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Acyl, Carbene, Vinyl, and Azavinylidene Ligands in Tungsten(II) Hydridotris(3,5-dimethylpyrazolyl)borate Alkyne Complexes

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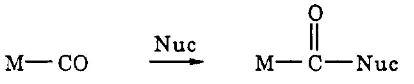
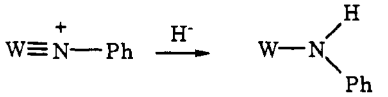
Reaction of [Tp′(CO)$_2$W(PhC$_2$Me)][BF$_4$] with LiCuR$_2$ (R = Ph, Me) generates neutral η^1-acyl complexes Tp′(CO)(PhC$_2$Me)W(η^1-C(O)R) in which the alkyne ligand remains as a four-electron donor. Deprotonation of the alkyne methyl in Tp′(CO)(PhC$_2$Me)W(η^1-C(O)Me) produces a nucleophilic propargyl synthon which reacts with MeI to yield an ethyl alkyne complex. Protonation or methylation of the neutral η^1-acyl complexes at the acyl oxygen results in the formation of Fischer-type hydroxy- or methoxycarbene cations, [Tp′(CO)(PhC$_2$Me)W═C(OE)R]$^+$ (E = H, Me; R = Me, Ph, *n*-C$_4$H$_9$). Crystals of the methoxybutylcarbene complex belong to the orthorhombic space group $P2_12_12_1$, $Z = 4$, with unit cell dimensions of $a = 15.090(6)$, $b = 16.562(4)$, and $c = 14.624(4)$ Å. Refinement of 273 variables over 2187 reflections led to an R value of 6.4% with $R_w = 6.7\%$. The alkyne ligand aligns itself parallel to the cis metal–carbonyl axis and perpendicular to the plane of the carbene ligand. Reaction of [Tp′(CO)(PhC$_2$Me)W═C(OMe)Me][CF$_3$SO$_3$] with NaOH in MeOH generates a neutral σ-vinyl complex, Tp′(CO)(PhC$_2$Me)W(η^1-C(OMe)═CH$_2$), via deprotonation of the carbene methyl group. Reaction of [Tp′(CO)(PhC$_2$Me)W═C(OMe)Ph][CF$_3$SO$_3$] with 2 equiv of KCN in MeOH yields a neutral azavinylidene complex, Tp′(CO)(PhC$_2$Me)WN═C(CN)CH(OMe)Ph, in which the lone pair of electrons on the nitrogen of the azavinylidene ligand competes with the alkyne $\pi_\perp$ donor orbital for donation to the lone vacant metal dπ orbital.

Introduction

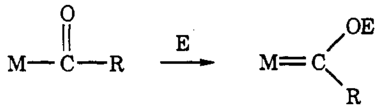
Nucleophilic and electrophilic additions constitute two fundamental classes of ligand transformations. Nucleophiles often add to a ligand α-position,[1a] as illustrated by the conversion of carbenes (E) to alkyls (F),[2] carbynes (C) to carbenes (E) (Scheme I),[3] carbonyls to acyls (eq 1),[4] and recently nitrenes to amidos (eq 2).[5,6] Addition of an electrophile to a ligand often occurs at the β-position,[1b] as illustrated by the conversion of acetylides (A) to vinylidenes (B),[7] vinylidenes (B) to carbynes (C),[7h,8] vinyls (D) to carbenes (E)[9] (Scheme I), and acyls to carbenes[10] (eq 3). Nucleophilic addition to the β-position of nitrile and imine ligands has formed azavinylidene and amido ligands which react with electrophiles at the nitrogen (α-site) to generate imine and amine ligands.[11]



$$\mathrm{M{-}CO} \xrightarrow{\mathrm{Nuc}} \mathrm{M{-}\overset{\overset{O}{\|}}{C}{-}Nuc} \qquad (1)$$



$$\mathrm{W{\equiv}\overset{+}{N}{-}Ph} \xrightarrow{\mathrm{H^-}} \mathrm{W{-}N}\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{Ph}} \qquad (2)$$



$$\mathrm{M{-}\overset{\overset{O}{\|}}{C}{-}R} \xrightarrow{\mathrm{E}} \mathrm{M{=}C}\genfrac{}{}{0pt}{}{\diagup \mathrm{OE}}{\diagdown \mathrm{R}} \qquad (3)$$

Nucleophilic addition to an alkyne ligand in tungsten monomers can form either η^1-vinyl[12] or η^2-vinyl[13] ligands, and addition of electrophiles to these distinct vinyl ligands can then generate carbenes or β-agostic carbenes, respectively[12,14] (Scheme II).

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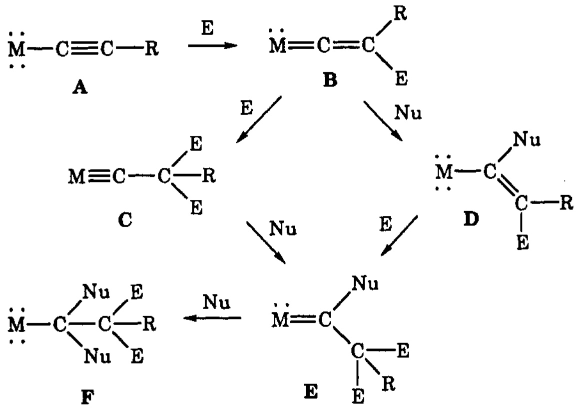
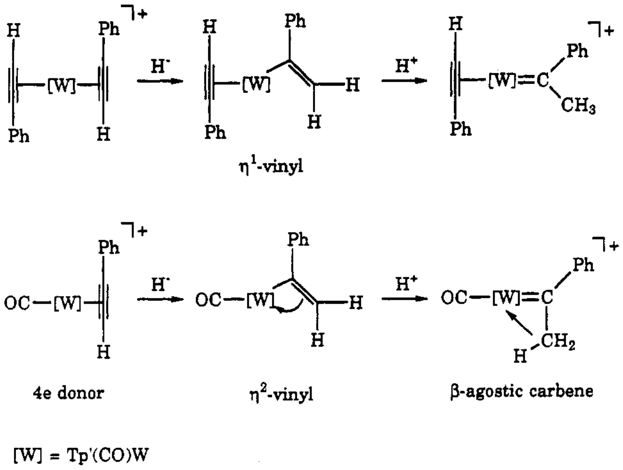
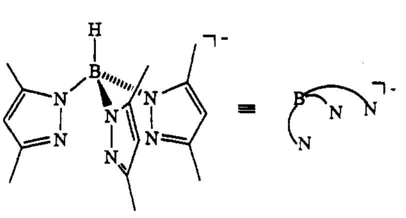
Scheme I



Scheme II



Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate



We now report Fischer carbene complexes in this series that complement the alkyne carbene monomers described previously. Specifically we report: (1) formation of acyl complexes by addition of nucleophiles to a carbonyl ligand; (2) formation of cationic Fischer carbenes of the type [Tp′(CO)(PhC≡CMe)W=C(OE)R]$^+$ from electrophilic addition to the η^1-acyl complexes (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate, see Scheme II); (3) a single crystal x-ray structure of the methoxy butyl carbene complex; (4) formation of an η^1-vinyl ligand from deprotonation of the methoxymethylcarbene ligand; and (5) formation of an azavinylidene complex, Tp′(CO)(PhC$_2$Me)W(N=C(CN)CH(OMe)Ph), from the reaction of cyanide with the carbene unit in [Tp′(CO)(PhC≡CMe)W=C(OMe)Ph]$^+$ in methanol solution.

Experimental Section

Materials and Methods. Manipulations involving air-sensitive reagents were performed under an atmosphere of pure dinitrogen using Schlenk techniques. Solvents were purified as follows: CH_2Cl_2 was distilled from P_2O_5. Et_2O, THF, and hexanes were distilled from potassium benzophenone ketyl. Other solvents were purged with nitrogen prior to use. Literature methods were employed in the synthesis of [Tp′W(CO)$_2$(PhC≡CMe)][BF$_4$][15] and Tp′(CO)(PhC≡CMe)W(η^1-C(O)Bu^n).[13] Methyl iodide was purified by passage through alumina. All other reagents were purchased from commercial sources and used as received.

Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 (400 MHz) spectrometer. Microanalyses were performed by Oneida Research Services, Whitesboro, NY.

Syntheses. Tp′(CO)(PhC$_2$Me)W[η^1-C(O)Me] (1). In a representative synthesis, a stoichiometric amount of LiCuMe$_2$, freshly prepared from reaction of CuI (0.40 g, 2.1 mmol) and MeLi (1.4 M in Et$_2$O, 3.0 mL, 4.2 mmol) at 0 °C in 20 mL of THF, was cannulated into a cold THF (−78 °C) solution of [Tp′W(CO)$_2$(PhC$_2$Me)][BF$_4$] (1.55 g, 2.1 mmol) resulting in an immediate color change from green to red-brown. The solution was warmed to room temperature and stirred for an additional 20 min. The solvent was removed and the solid residue was chromatographed on alumina with CH$_2$Cl$_2$/MeOH as the eluent. A band was collected, and the solvents were removed. The solid which remained was recrystallized from CH$_2$Cl$_2$/hexanes to yield red-wine crystals (0.92 g, 65%): IR (KBr, cm^{-1}) ν_{BH} = 2546, ν_{CO} = 1900, $\nu_{C=O}$ = 1578; ^{1}H NMR (CD$_2$Cl$_2$, δ) 7.29, 6.88 (m, C$_6$*H*$_5$), 5.91, 5.87, 5.67 (Tp′C*H*), 3.61 (3H, PhC$_2$C*H*$_3$), 2.56, 2.49, 2.45, 2.38, 1.36 (3:3:3:3:6, 18H, Tp′CC*H*$_3$), 1.76 (3H, C(O)C*H*$_3$); ^{13}C NMR (CD$_2$Cl$_2$, δ) 291.8 ($^1J_{WC}$ = 123 Hz, *C*(O)CH$_3$), 236.7 ($^1J_{WC}$ = 136 Hz, *C*O), 213.6 ($^1J_{WC}$ = 53 Hz, MeC*C*Ph), 208.6 ($^1J_{WC}$ = 14 Hz, PhC*C*Me), 154.0, 153.7, 149.3, 145.4, 145.2, 144.7 (Tp′*C*CH$_3$), 137.9, 129.2, 129.1, 128.9 (Ph), 108.1, 107.9, 106.8 (Tp′*C*H), 55.5 (C(O)*Me*), 21.8 (PhC$_2$*C*H$_3$), 16.6, 15.8, 15.5, 13.2, 13.0, 12.5 (Tp′C*C*H$_3$). Anal. Calcd for WC$_{27}$H$_{33}$N$_6$O$_2$B: C, 48.53; H, 4.94; N, 12.58. Found: C, 48.29; H, 4.58; N, 12.58.

Tp′(CO)(PhC$_2$Me)W[η^1-C(O)Ph] (2). This compound was prepared according to the procedure described above for 1 by using LiCuPh$_2$ in place of LiCuMe$_2$. The product was isolated as red-purple crystals (75%): IR (KBr, cm^{-1}) ν_{BH} = 2543, ν_{CO} = 1896, $\nu_{C=O}$ = 1543; ^{1}H NMR (CDCl$_3$, δ) 7.22, 6.88 (m, 10H, C$_6$*H*$_5$), 5.91, 5.83, 5.62 (Tp′C*H*), 3.26 (3H, PhC$_2$C*H*$_3$), 2.58, 2.54, 2.44, 2.40, 1.44, 1.38 (3H each, Tp′CC*H*$_3$); ^{13}C NMR (CDCl$_3$, δ) 293.8 ($^1J_{WC}$ = 120 Hz, *C*(O)Ph), 235.5 ($^1J_{WC}$ = 137 Hz, *C*O), 212.0 ($^1J_{WC}$ = 50 Hz, MeC*C*Ph), 208.3 ($^1J_{WC}$ = 15 Hz, PhC*C*Me), 160.5, 153.4, 153.1, 149.0, 144.6, 144.1, 143.9, 137.7 (Tp′*C*CH$_3$ and 2C$_{ipso}$), 128.5, 128.4, 128.3, 127.9, 127.4, 124.6 (Ph), 108.0, 107.9, 106.6 (Tp′*C*H), 21.4 (PhC$_2$*C*H$_3$), 16.5, 16.2, 15.6, 13.0, 12.4 (Tp′C*C*H$_3$). Anal. Calcd for Tp′(CO)(PhC$_2$Me)W(η^1-C(O)Ph)(CH$_2$Cl$_2$), WC$_{33}$H$_{37}$N$_6$O$_2$BCl$_2$: C, 48.61; H, 4.54; N, 10.31. Found: C, 48.65; H, 4.42; N, 10.48.

Tp′(CO)(PhC$_2$Et)W[η^1-C(O)Me] (3). A stoichiometric amount of butyllithium (2.5 M in hexanes, 0.3 mL) was added to a cold THF (−78 °C) solution of Tp′(CO)(PhC$_2$Me)W(–C(O)-Me) (0.5 g, 0.75 mmol), and the solution became yellow-brown. After 5 min, excess MeI (1.0 mL) was added through a layer of alumina, and the solution color returned to purple-brown. The solution was warmed to room temperature and stirred for an additional 20 min. The solvent was removed and the solid residue was chromatographed on alumina with THF as the eluent. A band was collected and the solvent was removed. The oily residue which remained was recrystallized from MeOH to yield red-wine crystals (0.41 g, 80%): IR (KBr, cm^{-1}) ν_{BH} = 2548, ν_{CO} = 1900, $\nu_{C=O}$ = 1572; ^{1}H NMR (CDCl$_3$, δ) 7.19, 6.70 (m, C$_6$*H*$_5$), 5.85, 5.72, 5.62 (Tp′C*H*), 4.10, 3.82 (each 1 H, PhC$_2$C*HH*CH$_3$), 2.50, 2.47, 2.42, 2.32, 1.42, 1.31 (3H each, Tp′CC*H*$_3$), 1.85 (3H, C(O)C*H*$_3$), 1.68 (t, $^3J_{HH}$ = 7.6 Hz, CH$_2$C*H*$_3$); ^{13}C NMR (CDCl$_3$, δ) 294.7 (*C*(O)-CH$_3$), 235.5 ($^1J_{WC}$ = 136 Hz, *C*O), 214.0 (EtC*C*Ph), 211.1 (PhC*C*Et), 153.5, 153.2, 148.6, 144.5, 144.4, 143.7 (Tp′*C*CH$_3$), 138.2, 128.6, 128.1, 128.0 (*Ph*), 107.9, 107.8, 106.5 (Tp′*C*H), 55.6

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($C(O)Me$), 30.9 (CH_2CH_3), 14.2 ($PhC_2CH_2CH_3$), 16.5, 15.8, 15.2, 13.0, 12.8, 12.4 (Tp′CCH_3). Anal. Calcd for Tp′(CO)(PhC_2CH_2Me)W(η^1-$C(O)CH_3$)·$^1/_2CH_2Cl_2$, $WC_{28.5}H_{36}N_6O_2BCl$: C, 47.23; H, 4.97; N, 11.60. Found: C, 47.99; H, 5.35; N, 11.59.

[Tp′(CO)(PhC$_2$Me)W=C(OH)Me][BF$_4$] (4). A purple-brown solution of Tp′(CO)(PhC_2Me)W(η^1-$C(O)CH_3$) (0.50 g, 0.75 mmol) in 30 mL of CH_2Cl_2/Et_2O (1:5) was cooled to 0 °C. A purple precipitate formed when a stoichiometric amount of HBF_4·Me_2O was added dropwise. The flask was put in the freezer (−40 °C) after 20 mL of Et_2O had been added. The powder which formed was isolated by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo (0.45 g, 80%). Recrystallization from CH_2Cl_2/Et_2O produced purple crystals, IR (KBr, cm^{-1}) $\nu_{BH} = 2560$, $\nu_{CO} = 1966$, $\nu_{BF} = 1069$. Two isomers are observed by ^1H NMR in a ratio of 9:1: ^1H NMR (CD_2Cl_2, major isomer only, δ) 7.46, 7.37, 6.95 (m, C_6H_5), 6.12, 6.00, 5.74 (Tp′CH), 3.86 (4.00 for the other isomer, 3H, PhC_2CH_3), 2.88, 2.61, 2.54, 2.48, 2.45, 1.33, 1.26 (3H each, Tp′CCH_3 and $=C(OH)Me$); the hydroxy proton was not located; ^{13}C NMR (CD_2Cl_2, major isomer only, δ) 329.8 ($^1J_{WC}$ = 131 Hz, $=C(OH)CH_3$), 220.3 ($^1J_{WC}$ = 130 Hz, CO), 218.5 ($^1J_{WC}$ = 48 Hz, $MeCCPh$), 214.2 ($^1J_{WC}$ = 14 Hz, $PhCCMe$), 155.3, 154.4, 150.0, 148.5, 146.9, 146.7 (Tp′CCH_3), 135.7, 132.0, 130.4, 129.6 (Ph), 109.8, 109.2, 107.9 (Tp′CH), 44.7 ($=C(OH)CH_3$), 23.3 (PhC_2CH_3), 16.6, 15.5, 15.4, 13.2, 13.0, 12.6 (Tp′CCH_3). Anal. Calcd for [Tp′(CO)(PhC_2Me)W=$C(OH)CH_3$][BF_4], $WC_{29}H_{34}N_6O_2B_2F_4$: C, 42.89; H, 4.50; N, 11.12. Found: C, 42.15; H, 4.37; N, 10.91.

[Tp′(CO)(PhC$_2$Me)W(=C(OMe)CH$_3$)][CF$_3$SO$_3$] (5). A purple-brown solution of Tp′(CO)(PhC_2Me)W(η^1-$C(O)CH_3$) (0.50 g, 0.75 mmol) in 5 mL of CH_2Cl_2 was cooled to 0 °C. Methyl triflate, [CH_3][CF_3SO_3], (0.10 mL, 0.88 mmol) was added dropwise. The flask was put in the freezer (−40 °C) after 20 mL of Et_2O had been added. The powder which formed was isolated by filtration, washed with Et_2O (2 × 10 mL), and dried in vacuo (0.53 g, 85%). Recrystallization from CH_2Cl_2/Et_2O yields purple crystals: IR (KBr, cm^{-1}) $\nu_{BH} = 2563$, $\nu_{CO} = 1966$, $\nu_{SO} = 1267$. Two isomers are observed (85%:15%): ^1H NMR ($CDCl_3$, δ), major isomer 7.30, 6.81 (m, C_6H_5), 5.99, 5.89, 5.65 (Tp′CH), 4.03, 3.82, 2.99 (PhC_2CH_3 and $=C(OMe)Me$), 2.55, 2.41, 2.40, 1.38, 1.21, 1.20 (3H each, Tp′CCH_3); significant signals for the minor isomer 7.39, 7.24, 6.78, 6.09, 4.14, 3.71, 2.61, 2.58, 2.44, 2.31, 1.15, 1.07; ^{13}C NMR ($CDCl_3$, major isomer only, δ) 330.8 ($^1J_{WC}$ = 133 Hz, $=C(OMe)CH_3$), 219.4 ($^1J_{WC}$ = 126 Hz, CO), 218.0 ($^1J_{WC}$ = 48 Hz, $MeCCPh$), 213.9 ($^1J_{WC}$ = 14 Hz, $PhCCMe$), 153.9, 153.4, 149.4, 146.8, 146.0, 145.5 (Tp′CCH_3), 135.3, 131.4, 129.6, 129.0 (Ph), 120.8 (q, $^1J_{FC}$ = 319 Hz, CF_3SO_3), 108.9, 108.7, 107.7 (Tp′CH), 63.0 (OMe), 40.7 ($=C(OMe)CH_3$), 23.1 (PhC_2CH_3), 16.4, 15.2, 12.9, 12.8, 12.4 (Tp′CCH_3). Anal. Calcd for [Tp′(CO)(PhC_2Me)W(=$C(OMe)CH_3$)][CF_3SO_3]$^1/_2CH_2Cl_2$, $WC_{29.5}H_{37}N_6O_5BClSF_3$: C, 40.50; H, 4.23; N, 9.61. Found: C, 40.54; H, 4.15; N, 9.89.

[Tp′(CO)(PhC$_2$Me)W(=C(OMe)Ph)][CF$_3$SO$_3$] (6). This compound was prepared according to the procedure described above for **5** but with **2** as the metal reagent (purple, 86%): IR (KBr, cm^{-1}) $\nu_{BH} = 2565$, $\nu_{CO} = 1977$, $\nu_{SO} = 1265$. Two isomers are observed (95%:5%): ^1H NMR ($CDCl_3$, major isomer only, δ) 7.55, 7.40, 7.33, 6.90, 6.72 (m, 10H, C_6H_5), 6.10, 6.02, 5.67 (Tp′CH), 3.72, 2.86 (3.95, 3.85 for the other isomer, PhC_2CH_3 and OMe), 2.61, 2.59, 2.42, 2.41, 1.56, 1.13 (3H each, Tp′CCH_3); ^{13}C NMR ($CDCl_3$, major isomer only, δ) 325.4 ($^1J_{WC}$ = 132 Hz, $=C(OMe)Ph$), 220.3 ($^1J_{WC}$ = 10 Hz, $PhCCMe$), 219.3 ($^1J_{WC}$ = 51 Hz, $MeCCPh$), 219.2 ($^1J_{WC}$ = 127 Hz, CO), 153.7, 153.0, 149.7, 147.8, 146.2, 135.4 (Tp′CCH_3 and 2C_{ipso}), 132.1, 130.2, 129.6, 129.5, 129.0, 122.4 (2Ph), 121.0 (q, $^1J_{FC}$ = 319 Hz, CF_3SO_3), 109.4, 109.0, 108.1 (Tp′CH), 65.2 (OMe), 22.1 (PhC_2CH_3), 16.5, 16.4, 15.2, 13.1, 13.0, 12.4 (Tp′CCH_3). Anal. Calcd for [Tp′(CO)(PhC_2Me)W(=$C(OMe)Ph$)][CF_3SO_3], $WC_{34}H_{38}N_6O_5BSF_3$: C, 45.65; H, 4.25; N, 9.40. Found: C, 44.83; H, 4.16; N, 9.27.

[Tp′(CO)(PhC$_2$Me)W(=C(OMe)CH$_2$CH$_2$CH$_2$Me)][CF$_3$SO$_3$] (7). This compound was prepared according to the procedure described above for **5** but with Tp′(CO)(PhC_2Me)W(η^1-$C(O)CH_2CH_2CH_2Me$)[13] as the metal reagent (purple, 89%): IR (KBr, cm^{-1}) $\nu_{BH} = 2563$, $\nu_{CO} = 1973$, $\nu_{SO} = 1270$; ^1H NMR (CD_2Cl_2, δ) 7.45, 7.37, 6.89 (m, C_6H_5), 6.09, 6.01, 5.73 (Tp′CH), 3.92, 3.86 (OMe and PhC_2CH_3), 2.62, 2.49, 2.47, 2.45, 1.27, 1.26 (3H each, Tp′CCH_3), 2.87, 2.00 (each a m, each 1 H, $CHHCH_2CH_2CH_3$), 1.55 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.06 (t, $^3J_{HH}$ = 7 Hz, 3H, $CH_2CH_2CH_2CH_3$); ^{13}C NMR (CD_2Cl_2, δ) 333.5 ($^1J_{WC}$ = 133 Hz, $=C(OMe)CH_2CH_2CH_2CH_3$), 220.7 ($^1J_{WC}$ = 126 Hz, CO), 218.9 ($^1J_{WC}$ = 49 Hz, $MeCCPh$), 213.9 (q, $^1J_{WC}$ = 14 Hz, $^2J_{HC}$ = 7 Hz, $PhCCMe$), 154.2, 153.6, 150.1, 147.8, 146.9, 146.5 (Tp′CCH_3), 135.7, 132.0, 130.1, 129.6 (Ph), 109.2, 109.1, 108.0, (Tp′CH), 62.9 (OMe), 55.1 ($CH_2CH_2CH_2CH_3$), 30.6 ($CH_2CH_2CH_2CH_3$), 23.4 (PhC_2CH_3), 23.3 ($CH_2CH_2CH_2CH_3$), 16.7, 15.7, 15.4, 13.8, 13.0, 12.6 (Tp′CCH_3 and $CH_2CH_2CH_2CH_3$). Anal. Calcd for [Tp′(CO)(PhC_2Me)W(=$C(OMe)CH_2CH_2CH_2CH_3$)][CF_3SO_3], $WC_{32}H_{42}N_6O_5BSF_3$: C, 43.95; H, 4.81; N, 9.61. Found: C, 43.66; H, 4.79; N, 9.52.

Tp′(CO)(PhC$_2$Me)W(η^1-C(OMe)=CH$_2$) (8). One equivalent of NaOH (0.034 g, 0.84 mmol) in 5 mL of MeOH was added to a cold MeOH (0 °C, 5 mL) solution of [Tp′(CO)(PhC_2Me)W(=$C(OMe)CH_3$)][CF_3SO_3] (0.70 g, 0.84 mmol), resulting in a color change from purple to green as a blue powder precipitated. The crystalline solid was isolated by filtration after putting the solution in a freezer (−40 °C) for 10 h. The product was recrystallized from CH_2Cl_2/MeOH to yield blue crystals (0.43 g, 75%): IR (KBr, cm^{-1}) $\nu_{BH} = 2542$, $\nu_{CO} = 1890$; ^1H NMR ($CDCl_3$, δ) 7.18, 6.69 (m, C_6H_5), 5.79, 5.77, 5.62 (Tp′CH), 4.49 (broad, 1H, $C(OMe)=CHH$), 3.43 (4H, PhC_2CH_3 and $C(OMe)=CHH$), 3.15 (OMe), 2.69, 2.56, 2.46, 2.35, 1.41 (3:3:3:3:6, 18H, Tp′CCH_3); ^{13}C NMR ($CDCl_3$, δ) 239.3 ($^1J_{WC}$ = 141 Hz, CO), 214.1, 206.8 ($MeC{\equiv}CPh$), 208.3 ($^1J_{WC}$ = 50 Hz, $C(OMe)=CHH$), 153.8, 153.7, 148.9, 143.9, 142.9 (Tp′CCH_3), 135.3 (C_{ipso}), 128.5, 128.1, 127.5 (Ph), 107.3, 107.0, 106.3 (Tp′CH), 91.0 (d of d, $^1J_{HC}$ = 157 Hz, $^1J_{HC}$ = 146 Hz, $C(OMe)=CHH$), 54.2 (OMe), 20.8 (PhC_2CH_3), 15.9, 15.1, 12.9, 12.5 (Tp′CCH_3). Anal. Calcd for Tp′(CO)(PhC_2Me)W(η^1-$C(OMe)=CH_2$)·$^1/_2CH_2Cl_2$, $WC_{28.5}H_{36}N_6O_2BCl$: C, 47.23; H, 4.97; N, 11.60. Found: C, 47.87; H, 5.37; N, 11.59.

Tp′(CO)(PhC$_2$Me)WN=C(CN)CH(OMe)Ph (9). KCN (0.11 g, 1.68 mmol) was added to a cold MeOH solution (0 °C, 20 mL) of [Tp′(CO)(PhC_2Me)W(=$C(OMe)Ph$)][CF_3SO_3] (0.70 g, 0.78 mmol). The solution was stirred for 10 h, resulting in a color change from purple to orange as an orange powder precipitated. The solvent was removed and the solid residue was redissolved in CH_2Cl_2, passed through a plug of alumina, and recrystallized from CH_2Cl_2/hexanes to yield orange crystals (0.47 g, 75%): IR (KBr, cm^{-1}) $\nu_{BH} = 2544$, $\nu_{CN} = 2187$, $\nu_{CO} = 1913$. Three isomers were observed (90%:5%:5%): ^1H NMR ($CDCl_3$, δ, major isomer only) 7.24, 7.03, 6.94, 6.45, 6.36 (m, 2C_6H_5), 6.00, 5.59, 5.35 (Tp′CH), 4.38 (4.59, 4.41 for the other two isomers, $CH(OMe)Ph$), 3.32, 3.26, 2.88, 2.53, 2.49, 2.41, 1.57, 1.01 [OCH_3, PhC_2CH_3 and Tp′CCH_3]; ^{13}C NMR ($CDCl_3$, δ, major isomer only) 222.5 ($^1J_{WC}$ = 151 Hz, CO), 160.7 ($^1J_{WC}$ = 44 Hz, $MeCCPh$), 159.4 (q, $^2J_{HC}$ = 8 Hz, $^1J_{WC}$ = 10 Hz, $MeCCPh$), 153.0, 152.0, 150.3, 144.4, 143.9, 142.9 (Tp′CCH_3), 139.3, 135.9 (2C_{ipso}), 134.3 [d, $^2J_{HC}$ = 4 Hz, $^2J_{WC}$ = 27 Hz, $WN=C(CN)CH(OMe)Ph$], 128.4, 127.8, 127.1, 126.7, 125.5 (Ph), 112.7 [d, $^3J_{HC}$ = 5 Hz, $N=C(CN)CH(OMe)Ph$], 107.8, 107.2, 106.6 (Tp′CH), 80.6 [d of q, $^1J_{HC}$ = 146 Hz, $^3J_{HC}$ = 5 Hz, $CH(OMe)Ph$], 56.7 [q of d, $^1J_{HC}$ = 141 Hz, $^3J_{HC}$ = 4 Hz, $CH(OMe)Ph$], 17.9, 16.9, 15.4, 13.7, 12.7, 12.6 [Tp′CCH_3 and PhC_2CH_3]. Anal. Calcd for Tp′(CO)(PhC_2Me)WN=$C(CN)CH(OMe)Ph$·$^1/_2CH_2Cl_2$, $WC_{35.5}H_{40}N_8O_2BCl$: C, 50.71; H, 4.76; N, 13.33. Found: C, 50.90; H, 4.67; N, 13.46.

X-ray Diffraction Data Collection for [Tp′(CO)(PhC≡CMe)W=C(OMe)CH$_2$CH$_2$CH$_2$CH$_3$][CF$_3$SO$_3$] (7). A purple block of **7** of dimensions 0.20 × 0.20 × 0.30 mm was selected and mounted on a glass wand with epoxy. Diffraction data were collected on a Rigaku automated diffractometer. Twenty centered reflections found in the region $20.0° < 2\theta < 25.0°$ and refined by least-square calculations indicated an orthorhombic cell. The cell parameters are listed in Table I.

Diffraction data were collected in the octant $+h, +k, +l$ under the conditions specified in Table I. Only data with $I > 2.5\sigma(I)$

Table I. Crystallographic Data Collection Parameters for [Tp′(CO)(PhC≡CMe)W=C(OMe)CH$_2$CH$_2$CH$_2$Me][CF$_3$SO$_3$]

molecular formula	WC$_{32}$H$_{42}$N$_6$O$_5$BF$_3$S
fw	874.43
crystal dimens, mm	0.20 × 0.20 × 0.30
space group	$P2_12_12_1$
cell params	
a, Å	15.090(6)
b, Å	16.562(4)
c, Å	14.624(4)
vol, Å^3	3655(2)
Z	4
density (calcd), g/cm^3	1.589
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.709 30)
monochromator	graphite
linear abs coeff, cm^{-1}	33.4
scan type	$\theta/2\theta$
2θ limit, deg	50
octant collected	$+h,+k,+l$
total no. of rflns	3597
data with $I \geq 2.5\sigma(I)$	2187
R, %	6.4
R_w, %	6.7
GOF	2.25
no. of params	273
largest param shift	0.189

were used in structure solution and refinement.[16] The data were corrected for Lorentz-polarization effects during the final stages of data reduction.

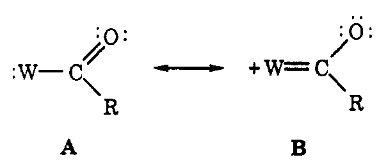
Solution and Refinement of the Structure. Space group $P2_12_12_1$ was confirmed and the position of the tungsten was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. The CF$_3$SO$_3$ anion is not well defined, and it has been input as a rigid group with idealized geometry. The phenyl group was refined as a rigid body.

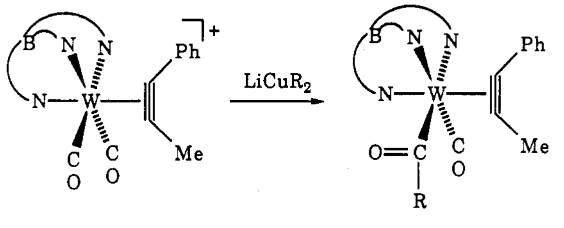
Only the tungsten atom was refined anisotropically due to the relatively small number of observed data. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å and an isotropic thermal parameter calculated from the anisotropic values for the atoms to which they were connected. The final residuals[17] for 273 variables refined against 2187 data with $I > 2.5\sigma(I)$ were $R = 6.4\%$ and $R_w = 6.7\%$.[18] The final difference Fourier map had no peak greater than 1.60 e/Å^3.[19]

Results and Discussion

An η^1-Acyl Alkyne Complex. Use of cuprate reagents, LiCuR$_2$ (R = Me, Ph), results in nucleophilic addition to one of the carbonyl ligands in [Tp′(CO)$_2$W(PhC≡CMe)]$^+$ to produce neutral η^1-acyl alkyne complexes (**1**, **2**) as stable crystals in good yields (eq 4). Hence nucleophiles are not restricted to attack at the alkyne ligand even though formation of η^2-vinyl ligands dominated earlier reports of related reactions.[13] That the carbonyls are susceptible to nucleophilic attack is not surprising given the high ν_{CO} stretching frequencies for this dicarbonyl cation (2060, 1970 cm^{-1}). Addition of nucleophiles to the alkyne ligands in this dicarbonyl system has previously generated not only η^2-vinyl ligands, but also η^3-allyl[13] and vinyl–amido[20] complexes through rearrangement processes.

Scheme III





(4)

R = Me (**1**), Ph (**2**)

The acyl products exhibit analogous spectroscopic properties to that of Tp′(CO)(PhC≡CMe)W-C(O)Bu^n which was reported earlier.[13] A strong infrared absorption [1900 (**1**), 1896 (**2**) cm^{-1}] is assigned as the lone metal carbonyl stretching frequency. Higher ν_{CO} stretching frequencies were observed in Alt's analogous Cp derivatives[21] (1938–1959 cm^{-1}), consistent with the fact that the Tp′ ligand is more electron rich than the Cp ligand. The acyl carbonyl absorption for **1** at 1578 cm^{-1} (and for **2** at 1543 cm^{-1}) is also lower than the comparable frequencies (~1600 cm^{-1}) in the analogous Cp systems. Two resonance structures, A and B, contribute to the bonding in the metal acyl fragment (Scheme III). An electron-rich metal center favors resonance form B and shifts the acyl $\nu_{C=O}$ absorption to lower energy.

Carbon-13 NMR data suggest formation of a complex containing a four-electron donor alkyne. As established earlier,[15] the alkyne ligand (PhC≡CMe) in Tp′(CO)(PhC≡CMe)WL^{n+} (n = 0, 1) complexes lies parallel to the cis carbonyl ligand with the phenyl group adjacent to the Tp′ ligand. The acetylenic carbon which is adjacent to the Tp′ ligand tends to have a lower chemical shift and a larger one-bond tungsten–carbon coupling constant than the acetylenic carbon distal to the Tp′. Here the proximal alkyne carbons appear at 213.6 ppm ($^1J_{WC}$ = 53 Hz) (**1**) and 212 ppm ($^1J_{WC}$ = 50 Hz) (**2**) for MeC≡CPh, and the distal carbons resonate at 208.6 ppm ($^1J_{WC}$ = 14 Hz) and 208.3 ppm ($^1J_{WC}$ = 15 Hz) for MeC≡CPh in **1** and **2**. These are all well downfield of signals observed for the Cp analogues where alkyne carbon signals range from 185 to 200 ppm.[21] The lone terminal metal carbonyl carbon resonates around 236 ppm ($^1J_{WC}$ = 130 Hz), comparable to the range of 231–237 ppm for the carbonyl in the Cp complexes.[21] The acyl carbon is located further downfield around 293 ppm ($^1J_{WC}$ = 120–123 Hz) which is substantially lower than the 261–265 ppm range observed for Cp(CO)(R″C$_2$R′)WC(O)R complexes.[21] An electron-rich metal center favoring resonance form B would be expected to shift the acyl carbon to lower field.

In the product here five electrons from the alkyne and the acyl ligand are required in the neutral counting formalism to produce an 18-electron compound. Both ligands are known as flexible electron donor ligands: two

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(16) 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.

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

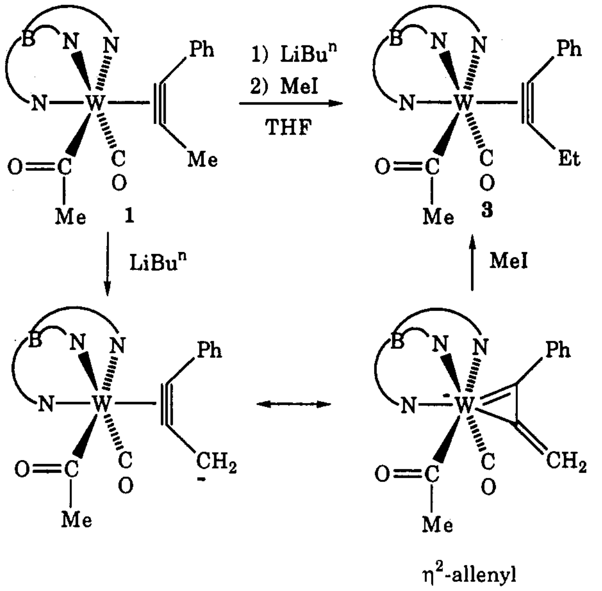
(18) $R_{\text{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{\text{weighted}} = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2}$.

(19) Scattering facters 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.

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

(21) Alt, H. G. *J. Organomet. Chem.* **1985**, *288*, 149.

Scheme IV

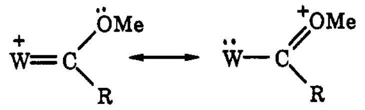


to four electrons for alkyne ligands; one to three electrons for acyl ligands. Possible extreme combinations then could be either an η^2-acyl (3 e$^-$) and a two-electron donor alkyne or an η^1-acyl (1 e$^-$) and a four-electron donor alkyne. The ground state properties clearly depend on which ligand wins this competition between $\pi_\perp$ of the alkyne and the lone pair on the oxygen of the acyl for electron donation into the lone vacant dπ orbital. In the product isolated here, $\pi_\perp$ donation dominates and the acyl acts as an η^1-ligand.

Deprotonation/Alkylation of Tp′(CO)(PhC$_2$Me)W(η^1-C(O)Me) (1). In order to find out which β-site is more susceptible to deprotonation, the acyl methyl[22] or the alkyne methyl,[23] the neutral alkyne acyl complex Tp′(CO)(PhC$_2$Me)W(η^1-C(O)Me) was allowed to react with butyllithium and then quenched with MeI. This reaction sequence generates a substituted η^2-alkyne complex, Tp′(CO)(PhC$_2$CH$_2$CH$_3$)W(η^1-C(O)Me) (Scheme IV). Deprotonation at C$_\beta$ of the alkyne presumably generates an anionic η^2-allenyl (Scheme IV). This species is highly moisture sensitive and immediately regenerates starting material when exposed to moist air. This result shows that the propargyl site of the alkyne ligand is activated more than the acyl methyl. Chromatography followed by recrystallization from CH$_2$Cl$_2$/hexanes produced high yields of wine-purple crystals.

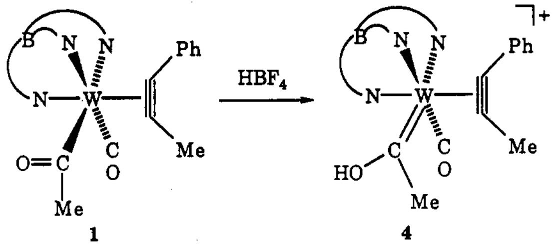
The substituted ethyl alkyne complex exhibits similar spectral properties to its parent methyl derivative. The infrared spectrum shows a single terminal ν_{CO} absorption at 1900 cm^{-1}. Unique resonances are present for each pyrazole ring of the Tp′ ligand in the NMR spectra and indicate an unsymmetrical environment for the Tp′ ligand. The diastereotopic methylene protons of the alkyne ethyl group resonate at 4.10 and 3.82 ppm, respectively. The alkyne ligand acts as a four-electron donor; the chemical shifts of the acetylenic carbons appear at 211.1 ($PhC\equiv CEt$) and 214.0 ($PhC\equiv CEt$). The metal carbonyl carbon appears downfield at 235.5 ppm with a one-bond W–C coupling of 136 Hz. The acyl carbonyl and methyl carbons resonate at 294.7 and 55.6 ppm, respectively.

Scheme V

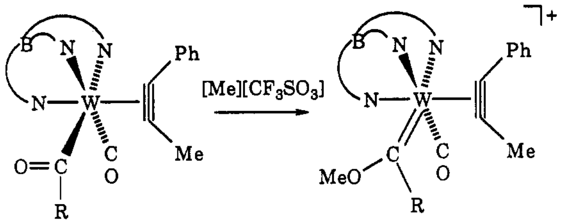


Alkyne elaboration reactions have previously been reported for both cationic and neutral alkyne complexes. This reaction provides another example of a neutral alkyne system in which alkyne deprotonation at the propargyl site can be followed by alkylation.[23]

Cationic Hydroxy- and Methoxycarbene Alkyne Complexes. Complexes 4–7 were synthesized by protonation or methylation of the carbonyl oxygen of the appropriate neutral η^1-acyl complex at 0 °C (eqs 5 and 6).



(5)



(6)

R = Me (5), Ph (6), n-Butyl (7)

The protonation reaction is rapid at 0 °C as judged by spontaneous product precipitation. Crystals of the hydroxycarbene were obtained by recrystallization from CH$_2$Cl$_2$/Et$_2$O. As is often the case, the heteroatom carbene complexes here are less reactive than carbene analogs which do not enjoy heteroatom stabilization.[12] Protonation of an η^1-vinyl complex yielded a related complex, [Tp′(CO)($PhC\equiv CMe$)W=C(Ph)Me][BF$_4$], with phenyl- and methylcarbene substituents.[12] Reduction of metal carbonyl ligands by sequential nucleophilic addition at the carbon and electrophilic addition at the oxygen is a common way to generate Fischer carbenes.[4,10] Alcohol addition across vinylidene ligands is another general route to Fischer carbenes.[7h,24]

Infrared spectra of carbene complexes 4–7 exhibit an absorption around 2564 cm^{-1} (ν_{BH}) which is ~15–20 cm^{-1} higher than the value for the Tp′ ligand in neutral complexes. This is characteristic of the Tp′ ligand in cationic compounds.[11-14] The single terminal carbonyl ν_{CO} absorptions appear between 1966–1977 cm^{-1} which is about 60–70 cm^{-1} lower than the corresponding frequency for [Tp′(CO)($PhC\equiv CMe$)W=C(Ph)Me]$^+$,[12] suggesting that the carbene oxygen atom indeed pushes substantial electron density toward the metal (Scheme V).

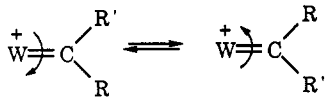
---

[22] (a) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550. (b) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (c) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1985**, 209. (d) Davies, S. G.; Easton, R. J. C.; Walker, J. C.; Warner, P. *J. Organomet. Chem.* **1985**, *296*, C40. (e) Ambler, P. W.; Davies, S. G. *Tetrahedron Lett.* **1985**, *26*, 2129.

[23] Collins, M. A.; Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 3771.

[24] Trost, B. M.; Kuluwiec, R. *J. Am. Chem. Soc.* **1992**, *114*, 5579.

Scheme VI



Unique sets of resonances for each pyrazole ring of the Tp′ in both ^{1}H and ^{13}C NMR spectra indicate an unsymmetrical environment for the Tp′ ligand. ^{1}H NMR assignments are straightforward. The hydroxy proton in 4 was not located; it may be buried under the pyrazole methyl signals. The low-field carbon-13 signals, located at 220 ppm (one-bond tungsten coupling of 50 Hz) for the phenyl-substituted alkyne carbon and 210 ppm (one-bond tungsten coupling of 10 Hz) for the methyl-substituted alkyne carbon, characterize the alkyne ligand as a 4-electron donor. The carbene carbon resonates at 325–334 ppm (with a one-bond tungsten coupling of 121 Hz), surprisingly close, although at somewhat higher field, than the value for Tp′(CO)(PhC≡CMe)W=C(Ph)Me$^+$ (341 ppm)[12]. The terminal carbonyl carbon in each complex resonates around 220 ppm with one-bond tungsten coupling of 130 Hz.

Two isomers are possible for carbene complexes bearing different substituents on the carbene unit based solely on alternative orientations of the carbene ligand and assuming restricted rotation about the metal–carbon double bond (Scheme VI). Unsymmetrical alkyne ligands are another potential source of isomerization, but we typically observe only one alkyne orientation for PhC≡CMe complexes. Observations in unsymmetrical monoalkyne complexes indicate that[11-13] a phenyl substituent on an alkyne ligand is most likely to be directed toward the pyrazole rings of the Tp′ ligand, while a terminal alkyne hydrogen exhibits an intermediate propensity to locate near the pyrazoles and an alkyl group is least likely to be proximal to the Tp′ ligand. Proximity to the pyrazole rings tends to shift ^{1}H signals to higher field by approximately 1 ppm. We conclude that the presence of a minor isomer for carbene complexes 4, 5, and 6 is due to restricted rotation around the tungsten–carbon double bond. Note that for the *n*-butyl-substituted carbene complex 7 only one isomer is detected. Although isomer interconversion did not occur on the NMR time scale, we did not separate and purify any single isomer.

Crystal Structure of [Tp′(CO)(PhC≡CMe)W=C(OMe)Bu^n][CF$_3$SO$_3$] (7). The coordination sphere of tungsten can be described as roughly octahedral for 7, considering the alkyne ligand as occupying a single coordination site. The Tp′ ligand occupies three coordination sites *trans* to the three remaining ligands: CO, PhC≡CMe, and the carbene ligand. Atomic positional parameters are listed in Table II. Selected intramolecular bond distances and angles are listed in Table III. An ORTEP drawing is shown in Figure 1.

Table II. Atomic Positional Parameters for [Tp′(CO)(PhC$_2$Me)W=C(OMe)CH$_2$CH$_2$CH$_2$Me][CF$_3$SO$_3$] (7)

	x	*y*	*z*	B_{iso}, Å^2
W1	0.11708(6)	0.00261(10)	0.07348(6)	3.67(6)
C1	0.1598(18)	0.0360(15)	–0.0502(17)	5.3(6)
O1	0.1923(12)	0.0589(11)	–0.1186(13)	6.5(5)
C2	0.1456(20)	0.2033(16)	0.0154(20)	6.5(7)
C3	0.1281(19)	0.1268(17)	0.0801(20)	6.1(6)
C4	0.1179(16)	0.1000(12)	0.1597(13)	2.9(4)
C5	–0.0125(13)	0.0010(23)	0.0235(13)	4.6(4)
O6	–0.0565(13)	–0.0687(12)	0.0163(13)	4.7(5)
C7	–0.1376(24)	–0.0759(19)	–0.0220(23)	8.5(9)
C9	–0.0575(24)	0.0763(21)	–0.0034(25)	6.4(9)
C10	–0.0723(21)	0.1014(19)	–0.0986(21)	7.2(8)
C17	–0.128(3)	0.172(3)	–0.105(3)	12.7(14)
C18	–0.154(4)	0.182(3)	–0.182(4)	17.3(20)
B1	0.1869(19)	–0.1703(17)	0.1685(19)	4.0(6)
N21	0.2493(12)	–0.0360(10)	0.1243(12)	3.8(4)
N22	0.2628(12)	–0.1123(11)	0.1576(11)	3.8(4)
C23	0.3474(18)	–0.1269(16)	0.1796(17)	4.9(6)
C24	0.3890(21)	–0.0523(17)	0.1538(19)	6.3(7)
C25	0.3268(14)	0.0026(22)	0.1220(14)	4.5(4)
C26	0.3862(21)	–0.1994(17)	0.2194(21)	7.0(7)
C27	0.3425(19)	0.0809(17)	0.0805(22)	7.0(7)
N31	0.1258(13)	–0.1232(10)	0.0167(12)	3.8(4)
N32	0.1456(12)	–0.1873(12)	0.0780(15)	4.6(4)
C33	0.1326(16)	–0.2574(14)	0.0335(15)	4.2(5)
C34	0.1012(16)	–0.2397(15)	–0.0576(16)	4.9(6)
C35	0.0985(14)	–0.1577(13)	–0.0622(16)	3.7(5)
C36	0.1452(19)	–0.3358(16)	0.0842(20)	6.5(7)
C37	0.0883(21)	–0.1089(19)	–0.1436(22)	7.8(8)
N41	0.0649(13)	–0.0623(12)	0.1926(13)	4.2(4)
N42	0.1134(14)	–0.1285(10)	0.2305(12)	3.4(4)
C43	0.0723(17)	–0.1471(15)	0.3115(17)	4.6(6)
C44	0.0052(17)	–0.0989(15)	0.3255(16)	4.4(6)
C45	0.0001(19)	–0.0496(15)	0.2558(17)	4.6(5)
C46	0.1171(23)	–0.2173(18)	0.3673(22)	7.7(8)
C47	–0.0669(17)	0.0174(16)	0.2363(16)	6.0(7)
S1	0.6462(11)	0.0940(9)	0.0775(13)	31.6(17)
C52	0.6599(12)	0.0343(10)	0.1811(13)	31.6(17)
O11	0.5665(14)	0.1378(12)	0.0947(19)	31.6(17)
O12	0.7248(15)	0.1415(14)	0.0753(20)	31.6(17)
O13	0.6402(19)	0.0342(14)	0.0079(13)	31.6(17)
F21	0.7322(13)	–0.0101(14)	0.1751(20)	31.6(17)
F22	0.6665(21)	0.0822(16)	0.2525(13)	31.6(17)
F23	0.5910(14)	–0.0134(13)	0.1924(19)	31.6(17)
C11	0.1229(15)	0.1339(11)	0.2484(9)	6.0(6)
C12	0.0957(13)	0.2133(10)	0.2634(10)	6.0(6)
C13	0.0944(13)	0.2446(8)	0.3519(13)	6.0(6)
C14	0.1201(13)	0.1964(10)	0.4255(9)	6.0(6)
C15	0.1473(12)	0.1170(10)	0.4106(10)	6.0(6)
C16	0.1487(13)	0.0857(8)	0.3220(12)	6.0(6)

Salient geometrical features of [Tp′(CO)(PhC≡CMe)W=C(OMe)Bu^n]$^+$ are consistent with those established by previous monocarbonyl alkyne complexes. (1) The alkyne is *cis* to the CO and parallel to the M–CO axis. As commonly observed, the alkyne lies between two pyrazole rings with the phenyl group up toward the Tp′ ligand.[15] (2) The W–C alkyne bond distances of 2.07(2) and 2.05(2) Å and the C≡C bond distance of 1.26(4) Å and the C–W–C angle of 36(1)° are typical for four-electron donor alkyne ligands.[12,15,25] (3) A standard alkyne ligand feature found in 7 is the *cis* bent geometry of the alkynes, as the C≡C–C angles are swept back to 147(3)° and 135(2)°. The tungsten–nitrogen bond distances cluster near 2.2 Å (W–N(15) = 2.17(2) Å, W–N(25) = 2.22(2) Å, W–N(35) = 2.18(2) Å).

The carbene W=C distance of 2.09(2) Å is close to distances characterizing low oxidation state Fischer carbenes (Ph$_2$C=W(CO)$_5$, 2.14 Å).[26] It is longer than distances in high oxidation state Schrock alkylidenes (Bu^{t}CH=W(dmpe)(CBu^t)(CH$_2$Bu^t), 1.94 Å).[27]

It is well established that the linearly ligating carbonyl ligand will mix CO π^* with d_{xz} and d_{yz} to lower the energy of these metal-based orbitals. The d^4 configuration then fills these two dπ orbitals to leave d_{xy} vacant.[25] The alkyne invariably aligns itself parallel to the M–CO axis in d^4 L$_4$M(CO)(RC≡CR) complexes in order to optimize both

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Table III. Selected Bond Distances (Å) and Angles (deg) for [Tp′(CO)(PhC≡CMe)W=C(OMe)Bu^n][CF$_3$SO$_3$] (7)

W-C(1)	2.00(3)	W-N(41)	2.19(2)
W-C(3)	2.07(3)	C(2)-C(3)	1.60(4)
W-C(4)	2.05(2)	C(3)-C(4)	1.26(4)
W-C(5)	2.09(2)	C(4)-C(11)	1.42(2)
W-N(21)	2.22(2)	C(1)-O(1)	1.18(3)
W-N(31)	2.25(2)	C(5)-O(6)	1.34(4)
C(1)-W-C(3)	75(1)	C(5)-W-N(31)	85(1)
C(1)-W-C(4)	109.7(9)	C(5)-W-N(41)	86.3(9)
C(1)-W-C(5)	89(1)	N(21)-W-N(31)	78.7(7)
C(1)-W-N(21)	95.3(9)	N(21)-W-N(41)	85.2(7)
C(1)-W-N(31)	84.5(8)	N(31)-W-N(41)	82.0(7)
C(1)-W-N(41)	166.1(9)	W-C(1)-O(1)	173(2)
C(3)-W-C(4)	36(1)	W-C(3)-C(2)	141(2)
C(3)-W-C(5)	96(1)	W-C(3)-C(4)	71(2)
C(3)-W-N(21)	101.5(9)	C(2)-C(3)-C(4)	147(3)
C(3)-W-N(31)	159(1)	W-C(4)-C(3)	73(2)
C(3)-W-N(41)	119(1)	W-C(4)-C(11)	151(2)
C(4)-W-C(5)	103(1)	C(3)-C(4)-C(11)	135(2)
C(4)-W-N(21)	90.9(8)	W-C(5)-O(6)	120(2)
C(4)-W-N(31)	163.3(7)	W-C(5)-C(9)	121(2)
C(4)-W-N(41)	84.2(8)	O(6)-C(5)-C(9)	119(2)
C(5)-W-N(21)	163(1)	C(5)-O(6)-C(7)	124(2)

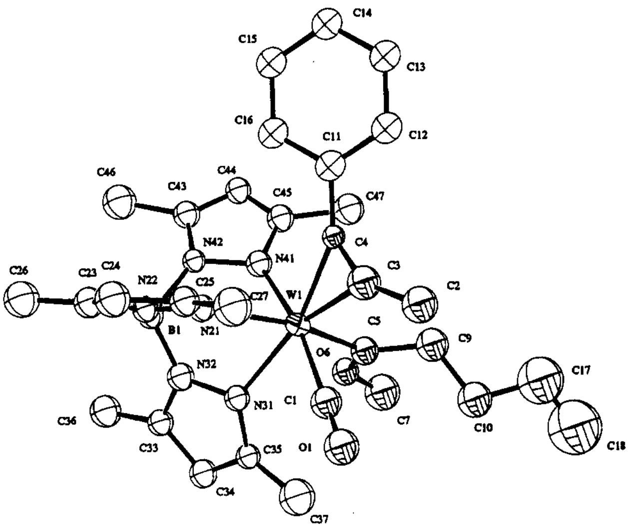


Figure 1. ORTEP drawing of [Tp′(CO)(PhC$_2$Me)W=C(OMe)CH$_2$CH$_2$CH$_2$Me][CF$_3$SO$_3$] (7).

d_{xz} to $\pi_{\|}$* back-bonding and $\pi_{\perp}$ to d_{xy} donation. This orientation optimizes the π-acid and π-donor interactions of the alkyne with the dπ orbitals on the tungsten while the CO can interact with both filled dπ orbitals. The single faced π-acceptor carbene ligand will be oriented so that the vacant carbene p orbital (considering the carbene fragment as neutral) can also overlap with metal d_{yz} to optimize back-bonding from the filled metal d_{yz} to the p orbital of the carbene unit (Figure 2). Mayr and coworkers[28] also found that the plane of the benzylidene ligand in (PMe$_3$)$_2$Cl$_2$(PhC≡CPh)W=CHPh was approximately orthogonal to and bisected the C≡C bond of the *cis* alkyne ligand.

Notice that the *cis* alkyne carbene fragment here is neither geometrically nor electronically poised to form a metallacyclobutene. Rotation of both the alkyne by 90° and rotation of the carbene by 90° would be required to set the stage for carbene–alkyne coupling. Furthermore, formation of a metallacyclobutene would lead to a "loss" of four electrons in the metal coordination shell, thus providing an additional barrier to coupling of these two *cis* ligands.

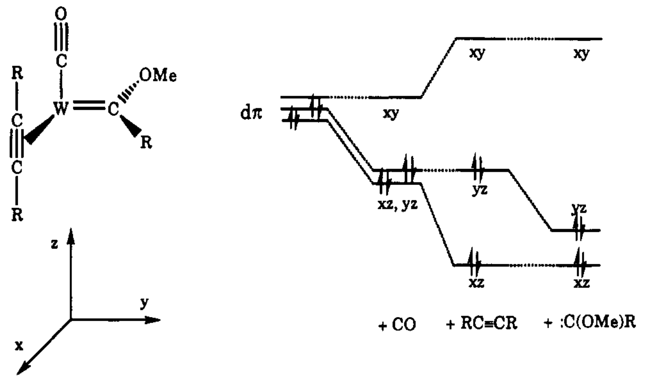
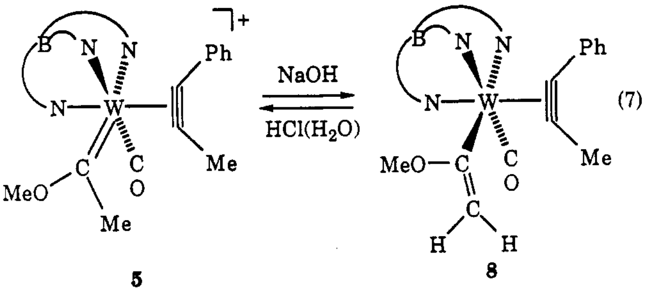


Figure 2. Qualitative molecular orbital scheme for the dπ-ligand interactions in Tp′(CO)(RC≡CR)W(=C(OMe)R).

A Neutral η^1-Vinyl Alkyne Complex. The cationic carbene complex containing a β-H on the carbene methyl substituent (5) reacts with base in methanol to form a neutral η^1-vinyl complex, Tp′(CO)(PhC$_2$Me)W(η^1-C(OMe)=CH$_2$) (8), in good yield (eq 7). This neutral air stable product was purified by recrystallization from CH$_2$Cl$_2$/MeOH. Protonation of 8 by HCl(aqueous) regenerated the methylmethoxycarbene cation 5 (eq 7).



The infrared spectrum of Tp′(CO)(PhC$_2$Me)W(η^1-C(OMe)=CH$_2$) displays a medium intensity absorption at 2548 cm^{-1} for ν_{BH} in the Tp′ ligand. This value is compatible with formation of a neutral compound.[11-13] The ν_{CO} absorption at 1893 cm^{-1} is comparable to that of the related neutral complex Tp′(CO)(PhC$_2$H)W(η^1-CPh=CH$_2$) (1896 cm^{-1})[12] which was prepared by hydride addition to [Tp′(CO)(PhC$_2$H)$_2$W]$^+$. Both ^{1}H and ^{13}C NMR spectra reveal the inequivalence of all three pyrazole rings, indicating C_1 symmetry. NMR data suggest that this complex is best described as containing a four-electron donor alkyne and an η^1-vinyl ligand rather than adopting an η^2-vinyl coordination with a two-electron donor alkyne. The ^{13}C NMR spectrum displays acetylenic ^{13}C resonances near 214 and 207 ppm. The two inequivalent vinyl protons (both broad) appear at 4.49 and 3.43 ppm. The vinyl protons in Tp′(CO)(PhC$_2$H)W(η^1-CPh=CH$_2$)[12] are doublets with a small geminal coupling of 4 Hz while the three-bond W-H coupling is 14.4 Hz for one proton and 8 Hz for the other proton. The C_α vinyl carbon here resonates near 208 ppm ($^1J_{WC}$ = 50 Hz), well downfield of that for C_α in Tp′(CO)(PhC$_2$H)W(η^1-CPh=CH$_2$) (162 ppm).[12] The C_β carbon appears near 90 ppm (as a doublet of doublets with one-bond proton–carbon coupling constants of 146 and 157 Hz) which is 30 ppm higher than the chemical shift for C_β in Tp′(CO)(PhC$_2$H)W(η^1-CPh=CH$_2$).[12]

Note that addition of nucleophiles to coordinated alkyne ligands is another common route to vinyl ligands: two-

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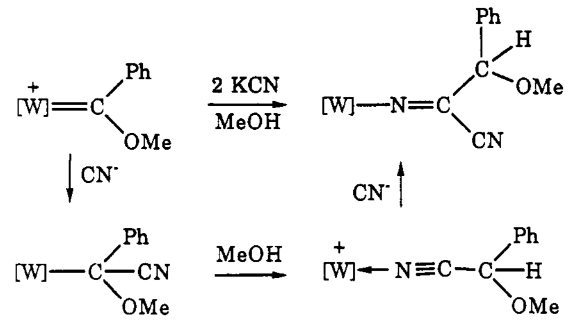
[28] Mayr, A.; Lee, K. S.; Kjelsberg, M. A.; Engen, D. V. *J. Am. Chem. Soc.* **1986**, *108*, 6079.

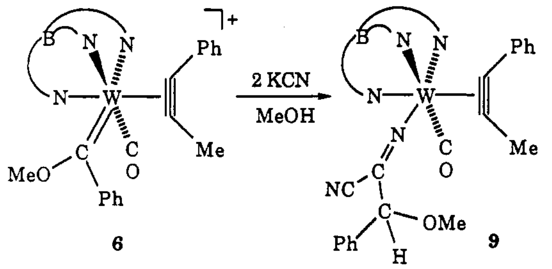
Scheme VII



[W] = Tp′(CO)(PhC≡CMe)W

electron donor alkynes form η^1-vinyls,[29] four-electron donor alkynes form η^2-vinyls,[13,30] and three-electron donor alkynes (in bis(alkyne) complexes) form either η^1-vinyls[12,31] or η^2-vinyls.[32]

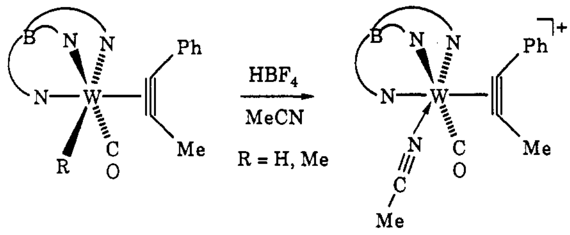
A Neutral Azavinylidene Alkyne Complex. Reaction of potassium cyanide with [Tp′(CO)(PhC$_2$Me)W(=C(OMe)Ph)]$^+$, at room temperature in methanol, results in formation of a neutral azavinylidene complex, Tp′(CO)(PhC$_2$Me)W(-N=C(CN)CH(OMe)Ph) (eq 8). Purification by chromatography on alumina followed by recrystallization from CH$_2$Cl$_2$/hexanes yields stable orange crystals. A color change from purple to orange and a 55 cm^{-1} drop in the single ν_{CO} absorption are consistent with formation of a neutral product.



(8)

The net reaction here incorporates two cyanide units and a proton to convert the carbene to the azavinylidene. This reaction may proceed by cyanide addition to the carbene ligand, protonation of the resulting alkyl ligand by methanol, nitrile coordination to the metal, and cyanide addition to the metal-bound nitrile C$_\beta$ (Scheme VII). Presumably the nitrile group could coordinate to the metal either before or after the MeOH protonation step. Protonation of related metal hydride[33] or metal alkyl[34] complexes in acetonitrile has generated an acetonitrile complex (eq 9).

The infrared spectrum of Tp′(CO)(PhC$_2$Me)W[N=C(CN)CH(OMe)Ph] displays medium intensity absorptions at 2544 cm^{-1} for ν_{BH} in the Tp′ ligand and at 2187 cm^{-1} for the nitrile triple bond. The ν_{CO} absorption at 1913 cm^{-1} is comparable to that for the related neutral complex Tp′(CO)(PhC$_2$Me)W(-N=C(CN)Me) (1917 cm^{-1})[11] which was prepared by cyanide addition to [Tp′(CO)(PhC$_2$Me)W(N≡CMe)]$^+$.



(9)

NMR data support the proposed formulation. The lone proton on the chiral carbon appears at 4.38 ppm as a singlet. ^{13}C NMR revealed the carbonyl carbon at 222.5 ppm ($^1J_{WC}$ = 151 Hz) and the azavinylidene carbon at 134 ppm (with two-bond tungsten–carbon coupling of 28 Hz, indicative of a linear W=N=C linkage). Azavinylidenes which have been structurally characterized have a linear M–N–C backbone.[35] We assume that donation from the nitrogen lone pair here is sufficient to dictate a linear geometry for the ground state. Even if there is some bending at nitrogen, we anticipate that the linear geometry is easily accessible, and therefore we interpret bonding and NMR properties in terms of a linear W=N=C linkage. We anticipate that the geometry of the metalloimine complex will place the plane of the N=CMeNu fragment perpendicular to the W–CO axis in order for the nitrogen lone pair to donate into the lone vacant dπ orbital. The alkyne carbons resonate at 161 ppm ($^1J_{WC}$ = 44 Hz, PhC≡CMe) and 159 ppm ($^1J_{WC}$ = 10 Hz, $^2J_{HC}$ = 7.5 Hz, PhC≡*C*Me) indicating that a shift from four-electron to "three-electron" donation from the alkyne ligand accompanied formation of the product. In other words, the alkyne $\pi_\perp$ electron pair in the product competes with the lone pair on nitrogen for the single vacant metal dπ orbital in the W^{2+} d^4 complex. Four-electron donor alkyne ligands normally have substantially lower field C-13 signals.[11-13]

Three isomers of the neutral azavinylidene complex **9** are evident by NMR in an 18:1:1 ratio. Isomers could potentially result from different alkyne orientations, restricted rotation around the tungsten nitrogen bond, or diastereomers from the chiral carbon and chiral metal center. The two isomers in Tp′(CO)(PhC$_2$Me)W(N=C(Nu)Me) result from restricted rotation about the metal–nitrogen bond[11] and are not due to different up and down orientations of the alkyne ligand. The chirality at carbon here presumably generates additional isomers.

Three-electron donor alkyne ligands are known in bis(alkyne)[12] and related complexes involving an alkyne and some other substantive π-donor ligand competing for a single vacant metal dπ acceptor orbital.[11]

Summary

Nucleophilic addition can occur at several sites in the monomers described here. The metal center, an alkyne carbon, or a nitrile carbon can add a nucleophile in related

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systems. Nucleophilic attack at a carbonyl ligand in [Tp'(CO)$_2$W(PhC$_2$Me)][BF$_4$] produces acyl complexes. Deprotonation of the neutral η^1-acyl alkyne complex Tp'(CO)(PhC$_2$Me)W(η^1-C(O)Me) occurs at C_β of the alkyne ligand instead of the acyl and when followed by addition of MeI yields a substituted η^2-alkyne complex, Tp'(CO)(PhC$_2$CH$_2$Me)W(η^1-C(O)Me), via an anionic η^2-allenyl intermediate. Protonation or methylation of the η^1-acyl complex at the acyl oxygen results in the formation of Fischer-type hydroxy- or methoxycarbene cations, Tp'(CO)(PhC$_2$Me)W=C(OE)R]$^+$. Restricted rotation about the metal–carbene double bond causes isomerization in some cases. A crystal structure of [Tp'(CO)(PhC$_2$Me)W=C(OMe)Bu^n][CF$_3$SO$_3$] shows a pseudooctahedral geometry with the alkyne ligand parallel to the carbonyl and perpendicular to the carbene ligand. Deprotonation of the methoxymethylcarbene ligand at the carbene methyl yields an alkyne η^1-vinyl complex, Tp(CO)(PhC$_2$Me)W(η^1-C(OMe)=CH$_2$). Cyanide addition to the carbene ligand in [Tp'(CO)(PhC$_2$Me)W=C(OMe)Ph][CF$_3$SO$_3$] in methanol solution initiates a double cyanide addition to form Tp'(CO)(PhC$_2$Me)WN=C(CN)(CH(OMe)Ph) in which the alkyne ligand competes with the azavinylidene nitrogen lone pair for donation to the lone vacant metal dπ orbital. Alkyne $\pi_\perp$ donation in our system competes with donation from the nitrogen lone pair of metalloimine or amido ligands,[11] but it dominates and inhibits additional donation from ancillary acyl, vinyl,[12] or carbene ligands.[12]

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Supplementary Material Available: Tables of anisotropic temperature factors and complete bond distances and angles for 7 (4 pages). Ordering information is given on any current masthead page.

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