Amine Addition to Coordinated Nitriles in Tungsten(II) Alkyne Complexes

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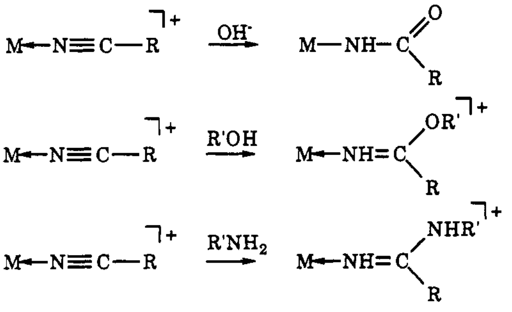
Reaction of [Tp′(CO)(PhC≡CR″)W(N≡CR)][BF$_4$] with NH$_2$R′ generates cationic amidine complexes of the type [Tp′(CO)(PhC≡CR″)W(NH=C(R)NHR′)][BF$_4$] (R = Me, R′ = H, R″ = Me (**1**), H (**2**); R = Me, R″ = Me, R′ = Ph (**3**), C(CH$_3$)$_3$ (**4**); R″ = H, R′ = Ph, R = Me (**5**), Ph (**6**)). These reactions reflect net addition of H—NHR′ across the nitrile triple bond. NMR spectra and a single crystal X-ray structure of **2** indicate that the alkyne ligand remains as a four-electron donor. Crystals of **2** belong to the monoclinic space group $P2_1/n$, $Z = 4$, with unit cell dimensions of $a = 12.919(3)$ Å, $b = 18.550(4)$ Å, $c = 15.989(4)$ Å, and $\beta = 99.08(2)°$. Refinement of 433 variables over 3974 reflections led to an R value of 3.4% with $R_w = 4.7\%$. Deprotonation of the α-nitrogen of [Tp′(CO)(PhC≡CH)W(NH=C(Ph)NHPh)][BF$_4$] (**6**) with ammonia results in the formation of a neutral azavinylidene alkyne complex, Tp′(CO)(PhC≡CH)W—N=C(Ph)NHPh (**9**). NMR spectra of **9** indicate that the alkyne ligand adopts a "three-electron donor" role. Reaction of [Tp′(CO)(PhC≡CH)W(N≡CR)][BF$_4$] with either gaseous or aqueous ammonia produces neutral metallocycle complexes of the type Tp′(CO)W=C(Ph)—C(H)=N—C(R)=N (R = Me (**7**), Ph (**8**)). An X-ray structure of **8** indicates that the six-membered metal—ligand ring is planar. The two metal—ligand bond distances in the ring are surprisingly short (W=C(Ph), 2.08(1) Å; W=N, 1.769(8) Å). The large W—N—C angle of 146.1(7)° in the ring is compatible with the two-bond tungsten—carbon coupling of 22 Hz here, which characterizes nearly linear W—N—C linkages. Complex **8** crystallized in the monoclinic space group $P2_1/c$ with unit cell dimensions of $a = 12.946(6)$ Å, $b = 14.259(5)$ Å, $c = 16.476(4)$ Å, and $\beta = 98.50(3)°$, with $Z = 4$. Refinement of 380 variables over 3293 reflections led to $R = 5.0\%$ and $R_w = 5.4\%$.

Introduction

Coordination of organic fragments or molecules to metals can activate sites which are usually inert. Alternatively, reactive functional groups can sometimes be stabilized by metal coordination. Metal nitrile complexes provide an example of activation as the electrophilicity of the α-carbon of nitriles is enhanced by coordination. We recently reported stepwise reduction of acetonitrile to chiral aminonitriles by using the chiral Tp′(CO)(RC$_2$Me)W (R = Me, Ph) moiety to control the stereochemistry of the addition reactions (Scheme I).[1] The stereoselectivity in this system is excellent, and the flexible electron donating ability of the alkyne ligand is important, as it allows isolation of the intermediate azavinylidene, imine, amido, and amine complexes. In stepwise reduction processes it is the nitrile nitrogen which is nucleophilic since it is the nitrogen that alternates between accommodating a lone pair and forming a covalent bond.[1] Reaction of metal nitriles with protic nucleophiles such as water, alcohols, and amines to generate the corresponding amides,[2] imidic esters,[2a–c,3] and amidines[2a–c,4] has been exploited (eqs 1–3). This one-step addition is attractive and contrasts with the stepwise nucleophile/electrophile sequence we have reported previously.[1]



(1)

(2)

(3)

In contrast the stepwise reduction of metal-bound acetylide reflects the nucleophilicity of C$_\beta$ and the electrophilicity of C$_\alpha$ in σ-bound unsaturated carbon ligands (Scheme II).[5] The difference here is that the metal houses electron lone pairs or forms π bonds to obey the 18-electron rule.

We have shown that alkyne ligands are subject to nucleophilic attack to form vinyl, allyl,[6] and vinyl amido ligands.[7] Terminal alkynes are particularly prone to

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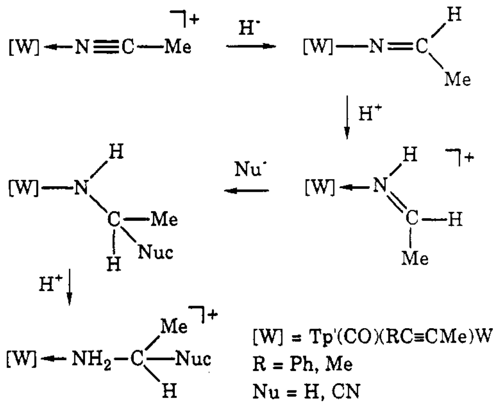
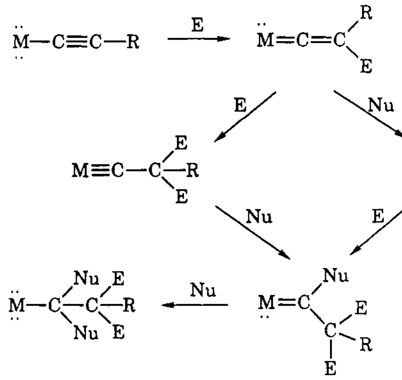
Scheme I



Scheme II



nucleophilic attack. This paper presents a study of reactions of alkyne nitrile complexes with amines. Amidine ligands and alkyne coupling products result, and we now report (1) formation of amidine complexes $[Tp'(CO)(PhC_2R)W{-}NH{=}C(NHR')R''][BF_4]$ (R = H, Me; R′ = H, Ph, t-Bu; R″ = Me, Ph) from the addition of H—NHR″ across the triple bond of the coordinated nitrile ligands, (2) a crystal structure of $[Tp'(CO)(PhC_2H)W{-}NH{=}C(NH_2)Me][BF_4]$, (3) formation of an alkyne metalloamidine complex from deprotonation of an amidine complex, (4) formation of a six-membered pseudoaromatic metallocycle, and (5) a crystal structure of Tp′(CO)W═C(Ph)—C(H)═N—C(Ph)═N.

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 hexanes were distilled from potassium benzophenone ketyl; acetonitrile was distilled from CaH_2; MeOH was dried over molecular sieves; other solvents were purged with N_2 prior to use. Reagents were used as obtained from commercial sources. Nitrile complexes, $[Tp'(CO)(PhC{\equiv}CR)W(N{\equiv}CR')][BF_4]$, were prepared according to literature methods.[8]

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 Oneida Research Services Inc., Whitesboro, NY.

Syntheses. $[Tp'(CO)(PhC_2Me)W{-}NH{=}C(NH_2)CH_3][BF_4]$ (1). Ammonia gas was bubbled through a blue slurry of $[Tp'(CO)(PhC_2Me)W(NCMe)][BF_4]$ (0.50 g, 0.66 mmol) in 15 mL of THF, resulting in a slight color change to a deeper blue and a shift in the CO stretching frequency to a lower energy (1906 cm^{-1}). Ammonia gas was removed after the CO absorption for the starting material (1940 cm^{-1}) had disappeared; precipitation of product was observed. Addition of 30 mL of Et_2O while the mixture was stirred caused more product to precipitate from the solution. The powder which precipitated was isolated by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo (0.45 g, 85%). Recrystallization from CH_2Cl_2/Et_2O yields ink-blue crystals of 1. IR (KBr, cm^{-1}): ν_{BH} = 2557; ν_{CO} = 1900; $\nu_{N{=}CN}$ = 1647, 1577; $\nu_{C{=}N(Tp')}$ = 1544; ν_{BF} = 1069. ^1H NMR (CD_2Cl_2, δ): 7.51, 6.55, 5.97 [broad, $NH{=}C(NH_2)Me$], 7.27, 6.64 (m, C_6H_5), 5.98, 5.96, 5.77 (Tp′CH), 3.76 (PhC_2CH_3), 2.59, 2.51, 2.41, 2.14, 1.44, 1.37 [$Tp'CCH_3$ and $NH{=}C(NH_2)CH_3$]. ^{13}C NMR (CD_2Cl_2, δ): 232.9 (CO), 210.6 (MeCCPh), 203.6 (MeCCPh), 170.2 [$NH{=}C(NH_2)Me$], 154.0, 152.4, 151.2, 147.1, 146.7, 146.0 ($Tp'CCH_3$), 136.1, 130.0, 129.4, 129.0 (Ph), 109.2, 108.4, 107.9 (Tp′CH), 22.4 [q, $^1J_{HC}$ = 129 Hz, $NH{=}C(NH_2)CH_3$], 22.2 (q, $^1J_{HC}$ = 130 Hz, PhC_2CH_3), 15.8, 15.5, 14.0, 13.0, 12.8 ($Tp'CCH_3$). Anal. Calcd for $[Tp'(CO)(PhC_2Me)W{-}NH{=}C(NH_2)CH_3][BF_4](CH_2Cl_2)$, $WC_{28}H_{38}N_8OB_2F_4Cl_2$: C, 39.33; H, 4.44; N, 13.10. Found: C, 38.84; H, 4.42; N, 12.65.

$[Tp'(CO)(PhC_2H)W{-}NH{=}C(NH_2)CH_3][BF_4]$ (2). This compound was prepared by the same procedure as described above for 1 but using ammonia gas and $[Tp'(CO)(PhC_2H)W(NCMe)][BF_4]$ as reagents (blue, 82%). IR (KBr, cm^{-1}): ν_{BH} = 2551; ν_{CO} = 1913; $\nu_{N{=}CN}$ = 1647, 1576; $\nu_{C{=}N(Tp')}$ = 1544; ν_{BF} = 1056. ^1H NMR (CD_2Cl_2, δ): 13.89 ($^2J_{WH}$ = 5 Hz, PhC_2H), 7.38, 6.73, 6.21 [broad, $NH{=}C(NH_2)Me$], 7.23, 6.67 (m, C_6H_5), 5.96, 5.95, 5.76 (Tp′CH), 2.58, 2.48, 2.44, 2.38, 2.16, 1.55, 1.38 [$Tp'CCH_3$ and $NH{=}C(NH_2)CH_3$]. ^{13}C NMR (CD_2Cl_2, δ): 232.1 ($^3J_{HC}$ = 6 Hz, CO), 214.7 (HCCPh), 194.5 (d, $^1J_{HC}$ = 215 Hz, HCCPh), 169.4 [$NH{=}C(NH_2)Me$], 153.8, 152.7, 149.8, 147.2, 146.8, 146.2 ($Tp'CCH_3$), 135.2, 130.7, 128.9 (Ph), 109.3, 108.4, 107.8 (Tp′CH), 22.4 [q, $^1J_{HC}$ = 130 Hz, $NH{=}C(NH_2)CH_3$], 15.8, 15.4, 14.2, 12.9, 12.8 ($Tp'CCH_3$). Anal. Calcd for $[Tp'(CO)(PhC_2H)W{-}NH{=}C(NH_2)CH_3][BF_4]\cdot 2CH_2Cl_2$, $WC_{28}H_{38}N_8OB_2F_4Cl_4$: C, 36.31; H, 4.11; N, 12.10. Found: C, 36.41; H, 4.00; N, 12.18.

$[Tp'(CO)(PhC_2Me)W{-}NH{=}C(NHPh)CH_3][BF_4]$ (3). Aniline (0.15 mL, 1.65 mmol) was added to a blue slurry of $[Tp'(CO)(PhC_2Me)W(NCMe)][BF_4]$ (0.5 g, 0.66 mmol) in 15 mL of THF, resulting in a slight color change to a deeper blue and a shift in the CO stretching frequency to a lower energy (1903 cm^{-1}). Addition of 30 mL of Et_2O while the mixture was stirred caused precipitation of product from the solution. The powder which precipitated was isolated by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo (0.47 g, 85%). Recrystallization from CH_2Cl_2/Et_2O yields blue crystals of **3**. IR (KBr, cm^{-1}): ν_{BH} = 2555, ν_{CO} = 1899, $\nu_{N{=}CN}$ = 1577, $\nu_{C{=}N(Tp')}$ = 1545, ν_{BF} = 1068. ^1H NMR (CD_2Cl_2, δ, two isomers are observed in an 85%:15% ratio), for the major isomer only: 9.07, 7.30 [broad, $NH{=}C(NHPh)CH_3$], 7.22, 7.21, 7.16, 6.79, 6.51 (m, $2C_6H_5$), 6.03, 5.75, 5.64 (Tp′CH), 3.69 (3.87 for the other isomer) (PhC_2CH_3), 2.66, 2.59, 2.50, 2.48, 2.42, 1.45, 0.82 [$Tp'CCH_3$ and $NH{=}C(NHPh)CH_3$]. ^{13}C NMR (CD_2Cl_2, δ, major isomer only): 232.6 ($^1J_{WC}$ = 148 Hz, CO), 208.8 ($^1J_{WC}$ = 51 Hz, MeCCPh), 205.3 ($^1J_{WC}$ = 15 Hz, $^2J_{HC}$ = 7 Hz, MeCCPh), 170.4 [$NH{=}C(NHPh)Me$], 153.2, 152.3, 151.4, 147.1, 146.5, 145.7 ($Tp'CCH_3$), 136.3, 134.3 ($2C_{ipso}$), 130.3, 129.8, 129.2, 128.9, 128.2, 125.0 (2Ph), 108.7, 108.4,

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107.9 (Tp′C*H*), 23.3 [NH=C(NHPh)CH$_3$], 22.2 (PhC$_2$CH$_3$), 16.0, 15.6, 13.8, 13.0, 12.9, 12.8 (Tp′CCH$_3$). Anal. Calcd for [Tp′(CO)(PhC$_2$Me)W=NH—C(NHPh)CH$_3$][BF$_4$], WC$_{33}$H$_{40}$N$_8$OB$_2$F$_4$: C, 46.84; H, 4.73; N, 13.25. Found: C, 46.82; H, 4.62; N, 13.01.

[Tp′(CO)(PhC$_2$Me)W—NH=C(NHC(CH$_3$)$_3$)CH$_3$][BF$_4$] (4). This compound was prepared by the same procedure as described above for 3 but with NH$_2$-*t*-Bu as the amine reagent (blue, 87%). IR (KBr, cm^{-1}): ν_{BH} = 2550, ν_{CO} = 1900, $\nu_{N=CN}$ = 1577, $\nu_{C=N(Tp')}$ = 1545, ν_{BF} = 1069. ^{1}H NMR (CDCl$_3$, δ, three isomers are observed in a 70%:15%:15% ratio), for the major isomer only: 7.41, 6.21 [broad, N*H*=C(N*H*C(CH$_3$)$_3$)CH$_3$], 7.24, 6.53 (m, C$_6$*H*$_5$), 5.92, 5.90, 5.71 (Tp′C*H*), 3.61 (3.78 and 3.72 for the other two isomers) (PhC$_2$C*H*$_3$), 2.61, 2.55, 2.48, 2.41, 2.32, 1.41, 1.29 [Tp′CC*H*$_3$ and NH=C(NHC(CH$_3$)$_3$)C*H*$_3$], 1.04 [NH=C(NHC(C*H*$_3$)$_3$)CH$_3$]. ^{13}C NMR (CDCl$_3$, δ, major isomer only): 231.4 ($^1J_{WC}$ = 151 Hz, *C*O), 207.7 ($^1J_{WC}$ = 52 Hz, Me*C*CPh), 204.4 ($^1J_{WC}$ = 14 Hz, $^2J_{HC}$ = 7 Hz, MeC*C*Ph), 170.9 [NH=*C*(NHC(CH$_3$)$_3$)Me], 153.2, 152.2, 150.8, 146.3, 145.7, 145.3 (Tp′*C*CH$_3$), 136.2 (*C*$_{ipso}$), 129.4, 128.7, 128.5 (Ph), 108.8, 108.2, 107.6 (Tp′*C*H), 52.3 (*C*(CH$_3$)$_3$), 28.9 (C(*C*H$_3$)$_3$), 25.0 [NH=C(NHC(CH$_3$)$_3$)*C*H$_3$], 21.7 (PhC$_2$*C*H$_3$), 15.7, 14.6, 12.9, 12.8 (Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)(PhC$_2$Me)W—NH=C(NHC(CH$_3$)$_3$)CH$_3$][BF$_4$], WC$_{31}$H$_{44}$N$_8$OB$_2$F$_4$: C, 45.07; H, 5.33; N, 13.57. Found: C, 44.64; H, 5.30; N, 13.46.

[Tp′(CO)(PhC$_2$H)W—NH=C(NHPh)CH$_3$][BF$_4$] (5). This compound was prepared by the procedure described above for 3 but with aniline and Tp′(CO)(PhC≡CH)W(N≡CMe)][BF$_4$] as the reagents (greenish-blue, 83%). IR (KBr, cm^{-1}): ν_{BH} = 2559, ν_{CO} = 1901, $\nu_{N=CN}$ = 1585, $\nu_{C=N(Tp')}$ = 1544, ν_{BF} = 1069. ^{1}H NMR (CDCl$_3$, δ, three isomers are observed in a 90%:5%:5% ratio), for the major isomer only: 13.61 (13.98 and 12.40 for the other two isomers) (PhC≡C*H*), 9.41, 7.51 [broad, N*H*=C(N*H*Ph)CH$_3$], 7.17, 7.09, 6.79, 6.53 (m, 2C$_6$*H*$_5$), 5.98, 5.70, 5.61 (Tp′C*H*), 2.70, 2.59, 2.49, 2.45, 2.39, 1.56, 0.74 [Tp′CC*H*$_3$ and NH=C(NHPh)C*H*$_3$]. ^{13}C NMR (CDCl$_3$, δ): 231.9 ($^1J_{WC}$ = 143 Hz, *C*O), 211.2 ($^1J_{WC}$ = 52 Hz, HC*C*Ph), 195.1 ($^1J_{WC}$ = 12 Hz, $^1J_{HC}$ = 215 Hz, H*C*CPh), 169.7 [NH=*C*(NHPh)Me], 152.6, 152.0, 149.4, 146.5, 146.0, 145.2 (Tp′*C*CH$_3$), 134.7, 133.8, 130.1, 130.0, 129.9, 128.5, 127.8, 124.5 (2*C*$_6$H$_5$), 108.5, 108.2, 107.6 (Tp′*C*H), 23.3 [NH=C(NHPh)*C*H$_3$], 15.7, 15.1, 13.5, 12.8, 12.7 (Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)(PhC$_2$H)W—NH=C(NHPh)CH$_3$][BF$_4$], WC$_{32}$H$_{38}$N$_8$OB$_2$F$_4$: C, 46.18; H, 4.57; N, 13.47. Found: C, 45.80; H, 4.46; N, 13.41.

[Tp′(CO)(PhC$_2$H)W—NH=C(NHPh)Ph][BF$_4$] (6). This compound was prepared by the procedure described above for 3 but with aniline and [Tp′(CO)(PhC≡CH)W(N≡CPh)][BF$_4$] as the reagents (blue, 84%). IR (KBr, cm^{-1}): ν_{BH} = 2558; ν_{CO} = 1911; $\nu_{N=CN}$ = 1589, 1526; $\nu_{C=N(Tp')}$ = 1545; ν_{BF} = 1069. ^{1}H NMR (CDCl$_3$, δ, three isomers are detected in a 70%:25%:5% ratio), for the two predominant isomers only: 14.41, 13.13 (13.04 for the third isomer) (PhC≡C*H*), 9.45, 8.43, 7.67, 7.66 [broad, N*H*=C(N*H*Ph)Ph], 7.40, 7.28, 7.17, 6.87, 6.60 (m, 3C$_6$*H*$_5$), 6.09, 6.01, 5.92, 5.76, 5.73, 5.68 (Tp′C*H*), 2.68, 2.62, 2.57, 2.53, 2.46, 2.43, 1.56, 1.48, 1.32, 1.16 (Tp′CC*H*$_3$). ^{13}C NMR (CDCl$_3$, δ), for the two predominant isomers only: 230.7, 228.6 (*C*O), 215.3, 209.3, 198.1, 196.0 (H*C*$_2$Ph), 170.7, 167.7 [NH=*C*(NHPh)Ph], 152.5, 152.2, 151.7, 149.5, 149.3, 146.4, 146.3, 145.9, 145.7, 145.1 (Tp′*C*CH$_3$), 137–124 (3*C*$_6$H$_5$), 109.1, 108.6, 108.5, 107.8, 107.6, 107.4 (Tp′*C*H), 15.6, 15.4, 15.3, 13.9, 13.7, 12.8, 12.7, 12.6, 12.5 (Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)(PhC$_2$H)W—NH=C(NHPh)Ph][BF$_4$], WC$_{37}$H$_{40}$N$_8$OB$_2$F$_4$: C, 49.69; H, 4.48; N, 12.53. Found: C, 48.89; H, 4.37; N, 12.30.

Tp′(CO)W=C(Ph)—C(H)=N—C(Me)=N (7). Aqueous ammonia (3 mL) was added to a blue slurry of [Tp′(CO)(PhC$_2$H)W(NH=C(NH$_2$)Me)][BF$_4$] (2) or to [Tp′(CO)(PhC$_2$H)W(N≡CMe)][BF$_4$] (0.50 g, 0.66 mmol) in 30 mL of THF, resulting in a color change to brown and a shift in the CO stretching frequency to 1927 cm^{-1}. The solvent was removed, and the solid residue was chromatographed on alumina with CH$_2$Cl$_2$/hexanes as the eluent. A brown band was collected, and the solvents were removed. The solid residue was recrystallized from CH$_2$Cl$_2$/hexanes to yield red-brown crystals of 7 (0.18 g, 40%). IR (KBr, cm^{-1}): ν_{BH} = 2552, ν_{CO} = 1924, ν_{CN} = 1544. ^{1}H NMR (CD$_2$Cl$_2$, δ): 8.03 [$^3J_{WH}$ = 14 Hz, W=C(Ph)—C(*H*)], 6.91, 6.48 (m, C$_6$*H*$_5$), 6.08, 5.70, 5.56 (3Tp′C*H*), 3.27 [N—C(*Me*)=N], 2.70, 2.50, 2.48, 2.43, 1.57, 0.81 (Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 227.4 ($^1J_{WC}$ = 175 Hz, CO), 221.6 [d, $^2J_{HC}$ = 3 Hz, $^1J_{WC}$ = 111 Hz, W=*C*(Ph)—C(H)], 157.6 [q, $^2J_{HC}$ = $^3J_{HC}$ = 6 Hz, W=C(*C*$_{ipso}$-Ph)—C(H)], 155.8, 153.1, 150.9, 147.1, 147.0, 145.2 (Tp′*C*CH$_3$), 151.6 [q of d, $^2J_{HC}$ = 7 Hz, $^3J_{HC}$ = 6 Hz, $^2J_{WC}$ = 23 Hz, N—*C*(Me)=N], 143.7 [d, $^1J_{HC}$ = 169 Hz, W=C(Ph)—*C*(H)], 128.2, 127.1, 125.0 (*Ph*), 107.7, 107.4, 106.9 (Tp′*C*H), 18.3 [N—C(*Me*)=N], 16.8, 16.6, 13.1, 12.7, 12.5, 11.3 (Tp′C*C*H$_3$).

Tp′(CO)W=C(Ph)—C(H)=N—C(Ph)=N (8). Ammonia gas was bubbled through a blue slurry of [Tp′(CO)(PhC$_2$H)W(N≡CPh)][BF$_4$] (1.00 g, 1.25 mmol) in 20 mL of THF, resulting in a color change to green and then brown and a slight shift in the CO stretching frequency to a lower energy (1930 cm^{-1}). Residual ammonia gas was removed after 10 min. The solvent was removed, and the solid residue was chromatographed on alumina with toluene as the eluent. A red-brown band was collected and toluene was removed. The oily residue was recrystallized from CH$_2$Cl$_2$/MeOH to yield red-brown crystals of 8 (0.55 g, 60%). IR (KBr, cm^{-1}): ν_{BH} = 2540, ν_{CO} = 1929, $\nu_{N=CN}$ = 1591, $\nu_{C=N(Tp')}$ = 1543. ^{1}H NMR (CD$_2$Cl$_2$, δ): 8.39 [$^3J_{WH}$ = 13.6 Hz, W=C(Ph)—C(*H*)], 8.41, 7.56, 7.22, 6.99, 6.55 (m, 2C$_6$*H*$_5$), 6.16, 5.72, 5.61 (3Tp′C*H*), 2.87, 2.55, 2.52, 2.48, 1.66, 0.81 (Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 230.9 [d, $^2J_{HC}$ = 3 Hz, $^1J_{WC}$ = 112 Hz, W=*C*(Ph)—C(H)], 222.4 ($^1J_{WC}$ = 175 Hz, *C*O), 157.5 [q, $^2J_{HC}$ = $^3J_{HC}$ = 6 Hz, W=C(*C*$_{ipso}$Ph)—C(H)], 155.8, 153.2, 151.5, 147.6, 147.1, 145.4 (Tp′*C*CH$_3$), 152.1 [d of t, $^3J_{HC}$ = 13 Hz, $^2J_{HC}$ = 4 Hz, $^2J_{WC}$ = 22 Hz, N—*C*(Ph)=N], 144.9 [d, $^1J_{HC}$ = 170 Hz, W=C(Ph)—*C*(H)], 133.6 [t, $^2J_{HC}$ = 8 Hz, N—C(*C*$_{ipso}$Ph)=N], 129.2, 128.4, 128.1, 127.8, 127.1, 125.4 (*Ph*), 107.8, 107.6, 107.2 (Tp′*C*H), 17.1, 16.8, 13.1, 12.7, 12.6, 11.3 (Tp′C*C*H$_3$). Anal. Calcd for Tp′(CO)W=C(Ph)—C(H)=N—C(Ph)=N·$^1/_2$CH$_2$Cl$_2$), WC$_{31.5}$H$_{34}$N$_8$OBCl: C, 49.08; H, 4.42; N, 14.54. Found: C, 49.15; H, 4.56; N, 14.49.

Tp′(CO)(PhC$_2$H)W—N=C(NHPh)Ph (9). Ammonia gas was bubbled through a blue slurry of 6 (1.00 g, 1.12 mmol) in 20 mL of THF, resulting in a color change to orange and a slight shift in the CO stretching frequency to a lower energy (1885 cm^{-1}). The solution was chromatographed on alumina with toluene/CH$_2$Cl$_2$ as the eluent. A band was collected, and solvents were removed. The oily residue was recrystallized from CH$_2$Cl$_2$/MeOH to yield brown crystals of 9 (0.54 g, 60%). IR (KBr, cm^{-1}): ν_{BH} = 2531; ν_{CO} = 1881; $\nu_{N=CN}$ = 1703, 1626, 1597; $\nu_{C=N(Tp')}$ = 1545. ^{1}H NMR (CD$_2$Cl$_2$, δ, three isomers are detected in a 70%:25%:5% ratio), for the predominant isomer only: 11.01 (11.24, 11.15 for the other two isomers) ($^2J_{WH}$ = 10 Hz, PhC≡C*H*), 7.3–6.2 (m, 3C$_6$*H*$_5$), 5.73, 5.67, 5.61 (3Tp′C*H*), 5.56 (N*H*Ph), 2.60, 2.45, 2.43, 2.10, 1.85, 1.40 (Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ), for the predominant isomer only: 234.8 ($^1J_{WC}$ = 155 Hz, $^3J_{HC}$ = 8 Hz, *C*O), 171.4 (d of t, $^3J_{HC}$ = 4 Hz, $^2J_{HC}$ = 9 Hz, $^1J_{WC}$ = 46 Hz, HC≡*C*Ph), 157.4 (d, $^1J_{HC}$ = 217 Hz, H*C*≡CPh) 153.7 [N=*C*(NHPh)Ph], 153.0, 152.9, 149.6, 144.5, 144.2, 143.9 (Tp′*C*CH$_3$), 142.7, 137.1, 136.0 (3*C*$_{ipso}$), 129–119 (3*Ph*), 107.4, 107.1, 106.7 (Tp′*C*H), 15.7, 15.6, 14.3, 12.9, 12.8, 12.7 (Tp′C*C*H$_3$). Anal. Calcd for Tp′(CO)(PhC$_2$H)W—N=C(NHPh)Ph(MeOH), WC$_{38}$H$_{43}$N$_8$O$_2$B: C, 54.43; H, 5.13; N, 13.37. Found: C, 54.01; H, 4.92; N, 13.51.

X-ray Diffraction Data Collection for [Tp′(CO)(PhC≡CH)WNH=C(NH$_2$)Me][BF$_4$] (2) and Tp′(CO)W=C(Ph)—C(H)=N—C(Ph)=N (8). A blue rectangular parallelepiped of 2 of dimensions 0.40 × 0.30 × 0.30 mm and a red-brown rectangular parallelepiped of 8 of dimensions 0.35 × 0.20 × 0.15 mm were selected. These crystals were mounted on glass wands and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer for 2 and on a Rigaku automated diffractometer for 8. A total of 25 centered reflections found in the region 30.0° < 2θ < 35.0° for 2 and in

Table I. Crystallographic Data Collection Parameters

	$2 \cdot 2CH_2Cl_2$	8
molecular formula	$WC_{28}H_{38}B_2F_4N_8OCl_4$	$WC_{31}H_{33}BN_8O$
fw	925.93	728.31
cryst dimens, mm	0.40 × 0.30 × 0.30	0.35 × 0.20 × 0.15
space group	$P2_1/n$	$P2_1/c$
cell params		
a, Å	12.919(3)	12.946(6)
b, Å	18.550(4)	14.259(5)
c, Å	15.989(4)	16.476(4)
β, deg	99.08(2)	98.50(3)
vol, Å^3	3784(1)	3008(2)
Z	4	4
density calcd, g/cm^3	1.625	1.608
Collection and Refinement Parameters		
temp, °C	−80	25
radiation (wavelength, Å)	Mo Kα (0.709 30)	Mo Kα (0.709 30)
monochromator	graphite	graphite
linear abs coeff, cm^{-1}	33.1	39.6
scan type	$\theta/2\theta$	$\theta/2\theta$
2θ limit	45°	50°
quadrant colled	$\pm h,+k,+l$	$\pm h,+k,+l$
total no. of reflns	4930	5307
no. of data with $I > 2.5\sigma(I)$	3974	3293
R, %	3.4	5.0
R_w, %	4.7	5.4
GOF	1.66	1.55
no. of params	433	380
largest param-shift	0.375	0.076

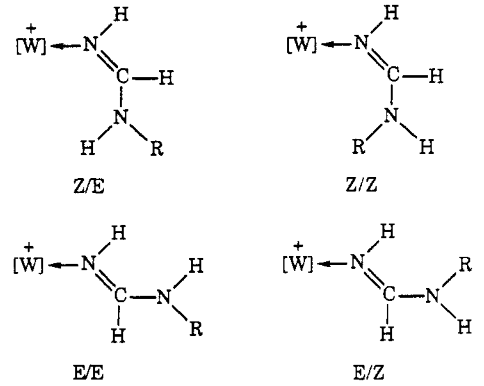
the region 26.0° < 2θ < 34.0° for 8 and refined by least-squares calculations indicated a monoclinic cell for each crystal. The cell parameters for 2 and 8 are listed in Table I.

Diffraction data for both crystals were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table I. Only data with $I > 2.5\sigma(I)$ were used in structure solution and refinement.[9] Absorption corrections were made using DIFABS for 2 and ψ scans for 8. The minimum and maximum transmission factors were 0.93 and 1.15 for 2 and 0.36 and 0.51 for 8. The crystals were checked for orientation every 200 reflections and were recentered if necessary.

Solution and Refinement of the Structures. Space group $P2_1/n$ was confirmed for 2 and $P2_1/c$ for 8. In each case the position of the tungsten 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. Data for 2 were collected at −80 °C because two molecules of methylene chloride found in each unit cell evaporated easily at room temperature and caused crystal collapse. The highest peaks in the final difference map were in the vicinity of the two solvent molecules. In particular C(61), C(13), and C(14) show quite high thermal parameters and are probably only partially occupied.

The non-hydrogen atoms, 48 for 2 and 42 for 8, were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. The final residuals[10] for 2 for 433 variables refined against 3974 data with $I > 2.5\sigma(I)$ were R = 3.4% and R_w = 4.7%.[11] The final difference Fourier map for 2 had no peak greater than 2.13 e/Å^3.[12] The final residuals[10] for 8 for 380 variables refined against 3293 data with $I > 2.5\sigma(I)$ were R = 5.0% and R_w = 5.4%.[11] The final difference Fourier map for 8 had no peak greater than 1.26 e/Å^3.[12]

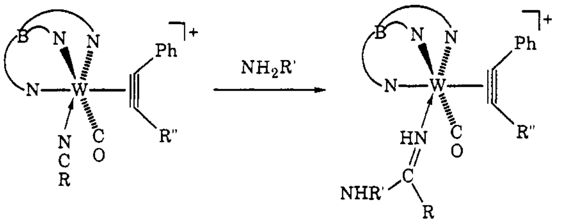
Scheme III



[W] = Tp'(CO)(RC≡CMe)W

Results and Discussion

Cationic Amidine Complexes. I. Synthesis. The cationic amidine complexes 1–6 were synthesized by reaction of the cationic nitrile complexes [Tp'(CO)(PhC$_2$R'')W(N≡CR)]$^+$ with NH$_2$R' reagents in THF (eq 4). A slight color change to a deeper blue and a shift in the carbonyl stretching frequency from about 1940 cm^{-1} to lower energies (1900–1913 cm^{-1}) were observed when NH$_2$R' was introduced to a THF slurry of the starting material. Crystalline products formed when Et$_2$O was added. Recrystallization from CH$_2$Cl$_2$/Et$_2$O produced blue crystals in 80–90% yields.



(4)

R = Me, R' = H, R'' = Me (**1**), H (**2**);
R = Me, R'' = Me, R' = Ph (**3**), C(Me)$_3$ (**4**);
R'' = H, R' = Ph, R = Me (**5**), Ph (**6**)

The net result of this reaction is addition of H—NHR across the nitrile triple bond. Similar nucleophilic reactions leading to the formation of amidines are known in other monomeric complexes.[4] The solid-state structure of 2 (vide infra) shows that trans H—NH$_2$ addition across the carbon—nitrogen triple bond has taken place. Note that protonation of the metalloimine fragment in Tp'(CO)(PhC≡CMe)W—N=CHMe at the nitrogen produced an imine complex with only the *E* isomer.[1] We hypothesized that the formation of the trans imine products was dictated by the metalloimine substituents rather than by the chiral metal center. Presumably protonation occurs in a late transition state which approaches the thermodynamically favored trans tungsten/methyl geometry.

Only one isomer was observed for 1 and 2, but two isomers were observed for 3 and 5, and three isomers were observed for 4 and 6. Eight potential isomers (2^3) reflect two possible alkyne orientations combined with restricted rotation about both carbon—nitrogen multiple bonds in the amidine ligand (Scheme III). The positive charge is highly delocalized over the N—C—N unit (Scheme IV).

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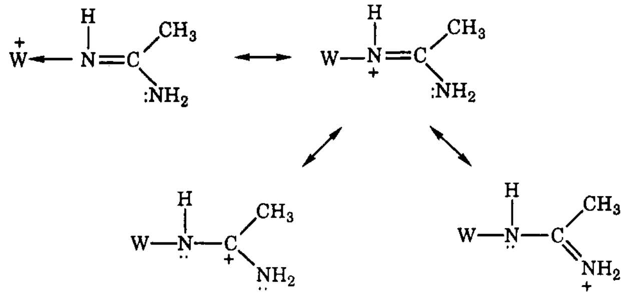
(9) Programs used during solution and refinement were from the NRCVAX structure determination package. Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Chem.* **1989**, *22*, 384.

(10) The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is based on counter statistics.

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

(12) 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 Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

Scheme IV



Isomerization based only on alkyne orientation has been observed for terminal acetylenes in Tp′(CO)(RC≡CH)WI and $[\mathrm{Tp'(CO)(RC{\equiv}CH)W(N{\equiv}CR)}]^+$, but not in $[\mathrm{Tp'W(CO)_2(RC{\equiv}CH)}]^+$.[8] Internal acetylene (PhC≡CMe) complexes of the type Tp′WL(CO)(PhC≡CMe) tend to favor a single alkyne orientation.[8,13] We have empirically observed that substituents on the alkyne ligand prefer to be close to the Tp′ ligand in the following order: Ph > H > Me. Given that only three isomers are observed for PhC≡CMe derivative **4**, we suggest that restricted rotation about both carbon—nitrogen bonds in the amidine ligand is responsible for the isomerization. Steric factors probably dictate the observed isomer ratios. Although the isomers do not interconvert on the NMR time scale we have been unable to separate and purify individual isomers.

II. Spectroscopic Properties. Complexes **1**–**6** all display similar IR properties with a slight variation in electron density at the metal center reflected in the range of metal carbonyl stretching frequencies (1899–1913 $\mathrm{cm^{-1}}$). A drop of 30–40 $\mathrm{cm^{-1}}$ in carbonyl stretching frequencies when the $\mathrm{NH_2R}$ addition products form is compatible with the net addition of a neutral nucleophile and suggests that the positive charge is delocalized between the two nitrogens and the carbon (Scheme IV). The IR carbonyl absorption in $\mathrm{Tp'(CO)(PhC_2Me)W[NH{=}C(NH_2)Me]^+}$ (1900 $\mathrm{cm^{-1}}$) is lower than that in $\mathrm{Tp'(CO)(PhC_2H)W[NH{=}C(NH_2)Me]^+}$ (1913 $\mathrm{cm^{-1}}$), consistent with the phenylpropyne being a better electron donor than phenylacetylene. A Tp′ B—H stretch at 2566 $\mathrm{cm^{-1}}$ is sufficiently high to be diagnostic for a cationic complex.[1,8,14] The B—F stretching frequency of the tetrahedral $\mathrm{BF_4^-}$ counterion appears around 1070 $\mathrm{cm^{-1}}$.

A chiral metal center and hence the absence of a mirror plane was indicated by the three inequivalent pyrazolyl rings evident in both ^{1}H and ^{13}C NMR spectra. The nitrogen-bound protons appear between 6 and 9.5 ppm as broad singlets. The terminal acetylene protons in complexes **2**, **5**, and **6** resonate far downfield between 12 and 14.5 ppm.

Three isomers were observed for PhC≡CH derivatives **5** and **6** with the acetylene proton resonating at 13.98, 13.61, and 12.40 ppm for **5** and 14.41, 13.13, and 13.04 ppm for **6**. Two are well downfield of the other one for **5** and one is well downfield of the other two for **6**, suggesting isomerization from different alkyne orientations. This suggests that the acetylene unit has the terminal acetylene proton distal to the Tp′ ligand for signals near 14 ppm since proximity to the pyrazole rings typically shifts ^{1}H signals to higher fields by about 1 ppm, say 12–13 ppm.[8,14] In the isomers observed for PhC≡CMe derivatives **3** and **4**, the chemical shift differences for the alkyne methyl ^{1}H signals are less than 1 ppm apart, in agreement with our previous observation that PhC≡CMe strongly prefers the orientation with the phenyl group close to the Tp′ ligand. The alkyne carbon signals are located from 194 to 215 ppm. The alkyne carbons which are close to Tp′ normally exhibit downfield chemical shifts and larger one-bond tungsten—carbon couplings (about 55 Hz) than the alkyne carbons which are away from Tp′, which have upfield chemical shifts and smaller $^1J_{\mathrm{WC}}$ couplings (about 15 Hz).[1,8,14] It is also interesting to note that the terminal alkyne carbons (~195 ppm) have a higher field chemical shift than the phenyl-substituted alkyne carbons (~210 ppm). The terminal acetylene carbons in **2** and **5** display a one-bond H—C coupling of 215 Hz. The chemical shifts of the acetylene proton in ^{1}H NMR (≥12 ppm) and the acetylene carbons in ^{13}C NMR (≥190 ppm) suggest that the alkynes remain as four-electron donors in these amidine complexes. The carbon of the amidine ligand resonates near 170 ppm in all of these complexes. The metal carbonyl carbon resonates at 228–233 ppm with a one-bond tungsten—carbon coupling of 143–151 Hz; a three-bond proton—carbon coupling of 6 Hz is evident to the acetylene proton for **2**.

III. Crystal Structure of $\mathrm{Tp'(CO)(PhC_2H)W[NH{=}C(NH_2)Me][BF_4]}$ (2). The coordination sphere of the tungsten(II) metal center can be described as roughly octahedral with the alkyne occupying a single coordination site. The Tp′ ligand occupies three facial coordination sites with each of the nitrogen donor atoms approximately trans to one of the remaining carbonyl, alkyne, or imine ligands. Atomic positional parameters are listed in Table II, and selected intramolecular bond distances and angles appear in Table III. An ORTEP drawing of the cation in $\mathrm{[Tp'(CO)(PhC_2H)W(NH{=}C(NH_2)Me)][BF_4]}$ is shown with the atomic numbering defined in Figure 1.

The salient geometrical features of this system agree with those observed for previous d^4 carbonyl alkyne monomers. (1) The alkyne is cis to the CO and parallel to the M—CO axis. This orientation optimizes both π-acid and π-donor interactions of the alkyne with the dπ orbitals on tungsten while the carbonyl can interact with both filled dπ orbitals. The alkyne lies between two pyrazole rings with the phenyl group proximal to the Tp′ ligand, apparently the preferred position. (2) The W—C alkyne bond distances of 2.040(7) and 2.011(8) Å are consistent with a four-electron donor alkyne description.[8,13,15] (3) The C≡C bond distance of 1.28(1) Å and the cis bent $\mathrm{C_{ipso}}$—C≡C angle of 138.2(7)° are typical of four-electron donor alkyne ligands.[8,13,15] (4) The planar imine ligand is located between the carbonyl and alkyne ligands with the methyl group up toward the Tp′ ligand and trans to tungsten and the $\mathrm{NH_2}$ group down and trans to the proton. The W—N bond distance is 2.105(6) Å which is compatible with a single bond; the W—N—C(11) angle is 135.1(5)°, reflecting sp^2 hybridization at the nitrogen. Bond distances for N(H)—C(11) and C(11)—$\mathrm{NH_2}$ are between C—N single bonds and double bonds at 1.314(9) and 1.31(1) Å, respectively, suggesting charge delocalization between the two nitrogens toward carbon. The angles around the C(11) carbon are 122.8(7)° [N(H)—C(11)—$\mathrm{NH_2}$],

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[13] Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.

[14] Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951.

[15] Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

Table II. Atomic Positional Parameters for $[Tp'W(CO)(PhC{\equiv}CH)W(NH{=}C(CH_3)NH_2)][BF_4]$ (2)

	x	y	z	B_{iso}, Å^2
W(1)	0.787697(23)	0.916312(15)	0.155599(17)	1.640(12)
C(1)	0.7861(6)	1.0169(4)	0.1895(5)	2.2(3)
O(1)	0.7863(4)	1.0777(3)	0.2087(3)	3.00(24)
C(2)	0.9343(6)	0.9522(4)	0.1947(5)	2.5(4)
C(3)	0.9419(6)	0.8882(4)	0.1658(4)	1.9(3)
C(4)	1.0251(6)	0.8381(4)	0.1499(5)	2.3(3)
C(5)	1.1243(6)	0.8465(4)	0.1955(5)	2.8(4)
C(6)	1.2028(7)	0.8016(5)	0.1789(6)	4.2(5)
C(7)	1.1859(7)	0.7493(6)	0.1179(6)	4.7(5)
C(8)	1.0862(8)	0.7408(5)	0.0731(6)	4.4(5)
C(9)	1.0048(6)	0.7845(5)	0.0896(5)	2.9(4)
N(10)	0.7444(5)	0.8781(3)	0.2692(4)	2.0(3)
C(11)	0.7652(6)	0.8972(4)	0.3492(5)	2.4(3)
N(12)	0.8310(6)	0.9486(4)	0.3763(4)	3.3(3)
C(13)	0.7127(8)	0.8589(5)	0.4138(5)	4.2(5)
B(1)	0.6363(7)	0.8440(5)	−0.0091(5)	2.2(4)
N(21)	0.6862(5)	0.7835(3)	0.0488(4)	2.2(3)
N(22)	0.7546(4)	0.8007(3)	0.1207(4)	1.90(25)
C(23)	0.7791(6)	0.7369(4)	0.1611(5)	2.7(4)
C(24)	0.7275(7)	0.6814(4)	0.1152(5)	3.0(4)
C(25)	0.6677(7)	0.7117(4)	0.0447(5)	3.0(4)
C(26)	0.8562(7)	0.7313(4)	0.2422(5)	3.3(4)
C(27)	0.5927(9)	0.6769(5)	−0.0255(6)	4.7(5)
N(31)	0.7214(5)	0.8920(3)	−0.0363(3)	1.82(24)
N(32)	0.7756(5)	0.9398(3)	0.0211(4)	1.88(25)
C(33)	0.8271(6)	0.9857(4)	−0.0226(5)	2.1(3)
C(34)	0.8086(6)	0.9660(4)	−0.1077(4)	2.4(3)
C(35)	0.7425(6)	0.9085(4)	−0.1146(5)	2.4(3)
C(36)	0.8891(6)	1.0474(4)	0.0168(5)	2.6(3)
C(37)	0.6970(7)	0.8654(5)	−0.1911(5)	3.5(4)
N(41)	0.5695(5)	0.8902(3)	0.0427(4)	2.1(3)
N(42)	0.6168(5)	0.9238(3)	0.1171(4)	2.0(3)
C(43)	0.5361(6)	0.9552(4)	0.1477(5)	2.5(4)
C(44)	0.4440(6)	0.9418(5)	0.0973(5)	3.0(4)
C(45)	0.4651(7)	0.9001(4)	0.0307(5)	3.0(4)
C(46)	0.5534(7)	0.9971(5)	0.2307(6)	3.7(4)
C(47)	0.3928(7)	0.8681(6)	−0.0413(6)	4.6(5)
C(51)	0.5067(9)	0.6954(5)	0.2491(7)	5.2(6)
Cl(1)	0.50486(18)	0.78174(12)	0.20546(16)	4.17(11)
Cl(2)	0.5065(3)	0.69586(17)	0.35650(20)	7.89(20)
B(2)	0.4003(9)	0.5480(6)	0.1180(6)	4.0(5)
F(1)	0.3564(5)	0.5232(5)	0.1846(4)	8.9(5)
F(2)	0.3732(5)	0.5044(3)	0.0484(3)	4.9(3)
F(3)	0.3644(6)	0.6170(3)	0.0947(4)	8.3(4)
F(4)	0.5066(4)	0.5507(3)	0.1421(3)	4.7(3)
C(61)	0.1465(13)	0.4422(12)	0.0555(11)	13.6(12)
Cl(3)	0.1083(4)	0.3708(3)	0.1084(3)	12.0(3)
Cl(4)	0.0772(5)	0.4382(3)	−0.0543(4)	13.5(4)

119.9(7)° [N(H)—C(11)—CH_3], and 117.3(7)° [NH_2—C(11)—CH_3], which add up to 360°, confirming the planarity of the imine ligand.

Neutral Metallocyclic-carbene-imine Complexes. I. Synthesis. Reaction of the imine complex, $[Tp'(CO)(PhC_2H)W(NH{=}C(NH_2)Me)]^+$ (2), with $NH_3(H_2O)$ or reaction of $[Tp'(CO)(PhC_2H)W(N{\equiv}CPh)]^+$ with NH_3 in THF generates neutral cyclic metallo—carbene—imine complexes 7 and 8, respectively (eqs 5 and 6). Purification by chromatography on alumina followed by recrystallization from CH_2Cl_2/hexanes yields brown crystals. Compound 8 is sufficiently stable to allow for accurate elemental analysis, but complex 7 is unstable. The intermediate on the way to 8, presumably $[Tp'(CO)(PhC_2H)W(NH{=}C(NH_2)Ph)]^+$, could not be isolated, which suggests that the NH_2 protons here are more acidic than those in 2. Phenyl is a better electron-withdrawing group than methyl and can stabilize the species generated by deprotonation.

Some sequence of deprotonation at NH_2, attack of a nitrogen lone pair to couple with the alkyne terminal site, and net H_2 loss would lead to formation of the observed products. Although net loss of H_2 is compatible with the formation of 8, we have not detected hydrogen. Indeed, any combination of redox events removing two electrons as well as two protons is a conceivable route from reagents to products. Another reaction corresponding to net hydrogen elimination without mechanistic implications results from the reaction of $Tp'W(CO)_2I$ with *n*-butylamine, which generates both amido and metalloimine complexes: W—N(H)CH_2R and W=N=C(H)R.[16] Reaction of a nitrile reagent, $Tp'W(CO)_3(N{\equiv}CMe)^+$, with *tert*-butylamine has generated an unusual amido species, $Tp'(CO)_2W\text{—}\overline{N(\text{—}C({=}CH_2)\text{—}N(t\text{-Bu})\text{—}C}(O))$, again consistent with a net loss of H_2.[17] The mechanism of these reactions is not clear.

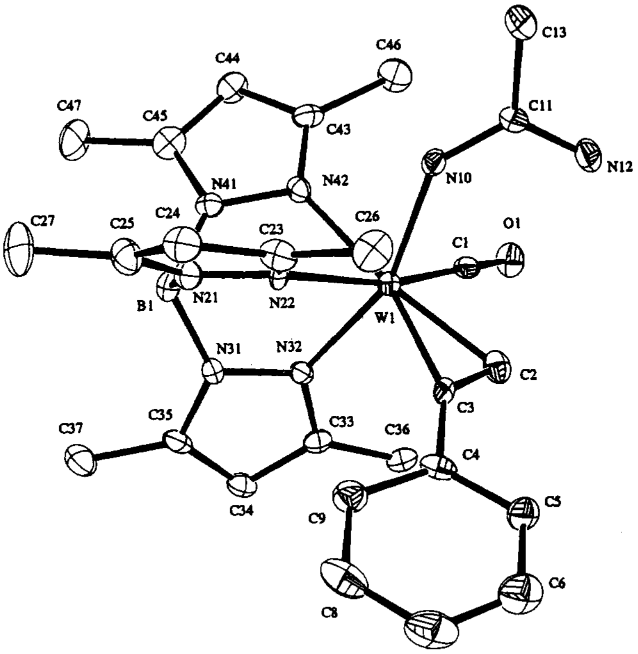

Figure 1. ORTEP drawing of $[Tp'W(CO)(PhC{\equiv}CH)W(NH{=}C(CH_3)NH_2)][BF_4]$ (2).

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Tp'(CO)(PhC{\equiv}CH)W(NH{=}C(NH_2)Me)][BF_4]$ (2)

W–C(1)	1.945(8)	C(1)–O(1)	1.168(9)
W–C(2)	2.011(8)	C(2)–C(3)	1.28(1)
W–C(3)	2.040(7)	C(3)–C(4)	1.47(1)
W–N(10)	2.105(6)	C(11)–N(12)	1.31(1)
W–N(22)	2.240(6)	C(11)–C(13)	1.50(1)
W–N(32)	2.175(6)	N(10)–C(11)	1.314(9)
W–N(42)	2.201(6)		

C(1)–W–C(2)	69.3(3)	N(10)–W–N(22)	80.0(2)
C(1)–W–C(3)	106.0(3)	N(10)–W–N(32)	158.8(2)
C(1)–W–N(10)	93.8(3)	N(10)–W–N(42)	82.6(2)
C(1)–W–N(22)	168.0(3)	N(22)–W–N(32)	88.0(2)
C(1)–W–N(32)	94.6(3)	N(22)–W–N(42)	81.2(2)
C(1)–W–N(42)	87.9(3)	N(32)–W–N(42)	78.4(2)
C(2)–W–C(3)	36.9(3)	W–C(1)–O(1)	178.7(6)
C(2)–W–N(10)	102.0(3)	W–C(2)–C(3)	72.8(5)
C(2)–W–N(22)	121.9(3)	W–C(3)–C(2)	70.3(5)
C(2)–W–N(32)	99.1(3)	W–C(3)–C(4)	151.3(6)
C(2)–W–N(42)	156.9(3)	C(2)–C(3)–C(4)	138.2(7)
C(3)–W–N(10)	103.5(2)	W–N(10)–C(11)	135.1(5)
C(3)–W–N(22)	85.5(3)	N(10)–C(11)–N(12)	122.8(7)
C(3)–W–N(32)	92.7(2)	N(10)–C(11)–C(13)	119.9(7)
C(3)–W–N(42)	164.2(3)	N(12)–C(11)–C(13)	117.3(7)

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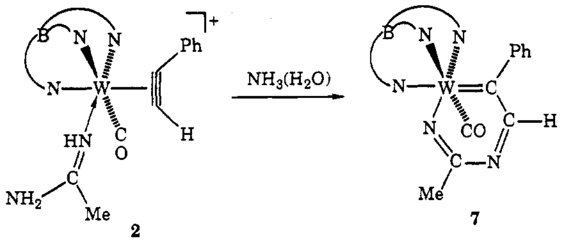
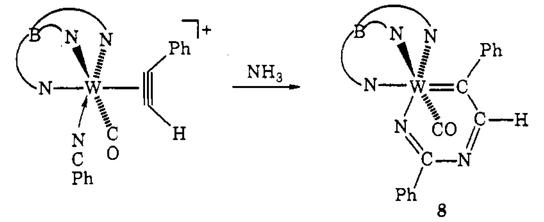
(16) Luan, L.; Brookhart, M.; Templeton, J. L. Manuscript in preparation.

(17) Feng, S. G.; White, P. S.; Templeton, J. L. Manuscript in preparation.



(5)



(6)

II. Spectroscopic Properties. Neutral complexes 7 and 8 have a less electron rich metal center than cationic complexes 1–6, as reflected in higher metal carbonyl stretching frequencies (1924 (7) and 1929 (8) cm^{-1}); recall that the IR carbonyl absorption in Tp′(CO)(PhC$_2$H)W-[NH═C(NH$_2$)Me]$^+$ is 1913 cm^{-1}. This surprising increase in the carbonyl stretching frequency on going from the cationic compound to the neutral complex suggests that chelation by linking the alkyne and amidine together coupled with the loss of a proton and two hydrogens actually takes electron density away from the metal center. Tp′ B—H absorbances at 2552 and 2540 cm^{-1} are diagnostic for neutral complexes.[1,8,14]

Assignment of the ^{1}H NMR spectra is straightforward. The three pyrazolyl rings are inequivalent in both ^{1}H and ^{13}C NMR spectra. The lone metallocycle ring proton (the original acetylene proton) of the chelating ligand in 7 and 8 resonates well downfield (8.03 and 8.39 ppm, respectively, both with $^3J_{WH}$ = 14 Hz). The metal carbonyl carbon resonates at 227.4 ppm for 7 and at 222.4 ppm for 8 with a large one-bond tungsten—carbon coupling of 175 Hz. The C$_\alpha$ carbon of the metallocycle exhibits a downfield chemical shift and one-bond tungsten—carbon and two-bond hydrogen—carbon couplings, suggesting multiple bonding between the metal and carbon (221.6 ppm, $^1J_{WC}$ = 111 Hz, $^2J_{HC}$ = 3 Hz for 7 and 230.9 ppm, $^1J_{WC}$ = 112 Hz, $^2J_{HC}$ = 3 Hz for 8). The C$_\beta$ carbon appears at higher field as a doublet with a one-bond hydrogen—carbon coupling of about 170 Hz (143.7 ppm, $^1J_{HC}$ = 169 Hz for 7 and 144.9 ppm, $^1J_{HC}$ = 170 Hz for 8). The carbon between the two nitrogens of the chelating ligand resonates near 152 ppm with a two-bond tungsten—carbon, three-bond hydrogen—carbon coupling to the ring proton, and two-bond hydrogen—carbon coupling to the methyl or the ortho protons of the phenyl group (151.6 ppm as a quartet of doublets, $^2J_{WC}$ = 23 Hz, $^2J_{HC}$ = 7 Hz, $^3J_{HC}$ = 6 Hz for 7 and 152.1 ppm as a doublet of triplets, $^2J_{WC}$ = 22 Hz, $^2J_{HC}$ = 4 Hz, $^3J_{HC}$ = 13 Hz for 8). Observation of two-bond tungsten—carbon coupling suggests that the W—N—C linkage is approaching linearity in solution, and indeed, the W—N—C angle is 146° in the crystal structure of 7. Tungsten coupling to C$_\beta$ carbons is commonly observed when the W—X—C linkage is linear, as in carbyne (W≡C—C)[18] and nitrene (W≡N—C)[19] moieties. It is also interesting to note that the ipso carbon of the C$_\alpha$-attached phenyl group resonates at about 157 ppm as a quartet coupled equally by the ring proton (three-bond) and the ortho protons of the phenyl group (two-bond) (157.6 ppm as a quartet, $^2J_{HC}$ = $^3J_{HC}$ = 6 Hz for 7 and 157.5 ppm as a quartet, $^2J_{HC}$ = $^3J_{HC}$ = 6 Hz for 8).

Table IV. Atomic Positional Parameters for Tp′(CO)W═C-(Ph)—C(H)═N—C(Ph)═N (8)

	x	y	z	B_{iso}, Å^2
W(1)	0.72921(3)	0.47699(3)	0.23706(3)	3.330(18)
N(1)	0.6577(6)	0.5426(5)	0.3009(5)	3.4(4)
C(2)	0.6593(8)	0.5853(7)	0.3758(6)	4.3(5)
N(3)	0.7515(7)	0.6005(6)	0.4207(5)	4.4(4)
C(4)	0.8405(8)	0.5748(8)	0.3930(6)	4.3(5)
C(5)	0.8540(8)	0.5274(7)	0.3201(6)	3.4(4)
C(6)	0.7106(9)	0.3673(8)	0.3003(7)	4.8(6)
O(7)	0.6984(7)	0.3007(7)	0.3392(6)	7.5(5)
C(11)	0.5629(9)	0.6095(7)	0.4065(7)	4.3(6)
C(12)	0.4710(10)	0.6278(9)	0.3520(8)	6.3(7)
C(13)	0.3797(10)	0.6529(9)	0.3817(10)	7.1(8)
C(14)	0.3755(11)	0.6560(9)	0.4648(9)	7.3(8)
C(15)	0.4669(11)	0.6380(9)	0.5185(8)	7.0(8)
C(16)	0.5581(10)	0.6172(8)	0.4909(8)	5.6(6)
C(21)	0.9684(8)	0.5183(7)	0.3126(6)	3.7(4)
C(22)	1.0455(9)	0.4933(8)	0.3785(7)	4.8(6)
C(23)	1.1491(9)	0.4850(9)	0.3695(8)	5.9(6)
C(24)	1.1811(9)	0.5028(8)	0.2957(8)	5.4(7)
C(25)	1.1100(9)	0.5270(8)	0.2299(7)	4.9(6)
C(26)	1.0042(8)	0.5371(7)	0.2368(6)	3.8(5)
B(1)	0.7541(10)	0.4517(8)	0.0399(7)	3.6(5)
N(31)	0.8389(6)	0.3865(5)	0.1780(4)	3.2(4)
N(32)	0.8340(6)	0.3876(5)	0.0931(4)	3.4(4)
C(33)	0.8967(8)	0.3219(7)	0.0696(6)	4.0(5)
C(34)	0.9434(9)	0.2757(8)	0.1383(7)	4.6(6)
C(35)	0.9073(8)	0.3167(7)	0.2040(6)	4.0(5)
C(36)	0.9087(10)	0.3055(10)	−0.0170(7)	6.5(7)
C(37)	0.9350(10)	0.2903(7)	0.2919(7)	5.0(6)
N(41)	0.7546(6)	0.5832(6)	0.1436(4)	3.2(4)
N(42)	0.7727(6)	0.5547(5)	0.0673(5)	3.3(4)
C(43)	0.7938(7)	0.6307(7)	0.0248(6)	4.0(5)
C(44)	0.7903(8)	0.7085(7)	0.0723(7)	4.3(5)
C(45)	0.7651(8)	0.6769(7)	0.1466(6)	3.6(5)
C(46)	0.8148(10)	0.6256(9)	−0.0623(7)	5.5(6)
C(47)	0.7524(10)	0.7308(7)	0.2207(8)	5.6(7)
N(51)	0.6193(6)	0.4219(6)	0.1326(4)	3.2(3)
N(52)	0.6428(6)	0.4222(6)	0.0533(5)	3.4(4)
C(53)	0.5607(9)	0.3906(7)	0.0016(6)	4.0(5)
C(54)	0.4837(8)	0.3678(7)	0.0472(7)	4.5(5)
C(55)	0.5220(8)	0.3880(7)	0.1288(7)	4.3(6)
C(56)	0.5605(9)	0.3800(8)	−0.0890(7)	4.9(6)
C(57)	0.4704(9)	0.3772(8)	0.2039(8)	5.3(6)

III. Crystal Structure of Tp′(CO)W═C(Ph)—C(H)═N—C(Ph)═N (8). The coordination sphere of this tungsten can also be described as roughly octahedral. The Tp′ ligand occupies three facial coordination sites with the carbonyl and metallocycle (carbon and nitrogen donor atoms) in the remaining coordination sites. Atomic positional parameters are listed in Table IV and selected intramolecular bond distances and angles appear in Table V. An ORTEP drawing of Tp′(CO)W═C(Ph)—C(H)═N—C(Ph)═N is shown with the atomic numbering defined in Figure 2.

The prominent geometrical features of 8 include the following: (1) The W—C and C═O bond distances of the carbonyl ligand are 1.92(1) and 1.17(2) Å and the W—C—O angle is 179(1)°. (2) The ring W═C$_\alpha$ bond distance of 2.08(1) Å is typical of Fischer-type carbene ligands.[20] (3) The ring imine W═N distance of 1.769(8) Å is approaching distances found for triple bonds in W≡NR complexes (~1.70 Å),[19] and it is substantially shorter than the formal

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[18] Jamison, G. M.; Bruce, A. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 5057.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Tp'(CO)\overline{W{=}C(Ph){-}C(H){=}N{-}C(Ph){=}N}$ (8)

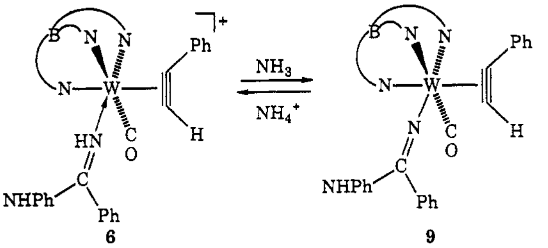
W–N(1)	1.769(8)	N(1)–C(2)	1.37(1)
W–C(5)	2.08(1)	C(6)–O(7)	1.17(2)
W–C(6)	1.92(1)	C(2)–N(3)	1.33(1)
W–N(31)	2.245(8)	N(3)–C(4)	1.35(1)
W–N(41)	2.218(8)	C(4)–C(5)	1.41(1)
W–N(51)	2.209(7)		

N(1)–W–C(5)	81.4(4)	N(31)–W–N(51)	80.4(3)
N(1)–W–C(6)	89.4(4)	N(41)–W–N(51)	81.2(3)
N(1)–W–N(31)	169.3(3)	W–N(1)–C(2)	146.1(7)
N(1)–W–N(41)	101.3(3)	N(1)–C(2)–N(3)	117.8(9)
N(1)–W–N(51)	108.5(3)	N(1)–C(2)–N(11)	121.2(9)
C(5)–W–C(6)	94.2(4)	N(3)–C(2)–N(11)	121(1)
C(5)–W–N(31)	90.2(3)	C(2)–N(3)–C(4)	120.6(9)
C(5)–W–N(41)	92.3(3)	N(3)–C(4)–N(5)	129.5(9)
C(5)–W–N(51)	168.9(3)	W–C(5)–C(4)	122.8(7)
C(6)–W–N(31)	84.6(4)	W–C(5)–C(21)	126.3(7)
C(6)–W–N(41)	168.2(4)	C(4)–C(5)–C(21)	110.9(8)
C(6)–W–N(51)	90.8(4)	W–C(6)–O(7)	179(1)
N(31)–W–N(41)	85.6(3)		

double bond distances in W—NR$_2$ complexes (~2.00 Å).[7,17,21] The three N—C distances of 1.37(1), 1.33(1), and 1.35(1) Å within the metallocycle ring are between the single and double bond ranges, suggesting that the resonance structures I and II (Scheme V) both contribute. The C$_\alpha$—C$_\beta$ bond (1.41(1) Å) is longer than a simple double bond. The Tp′ W—N distance trans to the imine nitrogen is 2.245(8) Å which is slightly longer than that trans to CO (2.218(8) Å) and carbene (2.209(7) Å), presumably reflecting the trans influence of the imine. Note that carbonyl and carbene are also strong trans influence ligands. In general, the trans influence observed for tungsten monomers in the Tp′ system (Table VI) correlates roughly with the metal—ligand bond strength, ≡C—R, =O, ≡N—R, =N=CR$_2$, alkyne, =CR$_2$, CO, -H, -NR$_2$, -I, here suggesting that the imine ligand is indeed bound to the tungsten through a multiple bond. (4) The six-membered metallocycle is basically planar. Noteworthy metallocycle angles are N—W—C$_\alpha$ at 81.4(4)° and W=N—C2 at 146.1(7)°; the rest of the ring angles are close to 120°.

The planar geometry of the six-membered metallocycle is reminiscent of benzene, and one can postulate that six π electrons are present to support an aromatic description of the bonding. Bleeke and co-workers have characterized aromatic metallobenzenes of iridium.[24] The ^{1}H and ^{13}C chemical shifts here are low and compatible with substantial ring current. A qualitative bonding scheme can be generated for this tungsten(II) d^4 system (counting the carbene as neutral) which places one metal-based electron pair in a d$_{xy}$ − d$_{xz}$ orbital combination to overlap with the CO π^* orbital. The filled d$_{xy}$ + d$_{xz}$ orbital combination is then available to be one of the six atomic π orbitals in the ring with a total of six electrons available to fill the bonding π combinations. This description places the nitrogen lone pairs in the plane of the ring rather than in the π system. The lone pair on N$_\alpha$ donates into the lone vacant dπ orbital on the metal, d$_{yz}$, to account for the large obtuse angle at M–N–C. The N$_\gamma$ lone pair is simply nonbonding in this picture (Scheme VI). A similar bonding picture results if the carbene is counted as a dianion bonding to tungsten(IV). In this description the only dπ electron pair of the d^2 metal resides in the d$_{xy}$ − d$_{xz}$ orbital combination stabilized by the carbonyl ligand. The d$_{xy}$ + d$_{xz}$ orbital which protrudes into the metallocycle ring is formally vacant, but now the σ-bound R$_2$C^{2-} unit also provides two electrons for the ring π system to again total six orbitals and six electrons and generate a pseudoaromatic description. The vacant d$_{yz}$ which lies in the plane of the metallocycle is once more a receptor orbital for π donation from the N$_\alpha$ lone pair.

Neutral Metalloamidine Complex. I. Synthesis. A plan was designed to form a metallocycle related to the putative precursor to 8 but one which could not eliminate H$_2$. This was attempted with the amidine complex containing a phenyl group bound to nitrogen to block the elimination. A reaction was initiated by adding ammonia. The result was simply deprotonation at the metal-bound nitrogen to form a metalloamidine complex. Thus reaction of [Tp′(CO)(PhC$_2$H)W(NH=C(Ph)NHPh)]$^+$ (6) with ammonia gas in THF results in formation of a neutral azavinylidene complex, Tp′(CO)(RC$_2$H)W—N=C(Ph)-NHPh (9) (eq 7). Deprotonation at the metal-bound nitrogen presumably reflects the enhanced acidity resulting from metal binding. Purification by chromatography on alumina followed by recrystallization from CH$_2$Cl$_2$/MeOH yields brown crystals. A color change from blue to brown and a 30-cm^{-1} drop in the single ν_{CO} absorption are consistent with formation of a neutral product. Protonation of 9 by a mild acid, NH$_4$$^+$, regenerates the amidine complex 6 (eq 7). Again eight isomers are possible considering potential isomers from restricted C—N rotation and alkyne orientations, and three isomers were observed for 9.



(7)

II. Spectroscopic Properties. The infrared spectrum of 9 displays a medium-intensity absorption at 2531 cm^{-1} for ν_{BH} in the Tp′ ligand. The ν_{CO} absorption at 1881 cm^{-1} is consistent with an electron-rich metal center and comparable to that for the related neutral complex Tp′(CO)(PhC$_2$Me)W(-N=C(H)Me) (1885 cm^{-1})[1] which was prepared by hydride addition to [Tp′(CO)(PhC$_2$Me)W(N≡CMe)]$^+$.

NMR data support the formulation of a metalloamidine alkyne complex. The proton on nitrogen appears at 5.56 ppm as a broad singlet. Three isomers of the neutral

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Table VI. Trans Influences in Tungsten Monomers As Reflected in W—N Bond Lengths in Tp′ Derivatives

d(W—N) trans to CO	X	d(W—N) trans to X	complex
2.23, 2.18	≡CR	2.29	[18] $[\mathrm{Tp'W(CO)_2({\equiv}CPMe_2Ph)}]^+$
2.23	=O	2.26	[22] $\mathrm{Tp'W(CO)({=}O)I}$
2.22	–N=CR$_2$	2.25	$\mathrm{Tp'(CO)W({-}N{=}C(Ph){-}N{=}C(H){-}C(Ph){=})}$
2.21	RC≡CR	2.24, 2.25	[14] $[\mathrm{Tp'W(CO)(PhC{\equiv}CH)_2}]^+$
2.17, 2.15	=NR	2.22	[19a] $[\mathrm{Tp'W(CO)_2({=}NPh)}]^+$
2.19	=CR$_2$	2.22	[23] $[\mathrm{Tp'W(CO)(PhC{\equiv}CMe)({=}C(OMe)\text{-}}n\mathrm{\text{-}Bu)}]^+$
2.24	–H	2.22	[13] $\mathrm{Tp'W(CO)(PhC{\equiv}CMe)H}$
2.23	–NR$_2$	2.18	[7] $\mathrm{Tp'W(CO)_2[{-}N(Bz)(CH{=}CHPh)]}$
2.27	–I	2.14	[8] $\mathrm{Tp'W(CO)(PhC{\equiv}CMe)I}$

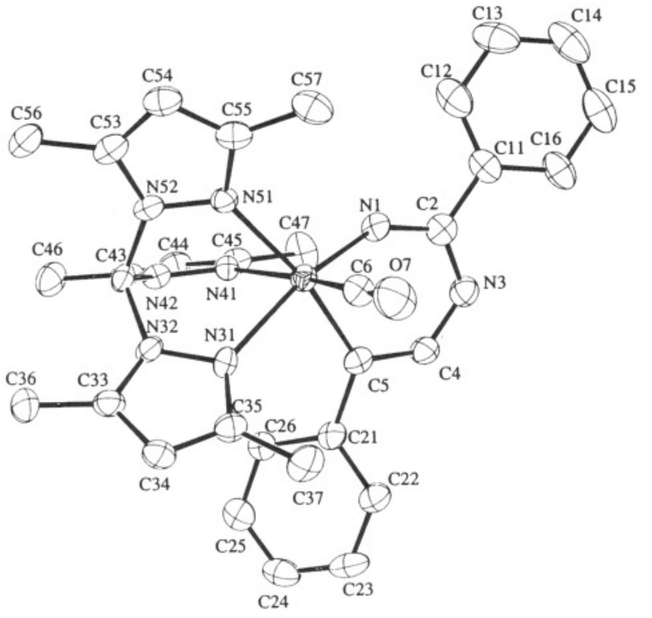
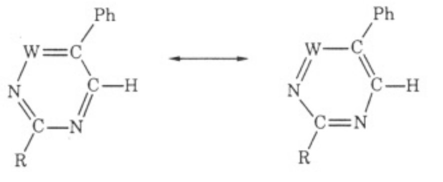


Figure 2. ORTEP drawing of $\mathrm{Tp'(CO)\overline{W{=}C(Ph){-}C(H){=}N{-}C(Ph){=}N}}$ (8).

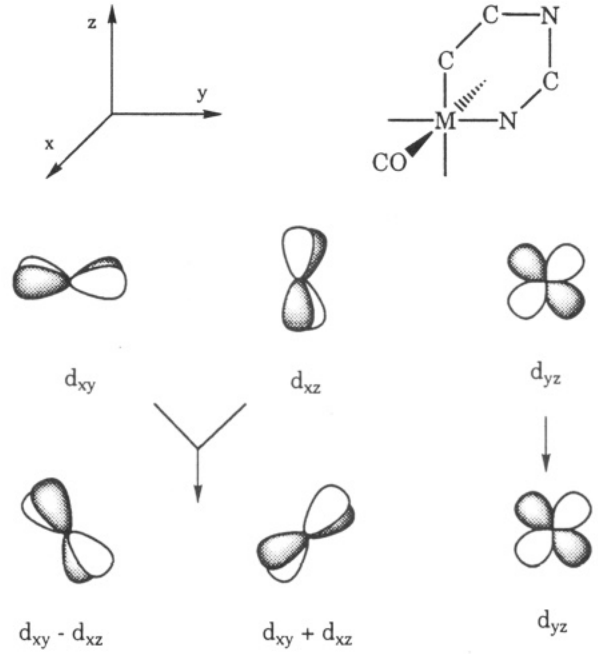
Scheme V



I II

azavinylidene complex **9** are evident by NMR in a 70%:25%:5% ratio. The acetylene proton resonates at 11.01, 11.24, and 11.15 ppm for the three isomers; the proximity of these chemical shifts to one another suggests that isomerization is not due to different alkyne orientations. We believe that restricted rotation around the two carbon—nitrogen bonds of the metalloamidine unit accounts for the isomerization. Two isomers in $\mathrm{Tp'(CO)(PhC_2Me)W({-}N{=}C(Nu)Me)}$ reflect restricted rotation about the metal—nitrogen bond.[1] ^{13}C NMR revealed the carbonyl carbon at 234.8 ppm ($^1J_{\mathrm{WC}}$ = 155 Hz, $^3J_{\mathrm{HC}}$ = 8 Hz) and the azavinylidene carbon at 153.7 ppm. The alkyne carbons resonate at 171.4 ppm as a doublet of triplets ($^1J_{\mathrm{WC}}$ = 46 Hz, $^3J_{\mathrm{HC}}$ = 4 Hz, $^2J_{\mathrm{HC}}$ = 9 Hz, PhC≡CH) and 157.4 ppm as a doublet ($^1J_{\mathrm{HC}}$ = 217 Hz, PhC≡CH), 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 this $\mathrm{W^{2+}}$ d^4 product. Four-electron donor alkyne ligands normally have lower field signals.[1,8,14]

Scheme VI. Qualitative Bonding Scheme for the dπ–Ligand Interactions in $\mathrm{Tp'(CO)W({=}C(Ph){-}C(H){=}N{-}C(R){=}N{-})}$



Note that three-electron donor alkyne ligands are unambiguously known in bis(alkyne) complexes[14,15] and the term is also used for related complexes involving a single alkyne in competition with some other π donor ligand for a single vacant metal dπ acceptor orbital.[1]

Summary

Metal-bound nitriles have previously been reduced in a stepwise manner by adding nucleophiles at carbon followed by addition of electrophiles at nitrogen. This stepwise reduction sequence has converted a coordinated nitrile to an amine.[1] We now report a one-step addition across the CN bond of the nitrile ligands with amines. The result is addition of H—NHR to the nitrile triple bond to yield NHR-substituted imine complexes. The alkyne ligands remain as four-electron donors, as indicated by NMR data and a crystal structure. An X-ray structure of the phenylacetylene derivative reveals a pseudooctahedral geometry with the alkyne roughly parallel to the M—CO axis. The phenyl group is found to lie near and bisect two pyrazole rings. Alkyne ligands are subject to intramolecular nucleophilic attack. Reaction of the $\mathrm{NH_2}$-substituted imine complexes containing a terminal alkyne with base yields cyclic metallo—imine—carbene complexes, presumably through deprotonation at $\mathrm{NH_2}$, coupling with the alkyne, and net H_2 loss. An X-ray structure of 8 shows the six-membered metallocycle is planar. The metalloimine unit of the ring has a short W═N distance of 1.768 Å and a large W═N═C angle of 146° along with a two-bond tungsten coupling of 27 Hz to the β-carbon in the ^{13}C NMR. In contrast, reaction of the NHPh-substituted imine, terminal alkyne complexes with base yields a metalloamidine complex, through deprotonation of the metal-bound nitrogen. The lone pair electrons on the nitrogen compete with the $\pi_\perp$ electrons of the alkyne to donate to the vacant metal dπ orbital at the neutral azavinylidene stage. This competitive donation results in a "three-electron donor" role for the alkyne ligand, and isomers result from restricted rotation around the metal—nitrogen multiple bond.

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Supplementary Material Available: Tables of anisotropic temperature factors and complete bond distances and angles and labeled diagrams for 2 and 8 (11 pages). Ordering information is given on any current masthead page.

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