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Conversion of Nitriles to Nitrenes via Azavinylidenes in Low-Valent Tungsten Carbonyl Complexes

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Abstract: Azavinylidene complexes of the type Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CRNu are available from the reaction of [Tp′(CO)$_3$W(N≡CR)][BF$_4$] with nucleophiles (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate; R = Me, Nu = H (**1a**); R = Ph, Nu = Et (**1d**); R = Me, Nu = MeO (**1e**)). Related azavinylidene complexes Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CHR (R = Me (**1a**); R = Et (**1b**); R = CH$_2$Ph (**1c**)) form via insertion of nitrile into the W–H bond of Tp′(CO)$_3$WH when the metal reagent is photolyzed in the presence of nitriles. Donation of the lone pair of electrons from the azavinylidene nitrogen to the tungsten center, compatible with electron counting guidelines, is reflected in the low IR stretching frequencies of the carbonyl ligands and their downfield carbon resonance in ^{13}C NMR. NMR spectra and an X-ray structure of Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CHCH$_2$Ph (**1c**) indicate that the azavinylidene ligand is nearly linear ($^3J_{WH}$ = 5.6 Hz, $^2J_{WC}$ = 27 Hz, and α(W–N–C) = 166.6(7)°). Complex **1c** crystallized in the monoclinic space group $P2_1/n$ with unit cell dimensions of a = 12.163(1), b = 17.207(2), and c = 13.312(1) Å and β = 102.103(7)°, with Z = 4. Refinement of 326 variables over 3538 reflections led to R = 4.2% and R_w = 5.8%. The short W–N distance of 1.871(6) Å indicates a tightly coordinated azavinylidene ligand. As in related dicarbonyl amido complexes, an acute OC–W–CO angle was found in the solid state. Protonation of azavinylidene complexes **1a–d** occurs at the ligand carbon atom to effectively oxidize the metal to tungsten(IV) and produce cationic nitrene complexes [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCHRR′][BF$_4$] (R = Me, R′ = H (**2a**); R = Et, R′ = H (**2b**); R = CH$_2$Ph, R′ = H (**2c**); R = Ph, R′ = Et (**2d**)). Reaction of the azavinylidene complexes **1a–c** with [Ph$_3$C][PF$_6$] produces cationic nitrene complexes of the type [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(R)CPh$_3$[PF$_6$] (R = Me (**3a**); R = Et **3b**); R = CH$_2$Ph (**3c**)) with a chiral substituent on the nitrene. The net result of this sequence of nucleophile, electrophile addition reactions to cationic nitrile complexes is formation of cationic nitrene complexes. These products reflect addition of both the nucleophile and the electrophile to the nitrile α-carbon.

Introduction

Metal imido (RN^{2-}) or nitrene (RN:) complexes are an important class of reagents in stoichiometric and catalytic transformation reactions. Numerous high oxidation imido complexes are known.[1] Low-valent nitrene complexes are less common because orbital conflicts can arise between filled metal orbitals and imido lone pairs. While π-donor ligands (such as imido and oxo ligands) are compatible with a high-oxidation-state metal center, π-acceptor ligands (such as a carbonyl ligand) require a low-valent metal center for back-bonding interactions. Mayer has demonstrated that a metal center with a d^2 configuration can accommodate both π-donor and π-acceptor ligands.[2] This will allow the π-donor ligand to interact with the two vacant dπ orbitals of an octahedral d^2 complex, while the lone filled dπ orbital can donate electron density to the π-acidic ligands.

Several routes to intermediate-oxidation-state nitrene complexes containing the Tp′(CO)W moiety are available. These include (1) oxidation following formation of an amido ligand (eqs 1 and 2),[3] (2) substitution of a carbonyl ligand using an organic azide as a nitrene source (eq 3),[4] (3) an oxo–amine exchange reaction (eq 4),[5] and (4) alkylation of a metal nitride species which had been prepared from inorganic azide, [PPN]-[N$_3$][6] (eq 5).

Coordinated nitriles are electrophilic at the α-carbon.[7,8] We have previously reported stepwise reduction of acetonitrile to chiral amino nitriles.[9] The chiral Tp′(CO)(PhC≡CMe)W moiety provided excellent stereocontrol of the addition reactions. The crucial role of the alkyne in moderating the dπ metal interactions with the nitrogen lone pair was emphasized in this work. Reactions of these same tungsten(II) nitrile complexes with amines generated the corresponding amidines.[10] This one-step addition of the H–NHR reagent across the nitrile triple bond is attractive and contrasts with the stepwise nucleophile/electrophile sequence.

$$\mathrm{Tp'(CO)_2WI} \xrightarrow{\mathrm{NH_2R}} \mathrm{Tp'(CO)_2W\overset{\leftarrow}{=}NHR} \xrightarrow{\mathrm{Ph_3C^+}} [\mathrm{Tp'(CO)_2W\overset{\leftarrow}{\equiv}NR}]^+ \tag{1}$$

$$[\mathrm{Tp'(CO)_2W(PhC{\equiv}CH)}]^+ \xrightarrow{\mathrm{NH_2CH_2Ph}} \mathrm{Tp'(CO)_2W\overset{\leftarrow}{=}N(CH_2Ph)CH{=}CHPh)} \xrightarrow{\mathrm{Ph_3C^+}} [\mathrm{Tp'(CO)_2W(\overset{\leftarrow}{\equiv}N{-}CH{=}CHPh)}]^+ \tag{2}$$

$$\mathrm{Tp'(CO)_3WI} \xrightarrow{\mathrm{N_3Ph}} \mathrm{Tp'(CO)IW(NPh)} \tag{3}$$

$$\mathrm{Tp'(CO)IW{=}O} \xrightarrow{\mathrm{NH_2Ph}} \mathrm{Tp'(CO)IW(NPh)} \tag{4}$$

$$\mathrm{Tp'(CO)_2WI} \xrightarrow{\mathrm{[PPN][N_3]}} \mathrm{Tp'(CO)_2W{=}N{:}} \xrightarrow{\mathrm{RX}} [\mathrm{Tp'(CO)_2W(NR)}]^+ \tag{5}$$

$$\mathrm{RX = HOTf,\ MeOTf,\ ClSO_2C_6H_4Me}$$

More recently we have generated [Tp′(CO)$_3$W(N≡CMe)]$^+$ in situ in order to study the results of nucleophilic addition to nitrile ligands in the absence of an auxiliary alkyne ligand. Reactions of amines with cationic nitrile complexes in the [Tp′-

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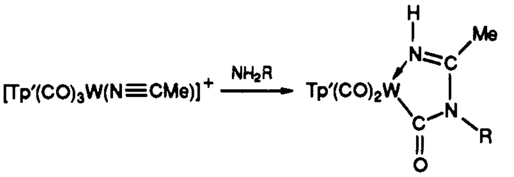
$(CO)_3W(N{\equiv}CMe)]^+$ system generated metallocyclic products which reflected activation of both nitrile and carbonyl ligands toward nucleophilic attack (eq 6).[11] The presence of an organic isocyanate moiety in the resulting metallocycle calls to mind numerous related but distinct products formed from metal-mediated coupling reactions of isocyanates with unsaturated substrates.[12]



(6)

This paper presents a study of nitrile reduction (and simultaneous oxidation of the metal) by sequential nucleophile and electrophile addition to the nitrile α-carbon to form azavinylidene and nitrene complexes, respectively. We now report (1) formation of azavinylidene complexes by nucleophilic addition to coordinated nitrile ligands and by nitrile insertion into the W–H bond of Tp′(CO)$_3$WH, (2) a crystal structure of a neutral azavinylidene complex, $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHCH_2Ph}$, and (3) formation of cationic nitrene complexes by electrophilic addition to azavinylidene ligands.

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. Other solvents were purged with N_2 gas prior to use. The tricarbonyl hydride, Tp′(CO)$_3$WH,[13] and iodide, Tp′(CO)$_3$WI,[14] and nitrile adducts, $\mathrm{Tp'(CO)_3W(N{\equiv}CR)^+}$ (R = Me, Ph),[11] were synthesized according to literature methods. Other reagents were used as obtained from commercial sources. Fisher 80–200-mesh alumina was used for the chromatographic separations.

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. $\mathbf{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHMe}$ (1a). This compound can be prepared in two ways. (a) To a cold (−40 °C) yellow solution of $\mathrm{[Tp'(CO)_3W(N{\equiv}CMe)][BF_4]}$ in 50 mL of acetonitrile, generated in situ from Tp′(CO)$_3$WI (2.0 g, 2.9 mmol) and $AgBF_4$ (0.58 g, 2.9 mmol) in MeCN,[11] was added $LiBH_4$ (0.13 g, 6.0 mmol) with stirring. The solution was allowed to warm to room temperature, resulting in a color change from yellow to green. Solvent removal left a green tar which was chromatographed on alumina with CH_2Cl_2/hexanes (1:3) as the eluent. The blue band that eluted was collected and the solvent was evaporated. Recrystallization from CH_2Cl_2/hexanes yielded blue crystals (0.92 g, 55%) of $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHMe}$ (**1a**). (b) Tp′(CO)$_3$WH (1.00 g, 1.76 mmol) was charged to a Schlenk tube. The vessel was purged of oxygen through three evacuation/nitrogen refill cycles, and then 40 mL of THF and 1 mL of MeCN were added. The solution was irradiated with a mercury vapor lamp (Hanovia, 679A36) for 15 h. A color change from yellow to blue-brown occurred. Solvent removal afforded a green tar which was chromatographed on alumina with CH_2Cl_2/hexanes (1:3) as the eluent. The blue band that eluted was collected and the solvent was evaporated to afford a blue solid (0.73 g, 71%). IR (KBr, cm^{-1}): ν_{BH} = 2543; ν_{CO} = 1922, 1811. ^{1}H NMR ($CDCl_3$, δ): 5.86, 5.85 (2:1, Tp′C*H*), 3.08 (q, $^3J_{HH}$ = 6 Hz, $^3J_{WH}$ = 6 Hz, N=C*H*Me), 2.49 (d, $^3J_{HH}$ = 6 Hz, N=CH*Me*), 2.46, 2.36, 2.29 (9:3:6, Tp′CC*H*$_3$). ^{13}C NMR ($CDCl_3$, δ): 241.5 ($^1J_{WC}$ = 173 Hz, 2*C*O), 145.0 ($^1J_{HC}$ = 173 Hz, $^2J_{HC}$ = 7 Hz, $^2J_{WC}$ = 27 Hz, N=*C*HMe), 157.0, 151.5, 145.4, 144.4 (1:2:1:2, Tp′*C*CH$_3$), 107.5, 106.3 (1:2, Tp′*C*H), 16.3, 16.2, 12.7, 12.5 (2:1:1:2, Tp′C*C*H$_3$), 10.4 ($^1J_{HC}$ = 128 Hz, $^2J_{HC}$ = 5 Hz, N=CH*Me*). Anal. Calcd for $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHMe}$ (**1a**), $WC_{19}H_{26}N_7O_2B$: C, 39.41; H, 4.52; N, 16.93. Found: C, 39.54; H, 4.34; N, 17.12.

$\mathbf{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHEt}$ (1b). This compound was prepared according to method b for **1a** described above by using EtCN in place of MeCN (blue, 70%). IR (KBr, cm^{-1}): ν_{BH} = 2533; ν_{CO} = 1921, 1805. ^{1}H NMR (CD_2Cl_2, δ): 5.93, 5.92 (2:1, Tp′C*H*), 3.03 (t, $^3J_{HH}$ = 6 Hz, $^3J_{WH}$ = 6 Hz, N=C*H*CH$_2$CH$_3$), 2.89 (qd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, N=CHC*H*$_2$CH$_3$), 1.02 (t, $^3J_{HH}$ = 8 Hz, N=CHCH$_2$C*H*$_3$), 2.50, 2.47, 2.40, 2.30 (6:3:3:6, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 241.8 ($^1J_{WC}$ = 172 Hz, 2*C*O), 151.7 ($^2J_{WC}$ = 27 Hz, N=*C*HCH$_2$CH$_3$), 157.5, 152.0, 146.5, 145.4 (1:2:1:2, Tp′*C*CH$_3$), 107.8, 106.7 (1:2, Tp′*C*H), 19.0 (*C*H$_2$CH$_3$), 16.4, 16.3, 14.1, 12.9, 12.7 (2:1:1:1:2, Tp′C*C*H$_3$ and CH$_2$*C*H$_3$). Anal. Calcd for $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHEt}$ (**1b**), $WC_{20}H_{28}N_7O_2B$: C, 40.50; H, 4.76; N, 16.53. Found: C, 41.02; H, 4.80; N, 16.05.

$\mathbf{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHCH_2Ph}$ (1c). This compound was prepared according to method b for **1a** described above by using PhCH$_2$CN in place of MeCN (blue, 78%). IR (KBr, cm^{-1}): ν_{BH} = 2542; ν_{CO} = 1928, 1813. ^{1}H NMR (CD_2Cl_2, δ): 7.32, 7.24 (m, C$_6$*H*$_5$), 5.94, 5.93 (2:1, Tp′C*H*), 4.21 (d, $^3J_{HH}$ = 6 Hz, N=CHC*H*$_2$Ph), 3.23 (t, $^3J_{HH}$ = 6 Hz, $^3J_{WH}$ = 5.6 Hz, N=C*H*CH$_2$Ph), 2.51, 2.48, 2.41, 2.31 (6:3:3:6, Tp′CC*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 241.4 ($^1J_{WC}$ = 171 Hz, 2*C*O), 151.7 (dt, $^1J_{HC}$ = 176 Hz, $^2J_{HC}$ = 8 Hz, $^2J_{WC}$ = 27 Hz, N=*C*HCH$_2$Ph), 157.5, 152.1, 146.6, 145.4 (1:2:1:2, Tp′*C*CH$_3$), 140.2, 129.0, 126.9 (*Ph*), 107.9, 106.8 (1:2, Tp′*C*H), 32.2 (t, $^1J_{HC}$ = 129 Hz, *C*H$_2$Ph), 16.5, 16.3, 12.9, 12.7 (2:1:1:2, Tp′C*C*H$_3$). Anal. Calcd for $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CHBz}$ (**1c**), $WC_{25}H_{28}N_7O_2B$: C, 45.80; H, 4.58; N, 14.96. Found: C, 45.66; H, 4.51; N, 14.95.

$\mathbf{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CEt(Ph)}$ (1d). To a cold (−40 °C) solution of $\mathrm{[Tp'(CO)_3W(N{\equiv}CPh)][BF_4]}$ in a 50 mL of THF, generated in situ from Tp′(CO)$_3$WI (2.0 g, 2.9 mmol) and $AgBF_4$ (0.58 g, 2.9 mmol), and 1 mL of N≡CPh was added EtMgBr (1.0 M in THF) (3 mL, 3.0 mmol) with stirring. The solution was allowed to warm to room temperature, resulting in a color change from yellow to green. Solvent removal left a green tar which was chromatographed on alumina with CH_2Cl_2/hexanes (1:3) as the eluent. The blue band that eluted was collected and the solvent was evaporated. Recrystallization from CH_2Cl_2/hexanes yielded a blue crystalline solid (0.79 g, 41%) of $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}C(Et)(Ph))}$ (**1d**). IR (KBr, cm^{-1}): ν_{BH} = 2529; ν_{CO} = 1928, 1825. ^{1}H NMR (CD_2Cl_2, δ): 7.40, 7.32, 7.16 (m, C$_6$*H*$_5$), 5.91, 5.87 (1:2, Tp′C*H*), 2.91 (b, N=C(C*H*$_2$Me)Ph), 2.49, 2.48, 2.38, 2.05 (6:3:3:6, Tp′CC*H*$_3$), 1.12 (t, $^3J_{HH}$ = 7 Hz, N=C(CH$_2$*Me*)Ph)). ^{13}C NMR (CD_2Cl_2, δ): 240.4 ($^1J_{WC}$ = 173 Hz, 2*C*O), 157.5 ($^2J_{WC}$ = 25 Hz, N=*C*(CH$_2$Me)Ph), 156.3, 152.7, 146.4, 145.6 (1:2:1:2, Tp′*C*CH$_3$), 130.2, 128.2, 128.1, 128.0 (*Ph*), 107.7, 106.8 (1:2, Tp′*C*H), 20.9 (t, $^1J_{HC}$ = 128 Hz, *C*H$_2$Me), 16.7, 16.4, 15.1, 12.9, 12.8 (2:1:1:2, Tp′C*C*H$_3$ and CH$_2$*Me*). Anal. Calcd for Tp′ $\mathrm{CO)_2W\overset{\leftharpoonup}{-}N{=}CEtPh}$ (**1d**), $WC_{26}H_{32}N_7O_2B$: C, 46.67; H, 4.78; N, 14.65. Found: C, 46.96; H, 4.81; N, 14.02.

$\mathbf{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}CMe(OMe)}$ (1e). To a cold (−40 °C) solution of $\mathrm{[Tp'(CO)_3W(N{\equiv}CMe)][BF_4]}$ in 50 mL of acetonitrile, generated in situ from Tp′(CO)$_3$WI (2.0 g, 2.9 mmol) and $AgBF_4$ (0.58 g, 2.9 mmol) in MeCN, was added NaOMe (0.2 g, 3.7 mmol) with stirring. The solution was allowed to warm to room temperature, resulting in a color change from yellow to green. Solvent removal left a green tar which was chromatographed on alumina with CH_2Cl_2/hexanes (1:3) as the eluent. The blue band that eluted was collected and the solvent was evaporated. Recrystallization from CH_2Cl_2/hexanes yielded blue crystals (0.62 g, 35%) of $\mathrm{Tp'(CO)_2W\overset{\leftharpoonup}{-}N{=}C(Me)(OMe)}$ (**1e**). IR (KBr, cm^{-1}): ν_{BH} = 2548; ν_{CO} = 1921, 1800. ^{1}H NMR (CD_2Cl_2, δ): 5.98, 5.90 (1:2, Tp′C*H*),

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3.61 (O*Me*), 2.61, 2.50, 2.44, 2.41, 2.20 (3:6:3:3:6, Tp′CC*H*$_3$ and N=C(OMe)*Me*). ^{13}C NMR (CD$_2$Cl$_2$, δ): 246.5 ($^1J_{WC}$ = 172 Hz, 2*C*O), 179.1 ($^2J_{WC}$ = 28 Hz, N=*C*(OMe)Me), 158.3, 152.7, 147.0, 145.6 (1:2:1:2, Tp′*C*CH$_3$), 108.2, 106.9 (1:2, Tp′*C*H), 54.9 (q, $^1J_{HC}$ = 144 Hz, O*Me*), 16.8, 13.0, 12.8, 12.7 (3:1:1:2, Tp′C*C*H$_3$ and N=C(OMe)*Me*). Anal. Calcd for Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=C(Me)OMe (**1e**), WC$_{20}$H$_{28}$N$_7$O$_3$B: C, 39.44; H, 4.63; N, 16.10. Found: C, 39.49; H, 4.51; N, 15.93.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NEt][BF$_4$] (2a). To a cold (0 °C) solution of Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CHMe (**1a**) (0.5 g, 0.86 mmol) in 20 mL of CH$_2$Cl$_2$ was added 1 equiv of HBF$_4$ with stirring, resulting in a color change from blue to red-brown. The solution was allowed to warm to room temperature. The solvent volume was reduced to ca. 5 mL by evaporation and the solution was filtered into 30 mL of Et$_2$O. The red crystalline solid which formed was isolated by filtration, washed with 2 × 5 mL of Et$_2$O, and dried in vacuo (0.53 g, 92%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded red crystals of **2a**. IR (KBr, cm^{-1}): ν_{BH} = 2569; ν_{CO} = 2080, 1997. ^{1}H NMR (CDCl$_3$, δ): 6.11, 5.94 (2:1, Tp′C*H*), 3.88 (q, $^3J_{HH}$ = 7 Hz, $^3J_{WH}$ = 9 Hz, C*H*$_2$CH$_3$), 2.42, 2.40, 2.35, 2.30 (6:6:3:3, Tp′CC*H*$_3$), 1.47 (t, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 215.9 ($^1J_{WC}$ = 157 Hz, 2*C*O), 153.4, 152.5, 149.1, 147.5 (1:2:1:2, Tp′*C*CH$_3$), 109.1, 108.3 (1:2, Tp′*C*H), 62.4 (tq, $^1J_{HC}$ = 141 Hz, $^2J_{HC}$ = 4 Hz, $^2J_{WC}$ = 26 Hz, *C*H$_2$CH$_3$), 15.8 (qt, $^1J_{HC}$ = 129 Hz, $^2J_{HC}$ = 5 Hz, CH$_2$*C*H$_3$), 15.6, 15.5, 12.9, 12.3 (2:1:1:2, Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NEt[BF$_4$] (**2a**), WC$_{19}H_{27}N_7O_2B_2F_4$: C, 34.22; H, 4.08; N, 14.70. Found: C, 34.21; H, 3.86; N, 14.58.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}NCH_2CH_2CH_3$][BF$_4$] (2b). This compound was synthesized according to the procedure described above for **2a** but with **1b** as the metal reagent (red, 91%). IR (KBr, cm^{-1}): ν_{BH} = 2563; ν_{CO} = 2085, 2002. ^{1}H NMR (CD$_2$Cl$_2$, δ): 6.18, 5.98 (2:1, Tp′C*H*), 3.75 (t, $^3J_{HH}$ = 8 Hz, $^3J_{WH}$ = 9 Hz, C*H*$_2$CH$_2$CH$_3$), 2.47, 2.46, 2.41, 2.36 (6:6:3:3, Tp′CC*H*$_3$), 1.94 (sextet, $^3J_{HH}$ = 8 Hz, CH$_2$C*H*$_2$CH$_3$), 1.04 (t, $^3J_{HH}$ = 8 Hz, CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 216.9 ($^1J_{WC}$ = 156 Hz, 2*C*O), 153.9, 153.0, 149.8, 148.3 (1:2:1:2, Tp′*C*CH$_3$), 109.3, 108.5 (1:2, Tp′*C*H), 69.4 (t, $^1J_{HC}$ = 146 Hz, $^2J_{WC}$ = 26 Hz, *C*H$_2$CH$_2$CH$_3$), 25.2 (t, $^1J_{HC}$ = 130 Hz, CH$_2$*C*H$_2$CH$_3$), 16.0, 16.9, 13.2, 12.6, (2:1:1:2, Tp′C*C*H$_3$), 11.7 (qt, $^1J_{HC}$ = 126 Hz, $^2J_{HC}$ = 4 Hz, CH$_2$CH$_2$*C*H$_3$). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}NCH_2CH_2$Me[BF$_4$] (**2b**), WC$_{20}H_{29}N_7O_2B_2F_4$: C, 35.25; H, 4.26; N, 14.39. Found: C, 35.49; H, 4.38; N, 14.18.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}NCH_2CH_2$Ph][BF$_4$] (2c). This compound was synthesized according to the procedure described above for **2a** but with **1c** as the metal reagent (red, 95%). IR (KBr, cm^{-1}): ν_{BH} = 2577; ν_{CO} = 2076, 1996. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.38–7.24 (m, C$_6$*H*$_5$), 6.17, 5.97 (2:1, Tp′C*H*), 4.12 (t, $^3J_{HH}$ = 7 Hz, $^3J_{WH}$ = 9 Hz, C*H*$_2$CH$_2$Ph), 3.16 (t, $^3J_{HH}$ = 7 Hz, CH$_2$C*H*$_2$Ph), 2.48, 2.40, 2.36, 2.33 (6:6:3:3, Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 216.9 ($^1J_{WC}$ = 157 Hz, 2*C*O), 153.8, 153.1, 149.7, 148.2 (1:2:1:2, Tp′*C*CH$_3$), 136.5, 129.3, 128.9, 127.8 (*C*$_6$H$_5$), 109.1, 108.5 (1:2, Tp′*C*H), 68.1 (t, $^1J_{HC}$ = 142 Hz, $^2J_{WC}$ = 26 Hz, *C*H$_2$CH$_2$Ph), 36.8 (t, $^1J_{HC}$ = 130 Hz, CH$_2$*C*H$_2$Ph), 15.8, 15.7, 13.1, 12.5 (2:1:1:2, Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}NCH_2CH_2$Ph[BF$_4$] (**2c**), WC$_{25}H_{31}N_7O_2B_2F_4$: C, 40.38; H, 4.17; N, 13.19. Found: C, 40.26; H, 4.11; N, 13.18.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(Et)Ph][BF$_4$] (2d). This compound was synthesized according to the procedure described above for **2a** but with **1e** as the metal reagent (red, 90%). IR (KBr, cm^{-1}): ν_{BH} = 2562; ν_{CO} = 2081, 2001. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.53–7.34 (m, C$_6$*H*$_5$), 6.20, 6.16, 5.98 (3Tp′C*H*), 4.74 (dd, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 6 Hz, C*H*(CH$_2$CH$_3$)Ph), 2.43, 2.24 (m, CH(C*HH*CH$_3$)Ph), 2.49, 2.47, 2.46, 2.35, 2.24 (3:3:3:6:3, Tp′CC*H*$_3$), 0.89 (t, $^3J_{HH}$ = 8 Hz, CH(CH$_2$C*H*$_3$)Ph). ^{13}C NMR (CD$_2$Cl$_2$, δ): 216.6, 216.2 ($^1J_{WC}$ = 156 Hz, 2*C*O), 153.9, 153.2, 153.0, 149.7, 148.4, 148.3 (Tp′(*C*CH$_3$), 138.0, 129.8, 129.6, 127.6 (*C*$_6$H$_5$), 109.2, 108.5 (1:2, Tp′*C*H), 82.7 (d, $^1J_{HC}$ = 140 Hz, $^2J_{WC}$ = 24 Hz, *C*H(CH$_2$CH$_3$)Ph), 30.3 (t, $^1J_{HC}$ = 139 Hz, CH(*C*H$_2$CH$_3$)Ph), 16.3, 15.9, 15.7, 13.1, 12.6, 12.5, 11.1 (Tp′C*C*H$_3$ and CH(CH$_2$*C*H$_3$)Ph). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(Et)Ph[BF$_4$] (**2d**), WC$_{26}H_{33}N_7O_2B_2F_4$: C, 34.61; H, 4.39; N, 12.95. Found: C, 34.54; H, 4.32; N, 12.80.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(Me)CPh$_3$][PF$_6$] (3a). To a cold (0 °C) solution of Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CHMe (**1a**) (0.5 g, 0.86 mmol) in 20 mL of CH$_2$Cl$_2$ was added 1 equiv of [Ph$_3$C][PF$_6$] (0.34 g, 0.87 mmol) with stirring, resulting in a color change from blue to brown-purple. The solution was allowed to warm to room temperature. The solvent volume was reduced to ca. 5 mL by evaporation and the solution was filtered into 30 mL of Et$_2$O. The purple crystalline solid which formed was isolated by filtration, washed with 2 × 5 mL of Et$_2$O, and dried in vacuo (0.79 g, 95%). Recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded purple crystals of **3a**. IR (KBr, cm^{-1}): ν_{BH} = 2565; ν_{CO} = 2081, 2002. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.39–7.26 (m, 3C$_6$*H*$_5$), 6.24, 6.05, 5.91 (Tp′C*H*), 5.83 (q, $^3J_{HH}$ = 7 Hz, $^3J_{WH}$ = 9 Hz, C*H*(CH$_3$)CPh$_3$), 2.53, 2.51, 2.41, 2.32, 2.29, 1.66 (Tp′CC*H*$_3$), 1.55 (d, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)CPh$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 220.5, 219.0 ($^1J_{WC}$ = 158 Hz, $^1J_{WC}$ = 159 Hz, 2*C*O), 154.2, 153.9, 153.6, 149.7, 148.7, 148.6 (Tp′*C*CH$_3$), 143.4, 130.0, 128.8, 127.7 (3 *C*$_6$H$_5$), 109.2, 109.0, 108.6 (Tp′*C*H), 77.4 (d, $^1J_{HC}$ = 138 Hz, $^2J_{WC}$ = 24 Hz, *C*H(CH$_3$)CPh$_3$), 62.9 (*C*Ph$_3$), 20.1 (q, $^1J_{HC}$ = 130 Hz, CH(*C*H$_3$)CPh$_3$), 16.0, 15.9, 15.7, 13.2, 12.8, 12.7 (Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(Me)CPh$_3$][PF$_6$] (**3a**), WC$_{38}H_{41}N_7O_2BPF_6$: C, 47.14; H, 4.24; N, 10.13. Found: C, 46.45; H, 4.20; N, 10.04.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(CH$_2CH_3$)CPh$_3$][PF$_6$] (3b). This compound was synthesized according to the procedure described above for **3a** but with **1b** as the metal reagent (purple, 94%). IR (KBr, cm^{-1}): ν_{BH} = 2561; ν_{CO} = 2079, 2002. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.37 (m, 3C$_6$*H*$_5$), 6.32, 6.01, 5.87 (Tp′C*H*), 5.43 (dd, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 1 Hz, C*H*(CH$_2$CH$_3$)CPh$_3$), 2.08 (dqd, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 1 Hz, CH(C*H*HCH$_3$)CPh$_3$), 1.33 (ddq, $^2J_{HH}$ = 13 Hz, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 8 Hz, CH(CH*H*CH$_3$)CPh$_3$), 2.94, 2.51, 2.44, 2.30, 2.22, 1.52 (Tp′CC*H*$_3$), 0.63 (t, $^3J_{HH}$ = 8 Hz, CH(CH$_2$C*H*$_3$)CPh$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 223.0, 219.5 ($^1J_{WC}$ = 159 Hz, 2*C*O), 154.4, 153.9, 153.3, 149.8, 148.8, 148.7 (Tp′*C*CH$_3$), 129.3, 128.9, 127.6 (3*C*$_6$H$_5$), 109.4, 109.0, 108.6 (Tp′*C*H), 83.6 (d, $^1J_{HC}$ = 137 Hz, $^2J_{WC}$ = 24 Hz, *C*H(CH$_2$MeCPh$_3$), 63.3 (*C*Ph$_3$), 27.3 (t, $^1J_{HC}$ = 130 Hz, CH(*C*H$_2$Me)CPh$_3$), 16.4, 16.2, 15.8, 13.1, 12.8, 12.7 (Tp′C*C*H$_3$), 11.4 (q, $^1J_{HC}$ = 125 Hz, (CH$_2$*C*H$_3$)CPh$_3$). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(CH$_2$Me)CPh$_3$][PF$_6$]($^1/_2CH_2Cl_2$), WC$_{39.5}H_{44}N_7O_2BPF_6$Cl: C, 46.30; H, 4.30; N, 9.57. Found: C, 46.47; H, 4.29; N, 9.90.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(CH$_2$Ph)CPh$_3$][PF$_6$] (3c). This compound was synthesized according to the procedure described above for **3a** but with **1c** as the metal reagent (purple, 90%). IR (KBr, cm^{-1}): ν_{BH} = 2562; ν_{CO} = 2087, 2010. ^{1}H NMR (CD$_2$Cl$_2$, δ): 7.60–7.30 (b, C*Ph*$_3$), 6.92, 6.78, 6.43 (m, C$_6$*H*$_5$), 6.17, 5.89, 5.81 (Tp′C*H*), 5.83 (d, $^3J_{HH}$ = 11 Hz, NC*H*(CH$_2$Ph)CPh$_3$), 3.46 (d, $^2J_{HH}$ = 14 Hz, NCH(C*H*HPh)CPh$_3$), 2.50 (dd, $^2J_{HH}$ = 14 Hz, $^3J_{HH}$ = 11 Hz, NCH(CH*H*Ph)CPh$_3$), 2.54, 2.44, 2.39, 2.26, 2.16, 1.59 (Tp′CC*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 222.9, 220.5 ($^1J_{WC}$ = 157 Hz, $^1J_{WC}$ = 158 Hz, 2*C*O), 154.2, 153.6, 153.1, 149.7, 149.0, 147.4 (Tp′*C*CH$_3$), 136.4, 129.1, 128.8, 128.2, 127.6 (4*C*$_6$H$_5$), 109.6, 109.1, 108.9 (Tp′*C*H), 83.8 (d, $^1J_{HC}$ = 140 Hz, $^2J_{WC}$ = 25 Hz, *C*H(CH$_2$Ph)CPh$_3$), 63.4 (*C*Ph$_3$), 39.9 (t, $^1J_{HC}$ = 132 Hz, CH(*C*H$_2$Ph)CPh$_3$), 16.1, 15.9, 15.8, 13.1, 12.7, 12.5 (Tp′C*C*H$_3$). Anal. Calcd for [Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(Bz)CPh$_3$][PF$_6$]($^1/_2CH_2Cl_2$), WC$_{44.5}H_{46}N_7O_2BPF_6$Cl: C, 49.17; H, 4.24; N, 9.02. Found: C, 48.63; H, 4.26; N, 8.77.

[Tp′(CO)$_2$W$\overset{\leftarrow}{\equiv}$NCH(Me)I][I] (4). To a cold (0 °C) solution of Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CHMe (**1a**) (45 mg) in 0.5 mL of CD$_2$Cl$_2$ in a 5-mm NMR tube was added excess I$_2$ with shaking, resulting in a color change from blue to brown. The solution was allowed to warm to room temperature. The sample was checked by NMR. ^{1}H NMR (CD$_2$Cl$_2$, δ): 6.24, 6.13, 5.97 (Tp′C*H*), 4.75 (b, C*H*(CH$_3$)I), 2.54, 2.51, 2.50, 2.44, 2.37, 2.35 (Tp′CC*H*$_3$), 1.55 (d, $^3J_{HH}$ = 7 Hz, CH(C*H*$_3$)I). ^{13}C NMR (CD$_2$Cl$_2$, δ): 216.9, 215.7 (2*C*O), 154.4, 153.1, 153.0, 150.1, 149.1, 148.8 (Tp′*C*CH$_3$), 109.5, 109.2, 109.0 (Tp′*C*H), 74.7 (d, $^1J_{HC}$ = 143 Hz, $^2J_{WC}$ = 26 Hz, *C*H(CH$_3$)I), 18.5, 17.4, 17.1, 16.6, 13.5, 13.1, 13.0 (CH(*C*H$_3$)I and Tp′C*C*H$_3$).

Collection of Diffraction Data. A blue cube of Tp′(CO)$_2$W$\overset{\leftarrow}{=}$N=CH(CH$_2$Ph) (**1c**) of dimensions 0.18 × 0.20 × 0.40 mm was selected and mounted on a glass wand coated with epoxy. Diffraction data were collected on a Rigaku automated diffractometer. Cell dimensions were obtained from 96 reflections with 2θ angles in the region $40.0° < 2\theta < 55.0°$, and when these were refined by least-square calculations, they indicated a monoclinic cell. The cell parameters are listed in Table 1. Diffraction data were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table 1. Only data with $I > 2.5\sigma(I)$ were used in structure solution and refinement.[15] The data were corrected for Lorentz–polarization effects during the final stages of data reduction. Absorption corrections were made. The transmission factors ranged from 0.516 to 0.998.

Solution and Refinement of the Structure. Space group $P2_1/n$ was confirmed and the position of the tungsten was deduced from the three-dimensional Patterson function. The positions of the remaining non-

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(15) 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.

Table 1. Crystallographic Data Collection Parameters for Tp'(CO)$_2$W$\overset{\leftarrow}{=}$N=CH(CH$_2$Ph) (**1c**)

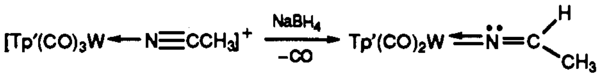
molecular formula	WC$_{25}$H$_{30}$BN$_7$O$_2$
formula weight, g/mol	655.21
crystal dimensions, mm	0.18 × 0.20 × 0.40
space group	$P2_1/n$
cell parameters	
a, Å	12.163(1)
b, Å	17.207(2)
c, Å	13.312(1)
β, deg	102.103(7)
vol, Å^3	2724.1(4)
Z	4
D$_{\text{calcd}}$, g/cm^3	1.598
Collection and Refinement Parameters	
radiation (wavelength, Å)	Cu Kα (1.54056)
monochromator	graphite
linear abs. coeff., cm^{-1}	82.2
scan type	$\theta/2\theta$
2θ limit	120°
quadrant collected	$\pm h, +k, +l$
total no. reflections	4009
data with I > 2.5σ(I)	3538
R, %	4.2
R_w, %	5.8
GOF	2.13
no. of parameters	326
largest parameter shift (shift/error ratio)	0.034

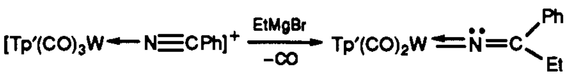
hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

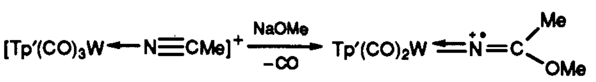
The 36 non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. The final residuals[16] for 326 variables refined against 3538 data with $I > 2.5\sigma(I)$ were R = 4.2% and R_w = 5.8%.[17] The final difference Fourier map had no peak greater than 1.46 e/Å^3.[18]

Results and Discussion

Neutral Azavinylidene Complexes (1a–e). Cationic nitrile complexes [Tp'(CO)$_3$W(N≡CR)]$^+$, prepared in situ from reaction of Tp'(CO)$_3$WI with AgBF$_4$ in the presence of nitriles, add diverse nucleophiles (LiBH$_4$, EtMgBr, NaOMe) to generate azavinylidene complexes **1a**, **1d**, and **1e** (eqs 7–9). Equation 7 reflects success in hydride addition to the acetonitrile adduct [Tp'(CO)$_3$W(N≡CMe)]$^+$. A better way to generate azavinylidene complexes of the type Tp'(CO)$_2$W($\overset{\leftarrow}{=}$N=CHR) is to photolyze the tricarbonyl hydride reagent with nitriles (N≡CR). Photolysis of Tp'(CO)$_3$WH with the appropriate nitrile in THF results in formation of analogous complexes **1a–c** through insertion of the nitrile N≡C triple bond into the W—H bond (eq 10). Purification of these neutral products by chromatography on alumina followed by recrystallization from CH$_2$Cl$_2$/hexanes yielded blue crystals. These complexes are slightly air and moisture sensitive, but they can be handled briefly in air as solids.


(7)


(8)


(9)

Formation of azavinylidene ligands from insertion of nitrile triple bonds into metal alkyl or hydride bonds is known.[19]

$$\mathrm{Tp'(CO)_2WH + N{\equiv}CR \xrightarrow{-CO} Tp'(CO)_2W\overset{\leftarrow}{=}N{=}CHR} \qquad (10)$$

1a, R = Me
1b, R = Et
1c, R = CH$_2$Ph

Nucleophilic addition to the carbon of nitrile ligands is rare, but attack at the carbon of a coordinated nitrile ligand has precedent in related systems.[9–11] Previous work with [Tp'(CO)(PhC≡CMe)W(N≡CMe)]$^+$ had shown that stepwise reduction to coordinated azavinylidene, imine, amido, and amine could be achieved by a series of H$^-$, H$^+$ additions.[9] The lone pair of electrons on the nitrogen of the azavinylidene or amido ligand in Tp'(CO)(PhC≡CMe)W$\overset{\leftarrow}{=}$N=CR$_2$ or Tp'(CO)(PhC≡CMe)W$\overset{\leftarrow}{=}$NR$_2$ competes with the $\pi_\perp$ electrons of the alkyne ligand donation into the lone vacant dπ orbital, resulting in a 3-center-4-electron bonding scheme for the nitrogen lone pair, the filled alkyne $\pi_\perp$ orbital, and the vacant metal dπ orbital. Nucleophilic addition to the nitrile carbon in [Tp'(CO)$_3$W(N≡CR)]$^+$ in the absence of an auxiliary alkyne ligand is accompanied by loss of carbon monoxide to create an acceptor dπ orbital for the azavinylidene nitrogen lone pair. Reaction of these same tricarbonyl nitrile cations with primary amines resulted in the coupling of nitrile and carbonyl ligands through an NR link to form five-membered metallocycle–imine–acyl complexes (eq 6).

Formation of Tp'(CO)$_2$W(N=CRNu) is easily achieved by nucleophilic addition to the nitrile carbon as one carbon monoxide ligand is lost. Note that the electron pair on the azavinylidene ligand here is required to donate to the metal in order to count 18 electrons in the product and optimally utilize all of the available metal orbitals. Unlike the alkyne case, there is no dπ competition among π-donor ligands here. In the absence of the ancillary alkyne, the addition of a nucleophile to the nitrile ligand causes irreversible loss of a carbon monoxide ligand. Loss of CO takes place here in order to accommodate the need for the —N=CHR ligand to find receptor orbitals on the metal for both σ and π donation.

Infrared spectra of **1a–e** display a medium intensity absorption for ν_{BH} in the Tp' ligand (2529–2548 cm^{-1}) and strong ν_{CO} absorptions (around 1925, 1810 cm^{-1}); the relatively low ν_{CO} frequencies are indicative of neutral complexes.[3,11,20] The carbonyl stretching frequencies are higher than those of related amido complexes (Tp'(CO)$_2$W$\overset{\leftarrow}{=}$NR$_2$: ~1900, 1790 cm^{-1}),[3,11,21] reflecting a less-electron-rich metal center in the azavinylidene complexes. This trend was also observed in the alkyne monocarbonyl system where net reduction from Tp'(CO)(RC≡CR)W$\overset{\leftarrow}{=}$N=CHR (1880 cm^{-1}) to the amido derivative Tp'(CO)(RC≡CR)W$\overset{\leftarrow}{=}$NHR' (1855 cm^{-1}) caused a decrease in the carbonyl stretching frequency.[9] Since the azavinylidene and amido ligands are related by addition of hydrogen across the N=C double bond (Scheme 1), it follows that the reduced form, the amido, is more electron rich.

Important NMR data that characterize the azavinylidene complexes are summarized in Table 2. The azavinylidene CH proton appears between 3.03 and 3.23 ppm (WN=C*H*R) for **1a–c** with three-bond tungsten–hydrogen coupling of about 6 Hz. The two equivalent terminal metal carbonyl carbons resonate downfield near 240 ppm with a large one-bond tungsten–carbon coupling of ~172 Hz; this low-field chemical shift and large one-bond tungsten–carbon coupling suggest that the azavinylidene

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[16] The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$, where ω is based on counter statistics.

[17] $R_{\text{unweighted}} = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_{\text{weighted}} = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2]^{1/2}$.

[18] 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.

[19] For example, see: Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443 and references therein.

[20] Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 2168.

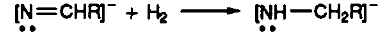
[21] Feng, S. G.; White, P. S.; Templeton, J. L. Manuscript in preparation.

Table 2. Selected NMR Data for Complexes **1a–e**, **2a–d**, and **3a–c**

	Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$N=C(R)R′		
	NC*H*R′	N*C*(R)R′	*C*O
1a (R = H, R′ = Me)	3.08 (6.1)[a]	145.0(27)	239.5(173)
1b (R = H, R′ = Et)	3.03(5.8)	151.7(27)	239.3(172)
1c (R = H, R′ = CH$_2$Ph)	3.23(5.6)	151.7(27)	239.5(171)
1d (R = Et, R′ = Ph)		157.5(25)	239.5(173)
1e (R = OMe, R′ = Me)		179.1(28)	239.5(172)
	[Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$NCH(R)R′$^+$		
	NC*H*(R)R′	N*C*H(R)R′	*C*O
2a (R = H, R′ = Me)	3.88(8.2)	62.4(26)	215.9(157)
2b (R = H, R′ = Et)	3.75(9.2)	69.4(26)	216.9(156)
2c (R = H, R′ = CH$_2$Ph)	4.12(8.8)	68.1(26)	216.9(157)
2d (R = Et, R′ = Ph)	4.71(—)	82.7(24)	216.6(156)
			216.2(156)
	[Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$NCH(R)CPh$_3$$^+$		
	NC*H*(R)CPh$_3$	N*C*H(R)CPh$_3$	*C*O
3a (R = Me)	5.83(8.7)	77.4(24)	220.5(158)
			219.0(159)
3b (R = Et)	3.75(—)	83.6(24)	223.0(159)
			219.5(159)
3c (R = CH$_2$Ph)	4.12(—)	83.8(25)	222.9(157)
			220.5(158)

[a] ppm ($J_{\mathrm{W-X}}$ in hertz.

Scheme 1



$$[\ddot{\underset{\cdot\cdot}{\mathrm{N}}}{=}\mathrm{CHR}]^- + \mathrm{H_2} \longrightarrow [\ddot{\underset{\cdot\cdot}{\mathrm{N}}}\mathrm{H}{-}\mathrm{CH_2R}]^-$$

ligand is a good π-donor ligand. The azavinylidene carbon (W$\stackrel{\leftharpoonup}{=}$N=*C*RR′) appears between 145 and 180 ppm with a two-bond tungsten–carbon coupling of ~26 Hz. Observation of tungsten coupling to the azavinylidene proton and carbon suggests a nearly linear azavinylidene unit.[3]

In order for the lone pair of electrons on the nitrogen of the azavinylidene ligand to donate into the lone vacant metal dπ orbital of this W(II) d^4 center, the plane of the azavinylidene ligand should position itself approximately perpendicular to the molecular mirror plane. Just as carbene and vinylidene ligands display orthogonal orientations relative to fixed metal fragments, amido and azavinylidene units should also alternate their orientations by 90°. An amido ligand bound to this Tp′(CO)$_2$W moiety with an acute OC–W–CO angle would lie in the molecular mirror plane, and indeed several Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$NRR′ structures have confirmed this amido orientation.[3,11,21] Even with the azavinylidene substituents positioned on either side of the molecular mirror plane, rapid rotation of the azavinylidene ligand will cause C_s symmetry to be observed by solution NMR even though there is no C_s symmetry in the molecular ground-state geometry.

The presence of a molecular mirror plane was indicated by the two equivalent pyrazolyl rings evident in both ^{1}H and ^{13}C NMR spectra. Either a static ground-state structure with the azavinylidene lying in the molecular mirror plane or rapid rotation of the azavinylidene fragment on the NMR time scale will effectively create a molecular mirror plane for NMR purposes. Variable-temperature ^{1}H NMR experiments on **1a** show two isomers at extremely low temperatures. This complex exhibits a low rotational barrier of about 9.5 kcal/mol as the two rotamers coalesced at −78 °C. Note that the rotational barrier about the W–N–C linkage will depend on the difference in donation of the lone pair of electrons on the nitrogen to the metal center as the azavinylidene ligand rotates from the minimum energy orientation through the maximum energy conformation. Here the distinction between the two dπ orbitals directed toward the azavinylidene unit will be differentiated by the distortion of the OC–W–CO angle away from 90°. So the distinction is a subtle one and the barrier is expected to be small. Regardless, rotational barriers typically decrease as multiple bonds cumulate away from the metal.

Table 3. Selected Bond Distances (angstroms) and Angles (deg) for Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$N=C(H)CH$_2$Ph (**1c**)

W–C(1)	1.971(7)	W–N(41)	2.228(5)
W–C(2)	1.942(7)	C(1)–O(1)	1.156(9)
W–N(3)	1.871(6)	C(2)–O(2)	1.155(9)
W–N(21)	2.182(5)	N(3)–C(4)	1.28(1)
W–N(31)	2.204(5)	C(4)–C(5)	1.36(2)
C(1)–W–C(2)	74.5(3)	N(3)–W–N(31)	93.5(3)
C(1)–W–N(3)	91.9(3)	N(3)–W–N(41)	88.1(3)
C(1)–W–N(21)	94.4(3)	N(21)–W–N(31)	81.7(2)
C(1)–W–N(31)	170.8(2)	N(21)–W–N(41)	80.4(2)
C(1)–W–N(41)	101.8(3)	N(31)–W–N(41)	85.9(2)
C(2)–W–N(3)	95.6(3)	W–C(1)–O(1)	172.8(6)
C(2)–W–N(21)	96.2(3)	W–C(2)–O(2)	176.8(7)
C(2)–W–N(31)	97.6(3)	W–N(3)–C(4)	166.6(7)
C(2)–W–N(41)	174.8(3)	N(3)–C(4)–C(5)	129(1)
N(3)–W–N(21)	167.8(2)	C(4)–C(5)–C(11)	114(1)

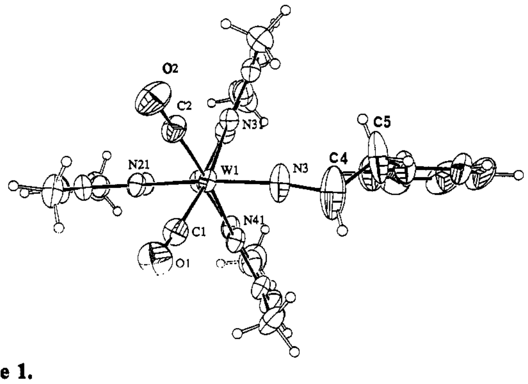


Figure 1.

Crystal Structure of Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$N=C(H)CH$_2$Ph (1c). The coordination sphere surrounding this tungsten center can be considered to be an octahedral geometry. The Tp′ ligand occupies three facial coordination sites with the two carbonyls and the azavinylidene ligand in the remaining coordination sites. Selected intramolecular bond distances and angles appear in Table 3. Two ORTEP drawings of Tp′(CO)$_2$W$\stackrel{\leftharpoonup}{=}$N=CHCH$_2$Ph (**1c**) are shown with the atomic numbering schemes defined in Figures 1 and 2.

Bond distances and angles for the Tp′ and the carbonyl ligands conform to expectations based on related dicarbonyl tungsten(II) structures.[3,11,21] The three tungsten-nitrogen bond distances to the Tp′ donor atoms cluster between 2.18 and 2.23 Å. The Tp′ W–N distance trans to the azavinylidene nitrogen is 2.182-

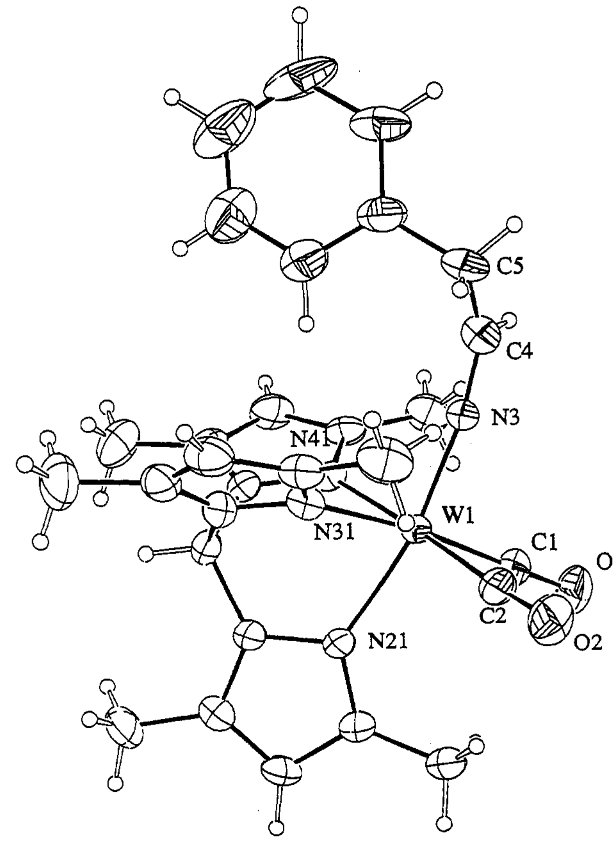


Figure 2.

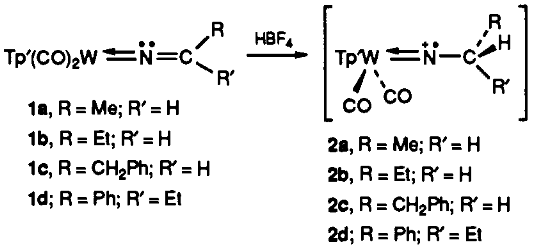
(5) Å, which is only slightly shorter than those trans to the carbonyls here (2.204(5) and 2.228(5) Å), suggesting that the azavinylidene ligand is comparable to carbon monoxide in its trans influence. The sum of the W–C and C–O distances for both carbonyl ligands is nearly constant (3.13 and 3.10 Å), and the W–C–O units approach linearity (172.8(6)° and 176.8(7)°).

The prominent geometrical features of **1c** are comparable to those of other structures of azavinylidene complexes.[22] The azavinylidene W–N distance of 1.871(6) Å is appropriate for a formal double bond and lies between values in related amido W$\overset{\leftarrow}{=}$NR$_2$ complexes (~2.00 Å)[3,11,21] and nitrene W$\overset{\leftarrow}{\equiv}NR^+$ complexes (~1.70 Å).[3] Azavinylidene complexes that have been structurally characterized have linear M–N–C backbones, and the angle of the W–N–C backbone here is 166.6(7)°. This nearly linear azavinylidene linkage suggests an sp hybridization at the nitrogen. The N(3)–C(4) distance is 1.28(1) Å, and the N(3)–C(4)–C(5) angle of 129(2)° suggests a N(3)–C(4) double bond with sp^2 hybridization at C(5).

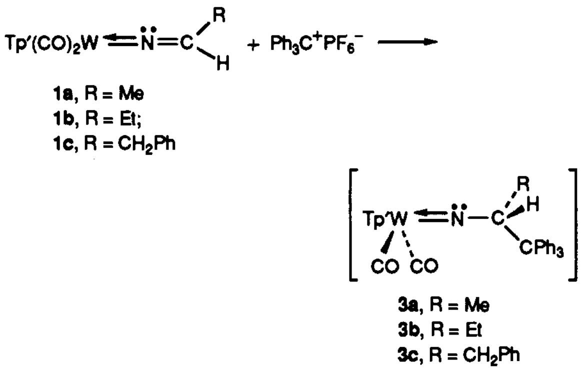
The phenyl group of the benzyl substituent on the azavinylidene unit is proximal to the Tp′ ligand and fits in between two pyrazoles of the Tp′ ligand. This orientation is consistent with our hypothesis that there are sometimes weak attractive interactions between Tp′ pyrazole rings and aromatic rings.[10,23,24] This causes a slight distortion of the azavinylidene ligand (bending of the W$\overset{\leftarrow}{=}$N=C(4) linkage and rotation about the C(4)–C(5) bond). The angle between the N(3)–C(4)–C(5) plane and the N(3)–W–C(1) plane is 34.1° while the N(3)–C(4)–C(5) plane and the N(3)–W–C(2) plane form an angle of 73.9°. As in the related amido structures, the angle of the two metal carbonyls at the metal center is acute, 74.5(3)°. This acute angle reflects preferential stabilization of the two filled dπ orbitals by back-bonding to the two π-acid carbonyl ligands.

The coordinate system we have chosen to describe the ligand–dπ bonding here puts the W–N–C linkage on the z axis and the two carbonyl ligands in the xy plane, 45° from the x and y axes (Chart 1). The carbonyl ligands mix CO π^* orbitals with metal-based dπ orbitals. Two electrons of this d^4 configuration then fill the d$_{x^2-y^2}$ orbital since this orbital will be stabilized more than d$_{xz}$ or d$_{yz}$ because of effective orbital overlap between d$_{x^2-y^2}$ and both CO π^* orbitals in the xy plane. Closure of the carbonyl angle from 90° to the observed 74.5° will preferentially stabilize d$_{yz}$ by increasing the overlap of the out-of-plane CO π^* orbitals with d$_{yz}$. The second pair of metal d electrons will then occupy the d$_{yz}$ orbital once the initial degeneracy of the d$_{xz}$ and d$_{yz}$ orbitals has been broken by decreasing the OC–M–CO angle. Note that the d$_{xz}$ orbital will be left vacant and can act as an acceptor dπ orbital for nitrogen lone pair donation. The orientation of the N=CRR′ unit between the cis carbonyls will allow donation from the nitrogen lone pair into this lone vacant dπ orbital of the tungsten center. The bonding description for an amido (NR$_2$) fragment and the metal in the related amido complexes is similar except that the amido ligand lies in the molecular mirror plane.[11] We consider d$_{yz}$ to be the HOMO stabilized by CO back-bonding and d$_{xz}$ to be the LUMO destabilized as the π^* component of the W–N double bond in these systems.

Cationic Nitrene Complexes. Complexes **2a–d** were synthesized by protonation of the azavinylidene carbon of the appropriate neutral complex, **1a–c**, at low temperature (eq 11). Cationic complexes **3a–c** with chiral substituents were synthesized by reaction of the appropriate neutral azavinylidene complex (1a–c) with [Ph$_3$C][PF$_6$] at low temperature (eq 12). Crystalline products were isolated in good yield by filtering the concentrated methylene chloride reaction solution into diethyl ether followed by recrystallization of the solid from CH$_2$Cl$_2$/Et$_2$O.



(11)



(12)

The site of electrophile addition here is reminiscent of the behavior of vinylidene ligands[25] and contrasts with the pattern

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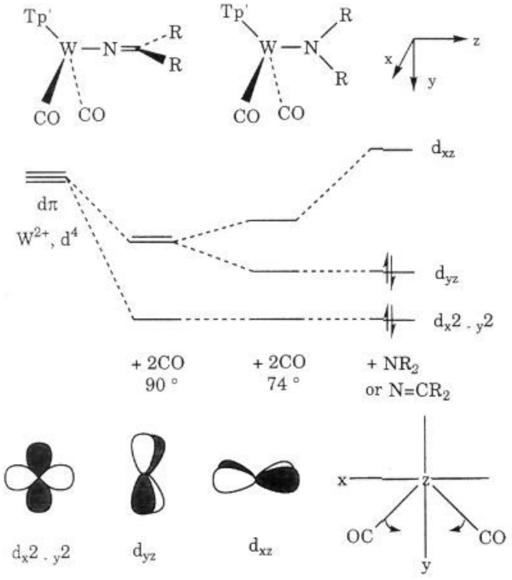
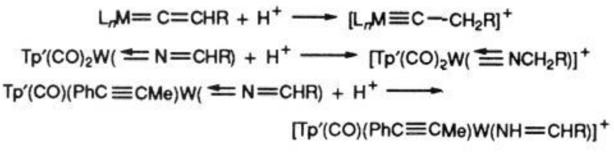
Chart 1. Qualitative Bonding Scheme for the dπ–Ligand Interactions in $\mathrm{Tp'(CO)_2W\overset{\leftarrow}{=}N{=}CR_2}$ and $\mathrm{Tp'(CO)_2W\overset{\leftarrow}{=}NR_2}$

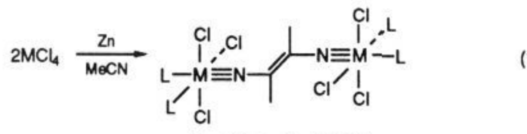


Scheme 2



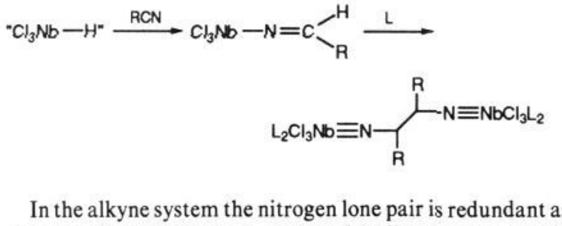
of addition seen with $[\mathrm{Tp'(CO)(PhC{\equiv}CMe)W(N{\equiv}CMe)}]^+$, where nucleophiles attacked at the position β to the metal and electrophiles added at nitrogen[9] (Scheme 2). Now it is the metal that acts as the electron reservoir and provides electrons to the nitrogen as protonation at carbon removes the N═C π-bonding electron pair. The net result is that the metal is oxidized to W(IV). The role of the auxiliary ligands in dictating the regiochemistry of the electrophilic addition step here is particularly noteworthy.

Conversion of nitriles to diimido-bridged dimers is known in tantalum and niobium complexes (eqs 13[26] and 14[27]), but systematic transformation of nitriles to nitrenes via formation of azavinylidene ligands has proven elusive. The route reported here provides a convenient synthetic procedure for the preparation of intermediate-oxidation-state metal nitrene monomers and complements the conversion of amines to nitrenes by net removal of hydrogen. The synthetic symmetry of $\mathrm{H^+}$, $\mathrm{H^-}$ removal from the nitrogen site of $\mathrm{H_2NR}$ to form $[\mathrm{Tp'(CO)_2W(NR)}]^+$ [3] and the addition of $\mathrm{H^-}$, $\mathrm{H^+}$ to the carbon site of NCR to form $[\mathrm{Tp'(CO)_2W(NCH_2R)}]^+$ is appealing.



M = Nb, Ta; L = MeCN

(13)



(14)

In the alkyne system the nitrogen lone pair is redundant as one component of a 3-center-4-electron bonding scheme, and hence it is effectively available for protonation.[9] As a result the addition of acid converts the —N═CHR ligand to a true imine ligand, HN═CHR, as the electrophile adds at nitrogen and the metal center remains as W(II). When $\mathrm{Tp'(CO)_2W(\overset{\leftarrow}{=}N{=}CHR)}$ is protonated, the metalloimine lone pair at nitrogen is tightly tied to the metal center in a 2-center-2-electron π-bond, and it is not available to electrophiles. Rather the regioselectivity of this simple protonation reaction is altered, and the imine carbon is the site of electrophilic addition. This regioselectivity resembles electrophilic addition to vinylidene ligands.[25] Here the metal is oxidized as the π electrons of the N═C unit are utilized by the incoming electrophile. The metal center then shares one of its lone pairs with the now electron deficient nitrogen atom, and the net result is conversion of $[\mathrm{Tp'(CO)_3W(N{\equiv}CMe)}]^+$ to $[\mathrm{Tp'(CO)_2W(NCH_2Me)}]^+$. Reversible deprotonation of nitrene ligands is a well-established reaction with $\mathrm{L_2Cl_3Re{=}NCH_3}$ providing an early example.[28]

Scheme 3

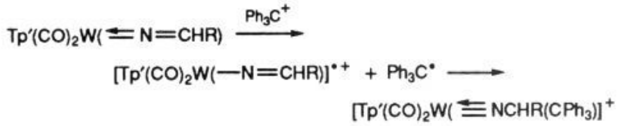


Table 4. Selected IR Data for Complexes **1a–e**, **2a–d**, and **3a–c**

	ν_{BH} (cm^{-1})	ν_{CO} cm^{-1}
$\mathrm{Tp'(CO)_2W\overset{\leftarrow}{=}N{-}C(R)R'}$		
1a (R = H, R′ = Me)	2543	1922, 1811
1b (R = H, R′ = Et)	2533	1921, 1805
1c (R = H, R′ = $\mathrm{CH_2Ph}$)	2542	1928, 1813
1d (R = Et, R′ = Ph)	2529	1928, 1825
1e (R = OMe, R′ = Me)	2548	1921, 1800
$[\mathrm{Tp'(CO)_2W\overset{\leftarrow}{\equiv}NCH(R)R'}]^+$		
2a (R = H, R′ = Me)	2569	2080, 1997
2b (R = H, R′ = Et)	2563	2085, 2002
2c (R = H, R′ = $\mathrm{CH_2Ph}$)	2577	2076, 1996
2d (R = Et, R′ = Ph)	2562	2081, 2001
$[\mathrm{Tp'(CO)_2W\overset{\leftarrow}{\equiv}NCH(R)CPh_3}]^+$		
3a (R = Me)	2565	2081, 2002
3b (R = Et)	2561	2079, 2002
3c (R = $\mathrm{CH_2Ph}$)	2562	2087, 2010

Attempts to methylate **1a** with MeOTf were not successful, perhaps indicating that the reaction with trityl cation proceeds by a radical pathway (Scheme 3).

Infrared spectra of these cationic nitrene complexes exhibit an absorption around 2565 cm^{-1} (ν_{BH}) which is 10–20 cm^{-1} higher than comparable values for the Tp′ ligand B–H stretches in neutral complexes.[11] The terminal carbonyl ν_{CO} absorptions appear at high frequencies (near 2080 and 2000 cm^{-1}) for these cationic W(IV) d^2 dicarbonyl complexes **2a–d** and **3a–c**. Selected IR data for complexes **1a–e**, **2a–d**, and **3a–c** are shown in Table 4. The trends mentioned earlier regarding the infrared stretches of the Tp′ ligand and of the metal carbonyl ligands are evident here.

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Chart 2. Metal Ligand Orbital Interactions in $Tp'(CO)_2W\overset{\leftarrow}{\equiv}NR^+$

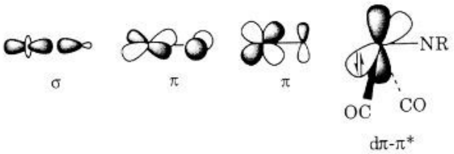

Table 5. Electron-Donating Abilities of Four-Electron Donor Ligands in $Tp'(CO)_2W^+$ Complexes As Reflected in Carbonyl Infrared Frequencies

ligand	ν_{CO} cm^{-1}
nitrene (cation) (R—N:=)	2080, 2000
alkyne (cation)[14] (RC≡CR)	2040, 1955
carbyne[29] (RC≡)	1975, 1880
η^2-vinyl[20] (CR=CR$_2$)	1950, 1860
metallofuran[30] (O—CR=CR—CR=)	1945, 1860
η^3-allyl[20] (CR$_2$—CR=CR$_2$)	1920, 1825
thiolate[31] (RS:$^-$)	1925, 1815
azavinylidene (R$_2$C=N:$^-$)	1925, 1810
alkoxide[32] (RO:$^-$)	1915, 1800
amide[3,11,21] (R$_2$N:$^-$)	1900, 1790

The average carbonyl stretching frequency for the nitrene complexes is about 170 cm^{-1} higher than that of their azavinylidene precursors. Net charge and metal oxidation state are the two major factors responsible for this difference. Note that W(IV) is d^2 so there is only one pair of d electrons available for back-donation to the two π-acid carbonyl ligands (Chart 2).

Table 5 lists carbonyl stretching frequencies for an array of 4-electron donor ligands in the $Tp'(CO)_2W^+$ system. Comparison of these frequencies provides information about the electron donor abilities of a wide range of effective 4-electron donor ligands. The neutral 4-electron donor nitrene (NR) and alkyne (RC≡CR) ligands result in carbonyl frequencies above 2000 cm^{-1}. Here the imido (NR^{2-}) oxidation state formalism would create a tungsten(IV) center with only a d^2 configuration, providing back-bonding to the two π-acid carbon monoxide ligands. The carbyne fragment, treated here as a 4-electron donor monoanion, also forms highly covalent metal–carbon bonds which leave relatively little electron density in the metal dπ orbitals. The order of increasing electron density from SR$^-$ to OR$^-$ to NR$_2^-$ is consistent with expectations for π-interactions in this series. Although different R groups characterize the carbyne, η^2-vinyl, and η^3-allyl complexes which have been studied, one can consider isomers of C_3H_5 as ligands in this system. Clearly the ethyl carbyne, CC_2H_5, would compete for dπ electron density most aggressively with the η^2-vinyl isomers (CH=CHCH$_3$) intermediate in its donor properties while the η^3-allyl isomer (CH$_2$CHCH$_2$) would be the most electron rich of the three ligands.

Important NMR data for the nitrene complexes are summarized in Table 2. The systematic changes in carbonyl chemical shifts and W–C coupling constants for the neutral and cationic complexes are obvious. A 2:1 symmetry pattern for the Tp′ ligand for **2a–c** was evident in both ^{1}H and ^{13}C NMR spectra, indicating retention of mirror symmetry in the cationic products. On the other hand, a 1:1:1 pattern of pyrazole ring signals was observed for the molecules with a chiral substituent attached to the nitrene nitrogen. ^{1}H NMR assignments are straightforward. The unique protons (NC*H*RR′) of the nitrene ligands in complexes **2a–d** and **3a–c** resonate between 3.75 and 5.83 ppm with slightly larger three-bond tungsten–hydrogen coupling constants (8–9 Hz) than their azavinylidene precursors (~6 Hz). The terminal metal carbonyl carbons resonate downfield near 216 ppm for **2a–d** and 220 ppm for **3a–c** with a one-bond tungsten–carbon coupling of ~158 Hz. These values are smaller than those of carbonyl ligands in the neutral complexes **1a–e** (240 ppm and 172 Hz), which reflects the fact that the cationic complexes are more electron deficient than the neutral precursors. The chirality of the nitrene substituents in **2d** and **3a–c** was reflected in diastereotopic carbonyl ligands. The nitrene carbon ($W\overset{\leftarrow}{\equiv}NCHRR'$ appears between 62 and 84 ppm with a two-bond tungsten–carbon coupling of ~25 Hz. The tungsten coupling to the nitrene proton and carbon is indicative of a nearly linear W–N–C linkage.[3]

A linear metal nitrene linkage here implies that the nitrogen adopts sp hybridization and acts as a 4-electron donor ligand in the neutral formalism to build a M≡N triple bond (Chart 2).

Compound **4**, formulated as $[Tp'(CO)_2W\overset{\leftarrow}{\equiv}NCHMeI]I$, can be generated in an NMR tube by treating **1a** with elemental iodine (eq 15). Although we were unable to isolate a clean solid product from this oxidation, NMR data support formation of a chiral nitrene molecule by net addition of I$^+$ to the azavinylidene carbon atom.

$$Tp'(CO)_2W(\overset{\leftarrow}{=}N{=}CHMe + I_2 \rightarrow [Tp'(CO)_2W\overset{\leftarrow}{\equiv}NCH(R)I^+I^- \quad (15)$$

Summary

Formation of nitrene ligands has been achieved by electrophilic addition to azavinylidene ligands at the carbon β to the metal. Since the azavinylidene ligand is formed from nucleophilic addition to a coordinated nitrile ligand, this nitrile reduction route reflects addition of both nucleophile and electrophile to the same carbon. The electronic factors which dictate the pattern of electrophilic addition to $Tp'(CO)_2W\overset{\leftarrow}{=}N{=}CR_2$, $Tp'(CO)(RC{\equiv}CR)W\overset{\leftarrow}{=}N{=}CR_2$, and $L_nM{=}C{=}CR_2$ are noteworthy. The acute OC–M–CO angle observed in the dicarbonyl complex containing the single-faced π-base azavinylidene ligand is the result of preferential stabilization of two filled metal dπ orbitals by back-bonding to the two π-acid carbonyl ligands with π-donation from the single-faced amido unit destabilizing the lone vacant metal dπ orbital. This acute OC–M–CO angle dictates that the azavinylidene fragment will be oriented perpendicular to the plane that bisects the two carbonyl ligands.

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Supplementary Material Available: Tables of anisotropic temperature factors and complete bond distances and angles for **1c** (5 pages); a listing of observed and calculated structure factors (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.