(*C*N)Me], 107.3, 106.8, 106.7 (Tp′ *C*H), 18.6, 17.9, 16.6, 15.5, 14.2, 14.1, 12.75, 12.7 [Tp′ C*C*H$_3$, N=C(CN)*Me*, and PhC$_2$*C*H$_3$]. Anal. Calcd for WC$_{28}$H$_{33}$N$_8$OB: C, 48.58; H, 4.77; N, 16.19. Found: C, 48.01; H, 4.89; N, 16.16.

[Tp′(CO)(PhC$_2$Me)W(NH=CHCH$_3$)][BF$_4$] (4). In a representative synthesis, an orange solution of 1 (1.04 g, 1.5 mmol) in 25 mL of CH$_2$Cl$_2$ was cooled to −78 °C and a stoichiometric amount of HBF$_4$·Me$_2$O was added dropwise with stirring, resulting in a color change to blue. The solution was transferred into 120 mL of Et$_2$O. The blue powder which precipitated was isolated by filtration, washed with Et$_2$O (2 × 10 mL), and dried in vacuo (1.2 g, 90%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded dark ink blue crystals. IR (KBr, cm^{-1}): ν_{CO} = 1920. ^{1}H NMR (CD$_2$Cl$_2$, δ): 10.86 (broad d, $^3J_{HH}$ = 20 Hz, N*H*=CHMe), 7.30, 6.82 (m, C$_6H_5$), 6.38 (d of q, $^3J_{HH}$ = 20 Hz, $^3J_{HH}$ = 5.6 Hz, NH=C*H*Me), 6.05, 5.90, 5.80 (Tp′ C*H*), 3.89 (PhC$_2$C*H*$_3$), 2.58, 2.54, 2.48, 2.45, 1.35, 1.20 (Tp′ CC*H*$_3$), 2.22 (d of d, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.4 Hz, NH=CHC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 228.5 ($^1J_{WC}$ 146 Hz, *C*O), 214.8 ($^1J_{WC}$ = 54 Hz, MeC*C*Ph), 214.3 ($^1J_{WC}$ = 15 Hz, $^2J_{HC}$ = 7 Hz, MeC*C*Ph), 176.9 (d of quintets, $^1J_{HC}$ = 171 Hz, $^2J_{HC}$ = 10 Hz, NH=*C*HMe), 153.6, 152.8, 150.7, 147.5, 147.4, 145.8 (Tp′ *C*CH$_3$), 137.0, 130.1, 129.7, 128.9 (Ph), 109.1, 109.0, 107.8 (Tp′ *C*H), 25.0 (q of t, $^1J_{HC}$ = 130 Hz, $^2J_{HC}$ = $^3J_{HC}$ = 15 Hz, NH=CH*C*H$_3$), 23.1, 15.9, 15.6, 14.2, 12.9, 12.8 (Tp′ C*C*H$_3$ and PhC$_2$*C*H$_3$). Anal. Calcd for WC$_{27}$H$_{35}$N$_7$OB$_2$F$_4$: C, 42.94; H, 4.64; N, 12.99. Found: C, 42.96; H, 4.62; N, 12.90.

[Tp′(CO)(MeC$_2$Me)W(NH=CHCH$_3$)][BF$_4$] (5): blue; 90%. This compound was prepared by acidification of 2 using reaction conditions described above for 4. IR (KBr, cm^{-1}): ν_{BH} = 2562; ν_{CO} = 1906; ν_{CN} = 1541; ν_{BF} = 1068. ^{1}H NMR (CD$_2$Cl$_2$, δ): 10.52 (d, $^3J_{HH}$ = 20.5 Hz, N*H*=CHMe), 6.35 (d of q, $^3J_{HH}$ = 20.5 Hz, $^3J_{HH}$ = 5.2 Hz, NH=C*H*Me), 6.11, 6.00, 5.78 (Tp′ C*H*), 3.63 (CH$_3$C$_2$C*H*$_3$), 2.92 (C*H*$_3$C$_2$CH$_3$), 2.53, 2.44, 2.40, 1.85, 1.41 (Tp′ CC*H*$_3$), 2.20 (d, $^3J_{HH}$ = 5.2 Hz, NH=CHC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 229.5 ($^1J_{WC}$ = 147 Hz, *C*O), 220.0 ($^1J_{WC}$ = 53 Hz, MeC*C*Me), 212.3 ($^1J_{WC}$ = 14 Hz, MeC*C*Me), 177.2 (d of quintets, $^1J_{HC}$ = 173 Hz, $^2J_{HC}$ = $^3J_{HC}$ = 7.5 Hz, NH=*C*HMe), 153.8, 152.3, 151.0, 147.6, 147.5, 146.2 (Tp′ *C*CH$_3$), 109.3, 109.2, 108.1 (Tp′ *C*H), 25.3 (q of d of d, $^1J_{HC}$ = 129 Hz, $^2J_{HC}$ = 10 Hz, $^3J_{HC}$ = 7 Hz, NH=CH*C*H$_3$), 22.4 (q, $^1J_{HC}$ = 132 Hz, CH$_3$C$_2$*C*H$_3$), 20.8 (q, $^1J_{HC}$ = 131 Hz, *C*H$_3$C$_2$CH$_3$), 16.2, 15.8, 15.1, 13.2, 13.1, 13.0 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{22}$H$_{33}$N$_7$OB$_2$F$_4$: C, 38.12; H, 4.77; N, 14.15. Found: C, 38.15; H, 4.80; N, 14.06.

Tp′(CO)(PhC$_2$Me)W[NH=C(CN)CH$_3$][BF$_4$] (6): green, 90%. This compound was prepared by acidification of 3 using reaction conditions described above for 4. IR (KBr, cm^{-1}): ν_{CO} = 1933. ^{1}H NMR (CD$_2$Cl$_2$, δ): 12.12 (broad, 1 H, N*H*), 7.32, 6.92 (m, C$_6H_5$), 6.04, 5.90, 5.80 (Tp′ C*H*), 3.87 (PhC$_2$C*H*$_3$), 2.66 [N-H=C(CN)C*H*$_3$], 2.57, 2.51, 2.47, 2.43, 1.28, 1.20 (Tp′ CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 224.0 ($^1J_{WC}$ = 142 Hz, *C*O), 216.1 ($^1J_{WC}$ = 52 Hz, MeC*C*Ph), 217.3 ($^1J_{WC}$ = 15 Hz, $^2J_{HC}$ = 7.2 Hz, MeC*C*Ph), 154.4 [NH=*C*(CN)Me], 154.3, 153.2, 150.5, 148.2, 147.7, 146.8 (Tp′ *C*CH$_3$), 136.8, 130.9, 130.1, 129.2 (Ph), 111.1 [d of q, $^3J_{HC}$ = 17 Hz, $^3J_{HC}$ = 5 Hz, NH=C(*C*N)CH$_3$], 109.0, 108.6, 108.1 (Tp′ *C*H), 28.2 [q of d, $^1J_{HC}$ = 132 Hz, $^3J_{HC}$ = 6 Hz, NH=C(CN)*C*H$_3$], 23.1 (q, $^1J_{HC}$ = 130 Hz, PhC$_2$*C*H$_3$), 15.8, 14.1, 13.0, 12.9, 12.8 (Tp′ C*C*H$_3$). Anal. Calcd for WC$_{28}$H$_{34}$N$_8$OB$_2$F$_4$: C, 43.10; H, 4.36; N, 14.37. Found: C, 43.03; H, 4.46; N, 14.36.

Tp′(CO)(PhC$_2$Me)W(−NHCH$_2$CH$_3$) (7). A stoichiometric amount of LiEt$_3$BH (1.33 mL) was dripped slowly into a cold THF (−78 °C) solution of [Tp′(CO)(PhC$_2$Me)W(NH=CHCH$_3$)][BF$_4$] (1.00 g, 1.33 mmol), resulting in an immediate color change to red-brown. The solution was warmed to room temperature and stirred for an additional 30 min. The solvent was removed, and the solid residue was chromatographed on alumina with toluene as the eluent. A red-orange band was collected, and toluene was removed. The solid formed was recrystallized from CH$_2$Cl$_2$/hexane to yield red-orange crystals (0.66 g, 75%). IR (KBr, cm^{-1}): ν_{CO} = 1854. ^{1}H NMR (CD$_2$Cl$_2$, δ): major isomer (80%), 7.11, 6.35 (m, C$_6H_5$), 6.86 (m, N*H*CH$_2$Me), 5.90, 5.87, 5.62 (Tp′ C*H*), 4.20 (m, 2 H, NHC*H*$_2$Me), 3.24 (PhC$_2$C*H*$_3$), 2.81, 2.57, 2.44, 2.39, 1.64, 1.61 (Tp′ CC*H*$_3$), 0.73 (t, $^3J_{HH}$ = 7.2 Hz, NHCH$_2$C*H*$_3$); significant minor isomer signals (20%), 7.05, 6.45 (m, C$_6H_5$), 6.60 (m, N*H*CH$_2$Me), 5.94, 5.79, 5.65 (Tp′ C*H*), 3.20 (PhC$_2$C*H*$_3$), 2.74, 2.54, 2.45, 2.41, 1.65 (Tp′ CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): major isomer only, 238.7 ($^1J_{WC}$ = 168 Hz, *C*O), 169.2 ($^1J_{WC}$ = 47 Hz, MeC*C*Ph), 167.1 (q, $^2J_{HC}$ = 7 Hz, MeC*C*Ph), 154.1, 152.0, 151.1, 145.0, 144.9, 144.8 (Tp′ *C*CH$_3$), 138.4, 129.0, 128.6, 126.8 (Ph), 108.8, 107.7, 106.8 (Tp′ *C*H), 60.7 (t of q, $^1J_{HC}$ = 133 Hz, $^2J_{HC}$ = 4 Hz, NH*C*H$_2$Me), 19.8, 18.8, 16.3, 16.1, 15.1, 14.8, 13.4, 13.3 (Tp′ C*C*H$_3$, PhC$_2$*C*H$_3$, and NHCH$_2$*C*H$_3$). Anal. Calcd for WC$_{27}$H$_{36}$N$_7$OB: C, 48.46; H, 5.38; N, 14.66. Found: C, 48.87; H, 5.65; N, 14.14.

Tp′(CO)(RC$_2$Me)W[-NHCH(CN)CH$_3$] (R = Ph, Me). In a representative synthesis, 1 equiv of KCN (0.043 g, 0.66 mmol)

Table I. Selected IR and NMR Data for Tp'(CO)(RC_2Me)W(N=$CHCH_3$)

R	IR ν_{CO}, cm^{-1}	^1H NMR, ppm[a]		^{13}C NMR, ppm[a]		
		N=C*H*	CH_3	N=CHCH_3	C≡C	CO
Ph (1; two isomers (80:20))	1885	6.26 (q) $^3J_{HH}$ = 6	1.78 (d) $^3J_{HH}$ = 6	144.6 (d of q) $^1J_{HC}$ = 167 $^2J_{HC}$ = 8	159.7 (≡*C*Ph) 158.7 (≡*C*Me)	232 $^1J_{WC}$ = 158
Me (2; two isomers (70:30))	1867	6.13 (q) $^3J_{HH}$ = 5.2	1.73 (d) $^3J_{HH}$ = 5.2	144.2 (d of q) $^1J_{HC}$ = 168 $^2J_{HC}$ = 7	157.2 (Me*C*$_2$Me)	233 $^1J_{WC}$ = 161

[a] *J* values are given in Hz.

was added to a cold MeOH (0 °C; 20 mL) solution of [Tp'(CO)(PhC_2Me)W(NH=$CHCH_3$)][BF_4] (0.5 g, 0.66 mmol), resulting in a color change from blue to wine red as a wine red powder precipitated. The solid was isolated by filtration after putting the solution in a freezer (−40 °C) for 10 h. The product was redissolved in CH_2Cl_2, passed through a plug of alumina, and recrystallized from CH_2Cl_2/hexane to yield wine red crystals (0.37 g, 80%).

Tp'(CO)(PhC_2Me)W[-NHCH(CN)CH_3] (8). IR (KBr, cm^{-1}): ν_{CO} = 1856. ^1H NMR (CD_2Cl_2, δ): 7.15, 6.41 (m, C_6H_5), 5.88, 5.84, 5.62 (Tp' C*H*), 5.49 [d, $^3J_{HH}$ = 10.4 Hz, N*H*CH(CN)Me], 5.11 [d of q, $^3J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 6.8 Hz, NHC*H*(CN)Me], 3.39 (PhC_2CH_3), 2.65, 2.54, 2.42, 2.35, 1.58, 1.57 (Tp' CCH_3), 1.33 [d, $^3J_{HH}$ = 6.8 Hz, NHCH(CN)CH_3]. ^{13}C NMR (CD_2Cl_2, δ): 236.2 ($^1J_{WC}$ = 162 Hz, *C*O), 178.6 ($^1J_{WC}$ = 49 Hz, MeC*C*Ph), 175.5 (q, $^1J_{WC}$ = 10 Hz, $^2J_{HC}$ = 7.4 Hz, MeC*C*Ph), 153.1, 151.8, 150.9, 145.0, 144.8, 144.7 (Tp' *C*CH$_3$), 137.7, 128.7, 128.2, 126.9 (Ph), 122.3 [NHCH(*C*N)CH$_3$], 108.6, 107.3, 106.6 (Tp' *C*H), 59.4 [d of q, $^1J_{HC}$ = 144 Hz, $^2J_{HC}$ = 4.2 Hz, NH*C*H(CN)Me], 25.0 [q of t, $^1J_{HC}$ = 129 Hz, $^2J_{HC}$ = $^3J_{HC}$ = 4.2 Hz, NHCH(CN)*C*H$_3$], 19.0 (q, $^1J_{HC}$ = 129 Hz, PhC_2CH_3), 15.7, 14.4, 12.9, 12.8, 12.7 (Tp' C*C*H$_3$). Anal. Calcd for $WC_{28}H_{35}N_8OB$: C, 48.44; H, 5.05; N, 16.14. Found: C, 48.71; H, 5.47; N, 15.84.

Tp'(CO)(MeC_2Me)W[NHCH(CN)CH_3] (9): orange; 80%. IR (KBr, cm^{-1}): ν_{CO} = 1852. ^1H NMR (CD_2Cl_2, δ): two isomers (55%/45%), 6.09, 5.86, 5.84, 5.59, 5.58 (Tp' C*H*), 5.60, 5.15 [d, $^3J_{HH}$ = 10.4 Hz, N*H*CH(CN)Me], 5.08 [m, NHC*H*(CN)Me], 3.15, 3.01, 2.79, 2.61 ($CH_3C_2CH_3$), 2.50, 2.37, 2.32, 2.31, 2.29, 2.20, 2.16, 1.61, 1.60 (Tp' CCH_3), 1.30, 0.91 [d, $^3J_{HH}$ = 7 Hz, NHCH(CN)CH_3]. ^{13}C NMR (CD_2Cl_2, δ): 237.6, 237.2 ($^1J_{WC}$ = 165 Hz, *C*O), 176.8, 173.7 ($^1J_{WC}$ = 53 Hz, MeC*C*Me), 168.1, 164.1 ($^1J_{WC}$ = 10 Hz, MeC*C*Me), 153.2, 153.0, 150.7, 150.5, 150.4, 150.3, 144.8, 144.7, 144.6, 144.2 (Tp' *C*CH$_3$), 124.8, 122.5 [NHCH(*C*N)Me], 108.2, 107.3, 107.2, 106.5, 106.4 (Tp' *C*H), 60.2, 59.1 [NH*C*H(CN)Me], 25.1, 23.4 [NHCH(CN)*C*H$_3$], 25.1, 23.4, 17.9, 16.0, 15.8, 15.7, 15.6, 15.5, 15.4, 15.3, 15.1, 12.9, 12.8, 12.7 (Tp' C*C*H$_3$ and *C*H$_3$C$_2$*C*H$_3$). Anal. Calcd for $WC_{23}H_{33}N_8OB$: C, 43.69; H, 5.22; N, 17.73. Found: C, 43.91; H, 5.34; N, 17.50.

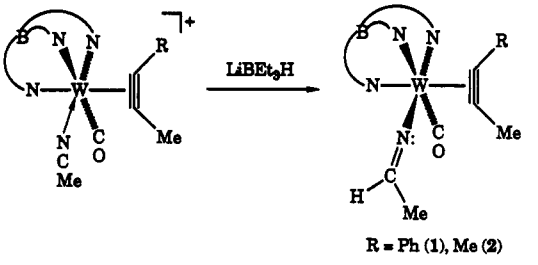
[Tp'(CO)(PhC_2Me)W($NH_2CH_2CH_3$)][BF_4] (10). In a representative synthesis, a red-orange solution of **7** (1.00 g, 1.5 mmol) in 80 mL of CH_2Cl_2/Et_2O (1:5) was cooled to −78 °C and a stoichiometric amount of HBF_4·Me_2O was added dropwise with stirring, resulting in a color change to blue. Addition of 20 mL of Et_2O and cooling in a freezer precipitated a blue powder, which was isolated by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo (1.02 g, 90%). Recrystallization from CH_2Cl_2/Et_2O yields deep blue crystals. IR (KBr, cm^{-1}): ν_{CO} = 1909. ^1H NMR (CD_2Cl_2, δ): 7.33, 6.76 (m, C_6H_5), 6.10, 5.98, 5.79 (Tp' C*H*), 3.78 (PhC_2CH_3), 4.10, 3.04 (m, NH_2CH$_2$Me), 2.84, 2.25 (m, NH$_2$CH_2Me), 2.74, 2.60, 2.53, 2.45, 1.51, 1.31 (Tp' CCH_3), 1.10 (t, $^3J_{HH}$ = 7.2 Hz, NH$_2$CH$_2$CH_3). ^{13}C NMR (CD_2Cl_2, δ): 230.8 ($^1J_{WC}$ = 148 Hz, *C*O), 214.5 (MeC*C*Ph), 213.0 (q, $^2J_{HC}$ = 8 Hz, MeC*C*Ph), 153.5, 152.3, 150.7, 147.8, 147.7, 146.2 (Tp' *C*CH$_3$), 136.4, 130.5, 129.5, 129.0 (Ph), 109.3, 109.1, 107.8 (Tp' *C*H), 46.4 (t, $^1J_{HC}$ = 140 Hz, NH$_2$*C*H$_2$Me), 22.9 (q, $^1J_{HC}$ = 135 Hz, PhC_2CH_3), 17.2, 16.0, 15.7, 13.8, 13.1, 12.9, 12.8 (Tp' C*C*H$_3$ and NH$_2$CH$_2$*C*H$_3$). Anal. Calcd for $WC_{27}H_{37}N_7OB_2F_4$: C, 42.83; H, 4.89; N, 12.95. Found: C, 43.05; H, 4.90; N, 12.86.

Tp'(CO)(PhC_2Me)W[NH_2CH(CN)CH_3][BF_4] (11): blue; 80%. This compound was prepared by acidification of **8** using reaction conditions described above for **10**. IR (KBr, cm^{-1}): ν_{CO} = 1915. ^1H NMR (CD_2Cl_2, δ): 7.33, 6.78 (m, C_6H_5), 6.12, 6.00, 5.78 (Tp' C*H*), 4.35 (m, NH_2CHCNMe), 3.90 (PhC_2CH_3), 3.78 [m, NH$_2$C*H*(CN)Me], 2.69, 2.59, 2.52, 2.45, 1.60, 1.32 (Tp' CCH_3), 1.61 [d, $^3J_{HH}$ = 6 Hz, NH$_2$CH(CN)CH_3]. ^{13}C NMR (CD_2Cl_2, δ): 229.8 ($^1J_{WC}$ = 148 Hz, *C*O), 218.4 ($^1J_{WC}$ = 52 Hz, MeC*C*Ph), 215.5 (q, $^1J_{WC}$ = 15 Hz, $^2J_{HC}$ = 7 Hz, MeC*C*Ph), 153.7, 152.5, 151.0, 148.1, 147.7, 146.3 (Tp' *C*CH$_3$), 136.7, 130.7, 129.6, 129.1 (Ph), 117.8 [NH$_2$CH(*C*N)CH$_3$], 109.5, 109.4, 108.0 (Tp' *C*H), 49.5 [d of q, $^1J_{HC}$ = 149 Hz, $^2J_{HC}$ = 4 Hz, NH$_2$*C*H(CN)Me], 23.9 (q, $^1J_{HC}$ = 130 Hz, PhC_2CH_3), 22.3 [q, $^1J_{HC}$ = 131 Hz, NH$_2$CH(CN)CH_3], 15.9, 14.2, 13.1, 13.0, 12.9 (Tp' C*C*H$_3$). Anal. Calcd for $WC_{28}H_{36}N_8OB_2F_4$: C, 43.00; H, 4.61; N, 14.33. Found: C, 43.05; H, 4.64; N, 14.29.

Tp'(CO)(MeC_2Me)W[NH_2CH(CN)CH_3][BF_4] (12): purple-blue; 80%. This compound was prepared by acidification of **9** using reaction conditions described above for **10**. IR (KBr, cm^{-1}): ν_{BH} = 2560; ν_{CO} = 1908; ν_{CN} = 1544; ν_{BF} = 1069. ^1H NMR (CD_2Cl_2, δ): 6.21, 6.06, 5.76 (Tp' C*H*), 4.28 [d, 2 H, $^3J_{HH}$ = 13.6 Hz, NH_2CH(CN)Me], 3.67 ($CH_3C_2CH_3$), 3.60 [m, NH$_2$C*H*(CN)Me], 3.30 ($CH_3C_2CH_3$), 2.71, 2.54, 2.42, 2.40, 2.17, 1.40 (Tp' CCH_3), 1.54 [d, $^3J_{HH}$ = 7.2 Hz, NH$_2$CH(CN)CH_3]. ^{13}C NMR (CD_2Cl_2, δ): 229.7 (*C*O), 223.2, 214.4 (MeC*C*Me), 153.8, 151.2, 151.0, 148.1, 147.4, 146.4 (Tp' *C*CH$_3$), 118.1 [NH$_2$CH(*C*N)Me], 109.3, 109.2, 108.0 (Tp' *C*H), 46.8 [d, $^1J_{HC}$ = 149 Hz, NH$_2$*C*H(CN)Me], 22.7, 21.0 ($CH_3C_2CH_3$), 21.4 [q, $^1J_{HC}$ = 130.8 Hz, NH$_2$CH(CN)*C*H$_3$], 16.0, 15.8, 14.2, 13.0, 12.9, 12.8 (Tp' C*C*H$_3$). Anal. Calcd for $WC_{23}H_{34}N_8OB_2F_4$: C, 38.36; H, 4.73; N, 15.57. Found: C, 38.31; H, 4.78; N, 15.61.

Results

Neutral Azavinylidene Complexes. Addition of a hydride reagent to cationic acetonitrile adducts, [Tp'(CO)(RC_2Me)W(NCMe)]$^+$, at low temperature in THF results in the formation of neutral azavinylidene complexes, Tp'(CO)(RC_2Me)W(N=CHMe) (**1** and **2**; eq 8).



(8)

Purification by chromatography on alumina followed by recrystallization from CH_2Cl_2/hexane yields stable orange crystals. A color change from blue to orange and a 55–65-cm^{-1} drop in the single ν_{CO} absorption are consistent with formation of a neutral product. Infrared spectra exhibit a carbonyl absorption for the phenylpropyne derivative **1** that is higher than that of the 2-butyne analogue **2**, consistent with the fact that 2-butyne is a better electron donor than phenylpropyne. Selected infrared and NMR data are presented in Table I.

NMR data indicated that the hydride had added to the acetonitrile carbon to form two isomeric products. The quartet evident at 6.26 ppm (1 H, $^3J_{HH}$ = 6 Hz) and the doublet at 1.78 ppm (3 H, $^3J_{HH}$ = 6 Hz) for the major isomer clearly point to a metal-substituted imine (also called an azavinylidene) product. ^{13}C NMR spectroscopy revealed the carbonyl carbon and azavinylidene carbon at 232 ppm ($^1J_{WC}$ = 158 Hz) and 145 ppm ($^1J_{HC}$ = 167 Hz, $^2J_{HC}$ = 8 Hz, $^1J_{WC}$ = 27 Hz), respectively. The alkyne

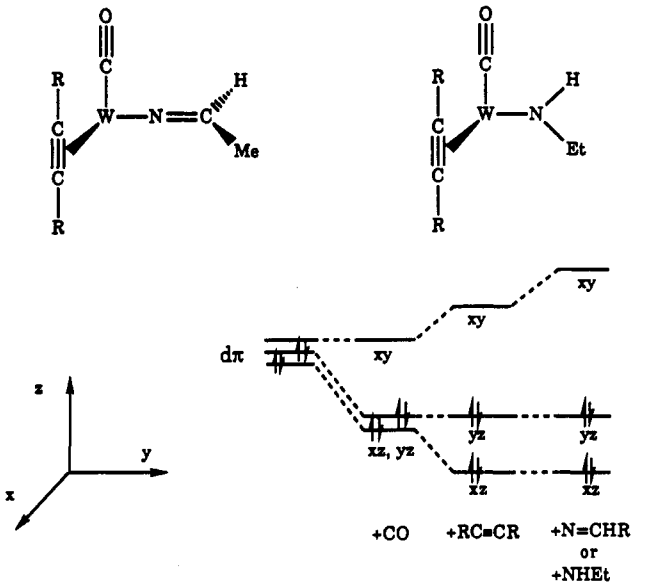


Figure 1. Qualitative molecular orbital scheme for the dπ–ligand interactions in Tp′(CO)(RC≡CR)W(–N=CHMe) and Tp′(CO)(RC≡CR)W(–NHEt).

carbons resonate at 160 and 159 ppm, indicating that a shift from four-electron to "three-electron" donation from the alkyne ligand accompanied formation of the product. In other words, the alkyne $\pi_\perp$ electron pair in the product competes with the lone pair on nitrogen for the single vacant metal dπ orbital in the W^{2+} d^4 complex.

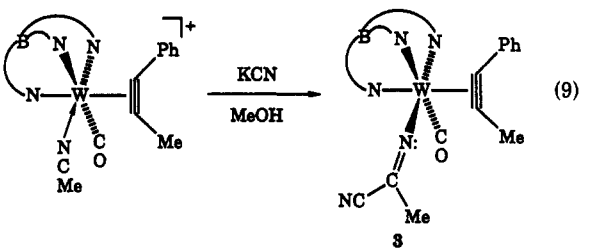
The geometric implications of donation from both the alkyne $\pi_\perp$ electron pair and the nitrogen lone pair into the lone vacant dπ orbital are straightforward (Figure 1). It is well established that the linearly ligating carbonyl ligand will mix CO π* with d_{xz} and d_{yz} to lower the energy of these metal-based orbitals. The d^4 configuration then fills these two dπ orbitals to leave d_{xy} vacant.[16] The alkyne invariably aligns itself parallel to the M–CO axis in d^4 $L_4M(CO)(RC{\equiv}CR)$ complexes in order to optimize both d_{xz} to $\pi_\parallel$* back-bonding and $\pi_\perp$ to d_{xy} donation. The azavinylidene will be oriented so that the lone pair on nitrogen can also overlap with d_{xy} to construct a three-center–four-electron bond involving d_{xy}, $\pi_\perp$, and p_x of nitrogen. The resultant antibonding combination is the vacant molecular orbital we designate simply as d_{xy}.

Azavinylidenes which have been structurally characterized have a linear M–N–C backbone.[17] We assume that donation from the nitrogen lone pair here is also sufficient to dictate a linear geometry for the ground state. Even if there is some bending at nitrogen, we anticipate that the linear geometry is easily accessible, and therefore, we interpret bonding and NMR properties in terms of a linear W=N=C linkage. In summary, we anticipate that the geometry of the metalloimine complex will place the plane of the N=CMeNu fragment perpendicular to the W—CO axis in order for the nitrogen lone pair to donate into the lone vacant dπ orbital.

Two isomers of the neutral azavinylidene complex **1** in a 4:1 ratio are evident by NMR spectroscopy. Isomers could potentially result from different alkyne orientations or restricted rotation around the tungsten–nitrogen bond. As discussed above, we are neglecting cis and trans metalloimine isomers since we believe they will rapidly interconvert at low temperatures via a linear intermediate even if present. The 2-butyne derivative (**2**) exhibits analogous spectral properties: distinct NMR singlets for each of the alkyne methyls were observed for **2**, indicating that alkyne rotation is slow on the NMR time scale. We again see two isomers just as observed for **1**, so we conclude that the two isomers are due to restricted rotation about the metal–nitrogen bond and not due to different up and down orientations of the alkyne ligand.

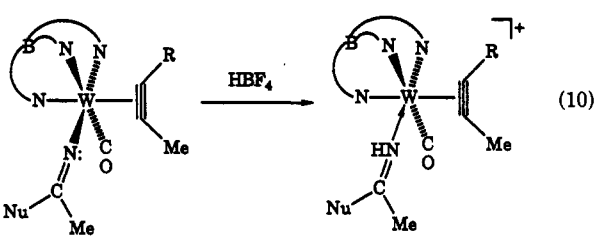
Note that the choice of hydride reagent is important; reaction of $[Tp'(CO)(RC_2Me)W(NCMe)]^+$ (R = Me, Ph) with $NaBH_4$ at room temperature results in substitution of acetonitrile by hydride.[18] This observation illustrates the delicate balance that exists in this and related systems. We have also observed nucleophilic attack on four-electron-donor alkynes to form η^2-vinyl and η^3-allyl ligands, as well as nucleophilic addition to a carbonyl ligand which produced a metal acyl fragment.[19]

When cyanide is used as a nucleophile, the reaction proceeds similarly to form **3** (eq 9). The product is isolated as two isomers in a 1:1 ratio. The cyanide-substituted azavinylidene complex exhibits a CO stretching frequency higher than that of **1**.



(9)

Cationic Imine Complexes. Low-temperature acidification of the neutral azavinylidene complexes (**1–3**) in CH_2Cl_2 results in protonation at nitrogen to form cationic imine complexes (**4–6**; eq 10). A color change from orange



(10)

to blue and an increase in ν_{CO} IR frequencies of approximately 40 cm^{-1} suggested that a cationic complex was formed. The product was isolated in 90% yield as blue powder after transferring the CH_2Cl_2 reaction solution to a large amount of Et_2O. Recrystallization from CH_2Cl_2/Et_2O yields ink blue crystals.

Selected infrared and NMR data are presented in Table II for **4** and **5**. The ^{13}C NMR spectrum indicated that formation of the imine returned the alkyne to a four-electron-donor role (alkyne carbons ~200 ppm). The

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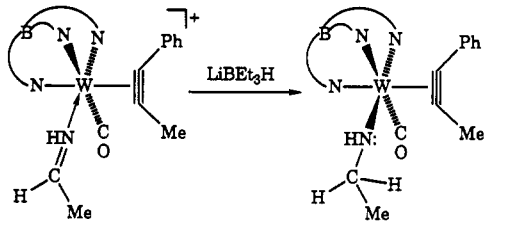
Table II. Selected IR and NMR Data for [Tp′(CO)(RC$_2$Me)W(NH=CHCH$_3$)][BF$_4$]

		^{1}H NMR, ppm[a]			^{13}C NMR, ppm[a]			
R	IR ν_{CO}, cm^{-1}	N*H*	C*H*	C*H*$_3$	NH=*C*H	*C*H$_3$	*C*≡*C*	*C*O
Ph (4)	1920	10.9 (d of q) $^3J_{HH}$ = 20 $^4J_{HH}$ = 1.4	6.4 (d of q) $^3J_{HH}$ = 20 $^3J_{HH}$ = 5.6	2.2 (d of d) $^3J_{HH}$ = 5.6 $^4J_{HH}$ = 1.4	176.9 (d of q) $^1J_{HC}$ = 171 $^2J_{HC}$ = 10	25 (q of t) $^1J_{HC}$ = 130 $^2H_{HC}$ = 15 $^3J_{HC}$ = 15	214.8 (≡*C*Ph) $^1J_{WC}$ = 54 214.3 (≡*C*Me) $^1J_{WC}$ = 15 $^2J_{HC}$ = 7	228.5 $^1J_{WC}$ = 146
Me (5)	1906	10.5 (d) $^3J_{HH}$ = 20.5	6.4 (d of q) $^3J_{HH}$ = 20.5 $^3J_{HH}$ = 5.2	2.2 (d) $^3J_{HH}$ = 5.2	177.2 (d of q) $^1J_{HC}$ = 173 $^2J_{HC}$ = 7.5	25 (q of d, d) $^1J_{HC}$ = 129 $^2J_{HC}$ = 10 $^3J_{HC}$ = 7	220 (≡*C*Me) $^1J_{WC}$ = 53 212.3 (≡*C*Me) $^1J_{WC}$ = 14	229.5 $^1J_{WC}$ = 147

[a] *J* values are given in Hz.

imine ligands were characterized by definitive coupling constants in both ^{1}H and ^{13}C NMR spectra. The vicinal coupling of 20 Hz across the C=N bond for **4** and **5** suggests that the hydrogens are trans to one another; thus, the trans tungsten and methyl substituents would define the *E* isomer. Rapid rotation about the W–N σ bond is possible, since there is no π component once the nitrogen lone pair has been protonated. Only one isomer is evident by NMR spectroscopy. Thus, the protonation reaction yields a specific geometry with respect to substituent location around the imine double bond. The presence of two NMR-distinguishable isomers in the azavinylidene reagents implies that the trans geometry of the cationic imine products is dictated by the metalloimine substituents rather than by the chiral metal center. Since the trans tungsten/methyl product is probably thermodynamically favored, a late transition state for the protonation step is consistent with formation of only the *E* imine complex. The 2-butyne derivative exhibits analogous spectral properties. Distinct NMR singlets for the two alkyne methyls were observed, indicating that alkyne rotation is slow on the NMR time scale. The cyanide-substituted complex **6** has a carbonyl stretching frequency higher than that of **4** or **5**, consistent with the electron-withdrawing nature of the CN group.

Neutral Amido Complexes. The coordinated imine complexes are susceptible to reduction. Addition of a hydride reagent to the imine carbon in [Tp′(CO)(PhC$_2$Me)W(NH=CHMe)]$^+$ (**4**) in cold THF generates the ethylamido complex **7** (eq 11). A color change from blue



(11)

4 **7**

to red-orange and a drop in IR CO stretching frequency from 1920 to 1856 cm^{-1} indicate that a neutral compound is formed. Purification by chromatography on alumina followed by recrystallization from CH_2Cl_2/hexane yields stable red-orange crystals. Amido complexes of the type Tp′(CO)$_2$W(NRR′)[20] also exhibit electron donation from the lone pair on the nitrogen, as evidenced by the low IR carbonyl stretching frequencies observed for these compounds.

The methylene protons of the amido ethyl group are diastereotopic since the metal is chiral, and assignment of

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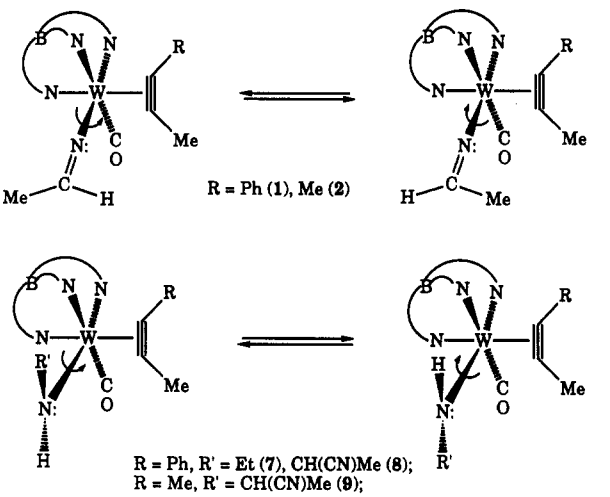
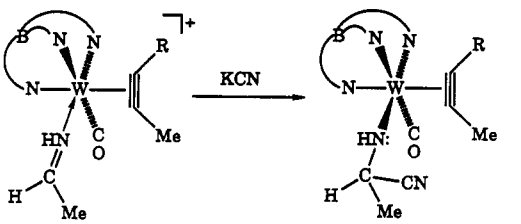
Scheme I



the ^{1}H NMR spectrum is straightforward. Chemical shifts of 169 and 167 ppm suggest that the alkyne ligand adopts approximately a three-electron-donor role. As in the neutral azavinylidene products, two isomers are evident in a 4:1 ratio in the ^{1}H and ^{13}C NMR spectra. These isomers are believed to result from restricted rotation around the metal–nitrogen bond (Scheme I). Again the nitrogen lone pair competes with the alkyne $\pi_\perp$ electrons for donation to the metal as in the neutral azavinylidene complex (Figure 1). At the amido stage we anticipate a geometry with the W–CO axis in the same plane as the NHR ligand will optimize metal–ligand π-bonding.

Addition of different nucleophiles at carbon forms chiral products with the stereochemistry determined by the metal fragment. Nitrile-substituted amido complexes were prepared from cyanide addition to the imine carbon in [Tp′(CO)(RC$_2$Me)W(NH=CHMe)]$^+$ (**4** and **5**) in methanol at 0 °C. The cyanide addition proceeds in high yield. A color change from blue to wine red followed by precipitation of the product indicated that a neutral complex had formed (**8** and **9**; eq 12). The product can be purified by passing the reaction solution through a plug of alumina followed by recrystallizing from CH_2Cl_2/hexane.



(12)

R = Ph (**4**), Me (**5**) R = Ph (**8**), Me (**9**)

Prominent IR and NMR data for the cyanoamido complexes are summarized in Table III. With regard to

Table III. Selected IR and NMR Data for Tp'(CO)(RC$_2$Me)W[NHCH(CN)CH$_3$]

		^{1}H NMR, ppm[a]			^{13}C NMR, ppm[a]				
R	IR ν_{CO}, cm^{-1}	N*H*	C*H*(CN)	C*H*$_3$	NHCH	*C*N	*C*H$_3$	*C*≡*C*	*C*O
Ph (**8**)	1856	5.49 (d) $^3J_{HH}$ = 10.4	5.11 (d of q) $^3J_{HH}$ = 10.4 $^3J_{HH}$ = 6.8	1.33 (d) $^3J_{HH}$ = 6.8	59.4 (d of q) $^1J_{HC}$ = 144 $^2J_{HC}$ = 4.2	122.3	25.0 (q) $^1J_{HC}$ = 129	178.6 (≡*C*Ph) $^1J_{WC}$ = 49 175.5 (MeC≡) $^1J_{WC}$ = 10 $^2J_{HC}$ = 7.4	236.2 $^1J_{WC}$ = 162
Me[b] (**9**)	1852	5.60 (d) 5.15 (d) $^3J_{HH}$ = 10.4	5.08 (m)	1.30 (d) 0.91 (d) $^3J_{HH}$ = 7.2	60.2 59.1	124.8 122.5	25.1 23.4	176.8 (≡*C*Me) 173.7 (≡*C*Me) $^1J_{WC}$ = 53 168.1 (MeC≡ 164.1 (MeC≡) $^1J_{WC}$ = 10	237.6 237.2 $^1J_{WC}$ = 165

[a] *J* values are given in Hz. [b] Two isomers are observed in a 45:55 ratio.

Table IV. Selected IR and NMR Data for {Tp'(CO)(RC$_2$Me)W[NH$_2$CH(CN)CH$_3$]}[BF$_4$]

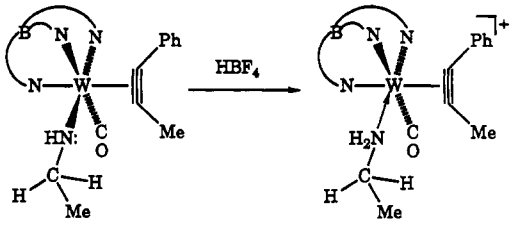
		^{1}H NMR, ppm[a]			^{13}C NMR, ppm[a]				
R	IR ν_{CO}, cm^{-1}	N*H*$_2$	C*H*(CN)	C*H*$_3$	NH$_2$*C*H	*C*N	*C*H$_3$	*C*≡*C*	*C*O
Ph (**11**)	1915	4.35 (m)	3.78 (m)	1.6 (d) $^3J_{HH}$ = 6	49.5 (d of q) $^1J_{HC}$ = 149 $^2J_{HC}$ = 4	117.8	22.3 (q) $^1J_{HC}$ = 131	218.4 (≡*C*Ph) $^1J_{WC}$ = 52 215.5 (≡*C*Me) $^1J_{WC}$ = 15 $^2J_{HC}$ = 7	229.8 $^1J_{WC}$ = 148
Me (**12**)	1908	4.28 (d) $^3J_{HH}$ = 13.6	3.60 (m)	1.54 (d) $^3J_{HH}$ = 7.2	46.8 (q) $^1J_{HC}$ = 149	118.1	21.4 $^1J_{HC}$ = 130.8	223.2 (≡*C*Me) 214.4 (≡*C*Me)	229.7

[a] *J* values are given in Hz.

diastereoselectivity, two isomers are evident in the ^{1}H and ^{13}C NMR spectra of Tp'(CO)(MeC$_2$Me)W[NHCH(CN)Me] in a 45:55 ratio. We believe the crucial cyanide addition is highly stereoselective. Recall that two isomers are also observed in the ethylamido analogue with no chiral carbon; presumably amido metal–ligand π bonding restricts rotation and accounts for the two isomers observed here.

Attempts to generate complex **8** through reaction of the cyanide-substituted imine complex **6** with a hydride reagent failed; instead, the neutral azavinylidene complex **3** is isolated. Therefore, deprotonation of the N–H group is favored in this case over nucleophilic attack at carbon due to the electron-withdrawing character of the cyano group.

Cationic Amine Complexes. Reaction of neutral amido complexes with HBF$_4$ at low temperature in a solvent mixture of CH$_2$Cl$_2$/Et$_2$O (1:5) generates cationic amine complexes **10** (eq 13). A color change from orange to blue

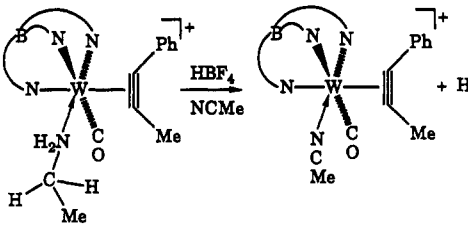


7 **10** (13)

and a shift in IR CO stretching frequency indicated that a cationic compound was formed. The product falls out of solution and is isolated as a blue powder which can be recrystallized from CH$_2$Cl$_2$/Et$_2$O to give deep blue crystals in high yield.

Selected IR and NMR data are presented in Table IV. Infrared spectra exhibit one carbonyl absorption at 1909 cm^{-1}. The ^{1}H NMR properties of the ethylamine ligand are very similar to those of the ethylamine ligand in [(triars)HRu(NH$_2$CH$_2$Me)$_2$]$^+$.[11] The diastereotopic protons attached to nitrogen in **10** appear at 4.10 and 3.04 ppm as multiplets. The methylene protons of the ethylamine ligand are also diastereotopic and appear at 2.84 and 2.25 ppm as multiplets. The acetylenic carbons resonate at 214.5 ppm (≡*C*Ph) and 213 ppm ($^2J_{HC}$ = 8 Hz, ≡*C*Me), suggesting that the alkyne ligand has returned to a four-electron-donor role. The lone carbonyl carbon resonates at 231 ppm with a one-bond W–C coupling constant of 148 Hz.

Protonation of the nitrile-substituted amido complexes cleanly generates the corresponding amine complexes. Only one diastereomer is evident by proton NMR spectroscopy, confirming that the cyanide addition reaction is highly diastereoselective. As with the simple ethylamine ligand, excess acid in acetonitrile regenerates the cationic [Tp'(CO)(PhC$_2$Me)W(NCMe)]$^+$ reagent (eq 14). Gladysz



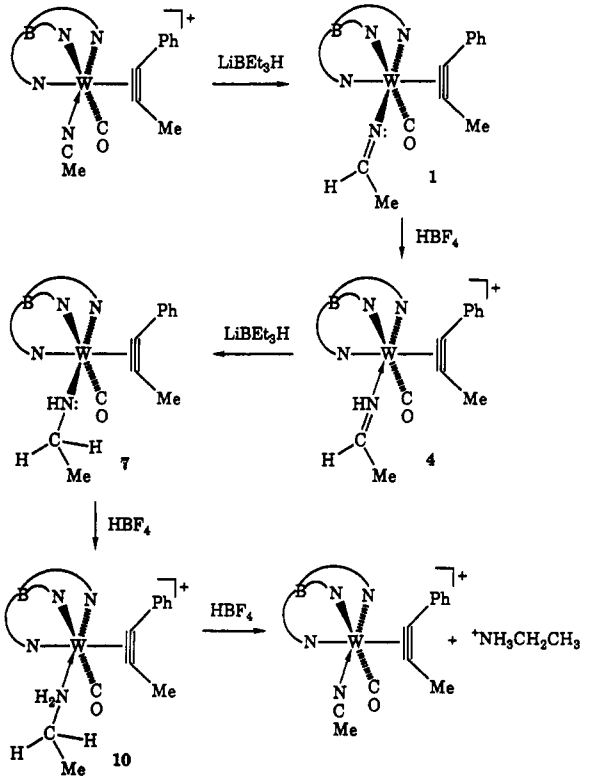
10 (14)

and co-workers have shown that facile substitution of the amine ligand in (π-Cp)Re(NO)(PPh$_3$)(NR$_3$)$^+$ complexes occurs with retention of configuration at rhenium.[5e]

Discussion

These reactions take advantage of nitrogen's ability to house a lone pair, stabilized by π-donation to the metal, or to accommodate a formal positive charge. Here nitrogen donates two electrons from :N≡CMe, :NH=CHMe, and :NH$_2$CH$_2$Me, and four electrons, both σ and π, from $^-$::N=CHMe and $^-$::NHCH$_2$Me. The electronic flexibility of the alkyne as an electron donor from $\pi_\perp$ and as an electron acceptor into $\pi_\parallel$* is crucial during the reduction sequence. The ability of the heteroatom to successfully house a lone pair or bind a proton requires a flexible metal dπ acceptor orbital. The tungsten–alkyne unit provides

Scheme II



Scheme III

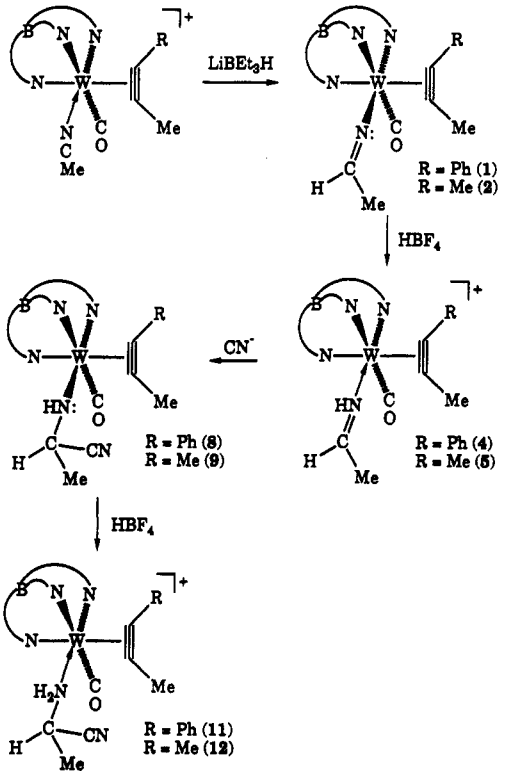


Table V.

complex	color	ν_{CO}, cm^{-1}	alkyne ^{13}C NMR, ppm
[Tp′(CO)(PhC≡CMe)W←N≡CMe][BF_4]	blue	1940	215, 213
Tp′(CO)(PhC≡CMe)W—N̈=CHMe (1)	orange	1885	160, 159
[Tp′(CO)(PhC≡CMe)W←NH=CHMe][BF_4] (4)	blue	1920	215, 214
Tp′(CO)(PhC≡CMe)W—N̈HCH_2Me) (7)	orange	1854	169, 167
[Tp′(CO)(PhC≡CMe)W←NH_2CH_2Me][BF_4] (10)	blue	1909	215, 213

the necessary electronic flexibility to keep the lone vacant metal dπ orbital satisfied with only alkyne $\pi_\perp$ donation in the protonated complexes, while the nitrogen lone pair competes with the alkyne $\pi_\perp$ donation in a three-center–four-electron bond in the neutral complexes.

Isolation of each of the intermediate metal complexes along this reaction pathway from MeCN to $MeCH_2NH_2$ (Scheme II) is promising for further synthetic studies. Complete reduction of nitriles to amines is easily accomplished by standard methods.[8,21] Our organometallic system offers two major advantages: control of stereochemistry and the ability to stop at the imine stage. Free imines are subject to isomerization to enamines or undergo oligomer formation, but the imine ligand here shows no signs of decomposition over time. Reduction of NCMe to an amine results in a net addition of electron density, as is evident by the decreasing frequency of the IR CO absorption of the cationic acetonitrile, imine, and amine complexes (Table V).

It is useful to contrast the nitrile triple bond, which undergoes stepwise reduction here, with the acetylide triple bond in Fp′—C≡CH, which undergoes stepwise reduction to form Fp′—CH_2CMe_3. The Fp′—C≡CH reaction sequence reflects the nucleophilicity of C_α and the electrophilicity of C_β in σ-bound unsaturated carbon ligands,[22] in accord with the ability of the metal to house lone pairs or form π bonds while adhering to the 18-electron rule.[23] The reactivity pattern in the acetonitrile reduction is reversed relative to the sites for electrophilic and nucleophilic additions, as expected, since it is the nitrogen that alternates between accommodating a lone pair and forming a covalent bond.

Summary

Sequential nucleophilic and electrophilic addition reactions of Tp′(CO)(RC_2Me)W(MeCN)$^+$ (R = Me, Ph) result in stepwise reduction of coordinated acetonitrile. Metal coordination activates the nitriles to add a nucleophile at the α-carbon. The resultant metalloimine is subject to protonation at nitrogen. The alkyne ligands, which serve as flexible electron donors, play an important role in isolation and characterization of the intermediate azavinylidene, imine, amido, and amine complexes. The lone-pair electrons on nitrogen compete with the $\pi_\perp$ electrons of the alkyne to donate to the vacant metal dπ orbital at the neutral azavinylidene and amido stages. This competitive donation results in a "three-electron-donor" role for the alkyne ligand, and two isomers result from restricted rotation around the metal–nitrogen multiple bond. Addition of the second nucleophile, at the imine complex stage, is highly stereoselective, as the nucleophile attacks from only one face of the imine ligand. Acidification of the amine ligands in acetonitrile frees the ammonium salt and regenerates the acetonitrile adducts. This system offers the potential to produce chiral amines from nitriles while retaining the integrity of the metal fragment

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(Scheme III). The yield for each of the reactions is high. Since one can regenerate the acetonitrile starting material, it may be possible to develop a system which will produce chiral amines from nitriles utilizing this metal fragment. Use of the $[Tp'(CO)(RC_2Me)W]^+$ moiety as an electronically flexible Lewis acid with a high degree of stereocontrol appears promising for further research.

Acknowledgment. We thank the National Science Foundation for support of this research. Helpful discussions with Professor M. S. Brookhart are gratefully acknowledged.

Four-Legged Piano Stool Molybdenum(II) Compounds without Carbonyl Ligands. 1. Synthesis, Properties, and Chloride Substitution Reactions of $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H, Me) and X-ray Crystal Structure of $[CpMoCl(PMe_3)_3]^+PF_6^-$

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Received September 19, 1991

The synthesis, solution structure, and redox properties of a series of cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) molybdenum-trimethylphosphine complexes is reported. $(\eta^5\text{-}C_5R_5)MoCl(PMe_3)_3$ (R = H (1), Me (1*)) compounds are prepared by sodium amalgam reduction of $CpMoCl_2$ or Cp^*MoCl_4, respectively, in the presence of PMe_3 and under an argon atmosphere. 1 is reversibly oxidized at $E_{1/2} = -1.46$ V with respect to $Cp_2Fe^{0/+}$. $[1]^+$ has been isolated as the PF_6^- salt and crystallographically characterized. Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 11.008$ (4) Å, $b = 15.195$ (4) Å, $c = 13.843$ Å, $V = 2315.7$ (14) Å^3, $Z = 4$, $R = 0.0884$, and $R_w = 0.0876$. Interaction between $CpMoCl_4$ and Zn, followed by addition of PMe_3, produces a compound of formula $[CpMoCl(PMe_3)_3]\cdot ZnCl_3$ (2), which displays EPR properties identical with those of $[1]^+$. Treatment of 1 with either $LiEt_3BH$ or K in heptane affords pure $CpMoH(PMe_3)_3$ (3), whereas 1* and $LiEt_3BH$ give a mixture of $Cp^*MoH(PMe_3)_3$ (3*) and $Cp^*MoH_3(PMe_3)_2$ (4*). Alkylation with MeLi affords the methyl derivatives, $(\eta^5\text{-}C_5R_5)MoCH_3(PMe_3)_3$ (R = H (5), Me (5*)), which are stable at room temperature for R = H and at $T = -20$ °C for R = Me. At higher temperatures, both compounds eliminate CH_4, but while 5 undergoes metalation of a PMe_3 ligand to form the compound $CpMo(\eta^2\text{-}CH_2PMe_2)(PMe_3)_2$ (6), compound 5* undergoes metalation at a Cp* methyl group, to form compound $(\sigma{:}\eta^5\text{-}CH_2C_5Me_4)Mo(PMe_3)_3$ (7*). Treatment of 1 with PhLi proceeds directly to compound 6 without detection of an intermediate containing the Mo–Ph linkage. The reaction of 1 and 1* with allylmagnesium bromide affords the allyl derivatives $(\eta^5\text{-}C_5R_5)Mo(\eta^3\text{-}C_3H_5)(PMe_3)_2$ (R = H (8), Me (8*)).

Introduction

We have recently been investigating the chemistry of paramagnetic molybdenum(III) monocyclopentadienyl derivatives,[1-3] which exhibit interesting electrochemical, EPR, structural, and bonding properties, as well as a peculiar halide exchange reactivity.[4-6] We have also attempted to replace the halide ligands with methyl groups, only to discover that the resulting $CpMo(CH_3)_2L_2$ (L = phosphine) derivatives are unstable and decompose with metal reduction to four-legged piano stool complexes of Mo(II). Of these products, $CpMo(o\text{-}C_6H_4PMe_2)(PMe_2Ph)_2$, which contains an ortho-metalated phenyl ring, has been structurally characterized.[7] The reaction of $CpMoCl_2(PMe_3)_2$ with MeLi, which ultimately gives $CpMo(CH_3)(PMe_3)_3$ in the presence of excess PMe_3, was proposed to occur through the intermediacy of $CpMoCl(PMe_3)_3$.[7] We were thus interested in synthesizing this Mo(II) material and verifying that it can be transformed into the methyl product. In this contribution, we report the synthesis of the $CpMoCl(PMe_3)_3$ compound (1) and its Cp* analogue (1*) and their transformation to the corresponding methyl derivatives, as well as a few other compounds obtained by exchanging the chloride ligand with other anionic ligands. In the following paper,[8] we report other derivatives obtained by replacing one or more of the PMe_3 ligands in 1 and 1* with other neutral ligands.

There is another interest in this cyclopentadienyl-containing Mo(II) chemistry, which is of a more structural nature. While comparing the structural features of 17-electron four-legged piano stool Mo(III) molecules synthesized in our laboratory with those of similar compounds, we discovered some general trends in the angle between bonds to the "basal" ligands and to the center of the ring (the θ angle), which depend on the metal electron count

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