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# An Investigation of Carbon−Fluorine Bond Functionalization. Versatile Reactivity of Tungsten(II) Fluoride Carbonyl Metallacycles with Alkynes

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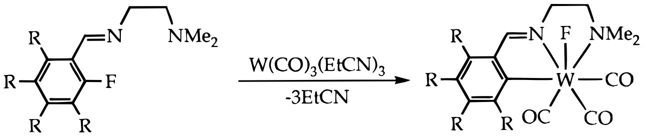
Metal-assisted functionalization of aromatic fluorocarbons is reported. Sequential carbon−fluorine oxidative addition and migratory insertion with electron-deficient alkynes are employed to construct novel tungsten(II) $\eta^2$-vinyl complexes in which net replacement of an aromatic carbon−fluorine bond by a carbon−carbon bond has ensued. A competitive reaction involving the formation of four-electron donor alkyne complexes is favored for electron-rich alkynes. Evidence suggests a two-electron donor alkyne complex may serve as a common intermediate in these transformations, which could either participate in the migratory insertion reaction or lose carbon monoxide to generate the four-electron donor alkyne complex. The observed partitioning of products appears to be controlled by the electronic profile of the coordinated alkyne as well as the nucleophilicity of the migrating aryl group. The migratory insertion reaction is regioselective for 1-phenyl-1-propyne with the insertion taking place at the phenyl-substituted alkyne carbon to afford **17**. Reaction of the nucleophilic tungsten(II) metallacycle **4** with the electronically unsymmetrical acetylene **18** affords two distinct and isolable $\eta^2$-vinyl isomers in a 56:44 ratio and suggests that there is not a significant electronic bias for the nucleophilic migration process. The solid state structures of the four-electron donor alkyne complex **9** and the $\eta^2$-vinyl complexes **16** and **17** have been determined.

## Introduction

Carbon−fluorine bond activation is an essential step in the design of useful transition metal reagents for the functionalization of fluorocarbons.[1] Our research group[2] has previously demonstrated that oxidative addition of an aromatic carbon−fluorine bond takes place at tungsten(0) to afford stable tungsten(II) metallacycles with the cleaved carbon and fluorine atoms both bound to the metal center as depicted below in eq 1.[3]



**1** R = F
**3** R = H

**2** R = F
**4** R = H

(1)

Although this chelate-assisted oxidative addition chemistry has been extended to other metals such as Mo,[4] Ni,[1a,4] and Pt,[5] little is known concerning the reaction chemistry of the resulting metallacycle systems which may lead to further elaboration of the C−F linkage.

The chemical modification of fluorocarbons presents a significant synthetic challenge, and examples describing the replacement of fluorine for groups other than hydrogen are rare.[2b,6] For the most part, chemistry

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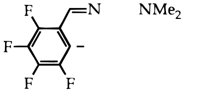
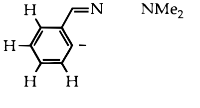
(3) Throughout the remainder of the manuscript, for convenience, (F$_4$-Pia) will refer to the ligand chelate fragment



and (Pia) will refer to the ligand chelate fragment



For the $\eta^2$-vinyl complexes, *cis* describes the stereochemistry between the inserted alkyne and the fluoride ligand.

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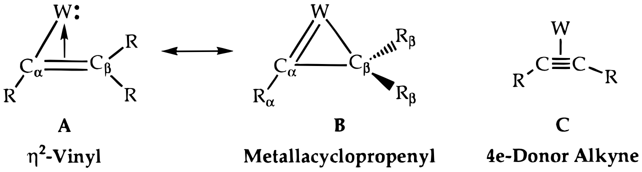
effecting the functionalization of fluorinated compounds has been limited to attack of highly fluorinated aromatic compounds by strong nucleophilic reagents; the usual stereochemistry is *para* to the unique groups present.[7] Transition metals have been shown to alter the site of attack to the *ortho* position in suitably designed ligand systems.[8] Recently, Crabtree and co-workers reported that a combination of $NH_3$ with mercury photosensitization can effect the functionalization of saturated fluorocarbons to unsaturated fluorinated amines.[9]

An alternative strategy for the functionalization of C−F bonds could involve the insertion of unsaturated organics into the metal−$C_{aryl}$ bonds formed in eq 1.[10] In this work we report that internal acetylenes react with **2** and **4** to afford $\eta^2$-vinyl **(A)**, or metallacyclopropenyl **(B)**, complexes by insertion into the W−$C_{aryl}$ bond or to yield four-electron donor coordination compounds **(C)** depending on the nature of the acetylene. The key feature of this work is that *net* replacement of an aromatic carbon−fluorine bond by a carbon−carbon linkage occurs under mild conditions via sequential C−F oxidative addition and alkyne insertion at a tungsten carbonyl complex. A portion of this work has been previously communicated.[11]



## Experimental Section

**General Procedures.** All manipulations involving air sensitive reagents were performed under an atmosphere of prepurified nitrogen using standard Schlenk techniques or a Vacuum Atmospheres glove box.[12] Solvents were purified as previously reported[13] except that acetonitrile was distilled under nitrogen from $CaH_2$ prior to use. Tungsten starting materials were prepared as previously reported.[2] All other chemicals were obtained from commercial sources and were used without further purification.

$^1H$, $^{13}C\{^1H\}$, $^{13}C\{^{19}F\}$, and $^{19}F$ NMR spectra were obtained on Varian XL-300 spectrometers at 300, 75, 75, and 281 MHz, respectively. All chemical shifts are reported in $\delta$ units with the following abbreviations: d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet, and apr = apparent. For $^{19}F$ and $^{13}C\{^{19}F\}$ NMR spectra, $CFCl_3$ was used as the external reference at $\delta$ 0.00. FTIR solution spectra were obtained in 0.1 mm $CaF_2$ cells. Melting points were obtained in open capillary tubes and reported in degrees Celsius. Mass spectra were obtained by Dr. Elliot Rachlin of the University of Utah on a Finnigan MAT 95 double-focusing high-resolution mass spectrometer operating with ionization by SIMS using a 20 keV cesium gun. Elemental analyses were performed by Atlantic Microlab, Norcross, GA, and Desert Analytics, Tucson, AZ.

**Preparation of *cis*-($F_4$-Pia)W(CO)$_2$(F)[$\eta^2$-C($C_6H_5$)=C-($C_6H_5$)] (7).** Under a nitrogen atmosphere, a 100 mL glass bomb sealed with a Teflon valve and equipped with a magnetic stir bar was charged with **2** (0.50 g, 0.93 mmol) ($\nu_{CO}$ 2020, 1934, and 1900 $cm^{-1}$) and diphenylacetylene (0.20 g, 1.1 mmol). Freshly distilled toluene (30 mL) was added by syringe, and the bright orange slurry was degassed, placed under reduced pressure, and heated to 60 °C for 18 h in an oil bath. Initial color change to dark red-orange was observed within 1 h; within 18 h the solution turned dark red-green. IR monitoring confirmed the reaction was complete ($\nu_{CO}$ 1966 and 1867 $cm^{-1}$). Precipitation was achieved by cooling the reaction mixture to room temperature over 12 h. Isolation by filtration followed by two washings with 5 mL of THF gave 0.22 g (0.32 mmol, 34% yield) of **7** as a green powder. X-ray quality crystals were grown by slow diffusion of pentane into a $CH_2Cl_2$ solution of **7**: mp 182−184 °C dec; IR $\nu_{CO}$ ($CH_2Cl_2$) 1970, 1873 $cm^{-1}$. Anal. Calcd for $WC_{27}H_{21}N_2O_2F_5 \cdot {}^1/_2\, CH_2Cl_2$: C, 45.45; H, 3.05; N, 3.85; F, 13.07. Found: C, 45.73; H, 2.96; N, 3.78; F, 12.84. Note that $CH_2Cl_2$ of crystallization was observed in the NMR spectra. $^1H$ NMR ($CDCl_3$) ($\delta$): N=CH 8.68 s, 1H; Ar *H* 7.69 m, 2H; Ar *H* 7.33 m, 3H; Ar *H* 7.11 m, 2H; Ar *H* 6.87 m, 1H; Ar *H* 6.49 m, 2H; C=N−C$H_2$ 4.65 m, 1H; C=N−C$H_2$ 3.78 m, 1H; N−C$H_3$ 3.19 s, 3H; N−$CH_3$ 2.94 d ($^4J_{HF}$ = 3 Hz), 3H; N−C$H_2$ 2.89 m, 1H; N−C$H_2$ 2.68 m, 1H. $^{13}C\{^1H\}$ NMR ($CDCl_3$) ($\delta$): W=$C_\alpha$ 230.1 s; W−*C*O 224.4 d ($^2J_{CF}$ = 5 Hz); W−*C*O 222.2 d ($^2J_{CF}$ = 56 Hz); N=*C*H 156.1 d ($^3J_{CF}$ = 6 Hz); $C_\alpha$−$C_{quat}$ 146.8 d ($^3J_{CF}$ = 3 Hz); $C_\beta$−$C_{quat}$ 144.2 s; Ar *C*H 129.4 s; Ar *C*H 129.4 s; Ar *C*H 128.4 s; Ar *C*H 127.9 s, 2C; Ar *C*H 127.6 s, 2C; Ar *C*H 127.3 s, 2C; Ar *C*H 123.6 s; C=N−*C*$H_2$ 62.3 s; N−*C*$H_2$ 60.9 s; N−*C*$H_3$ 55.8 s; N−*C*$H_3$ 50.5 d ($^3J_{CF}$ = 13 Hz); W−$C_\beta$ 25.7 s. Due to extensive C−F coupling, fluorinated aryl resonances could not be resolved. $^{19}F$ NMR ($CDCl_3$) ($\delta$): Ar *F* −126.6 m, 1F; Ar *F* −142.1 m, 1F; Ar *F* −142.9 m, 1F; W−*F* −152.9 s, 1F; Ar *F* −157.7 m, 1F.

**Preparation of ($F_4$-Pia)W(CO)(F)($CH_3CH_2C{\equiv}CCH_2CH_3$) (9).** As for **7**, compound **2** (0.32 g, 0.55 mmol), 3-hexyne (0.097 g, 1.2 mmol), and toluene (30 mL) were heated to 70 °C for 51 h in an oil bath. Initial color change to maroon was observed within 1 h, and within 51 h the solution turned dark blue. IR monitoring confirmed the reaction was complete ($\nu_{CO}$ 1912 $cm^{-1}$). Precipitation was achieved by addition of pentane to the reaction mixture and cooling the resulting solution to −10 °C. Isolation by filtration, followed by two washings with 10 mL of pentane afforded 0.24 g (1.0 mmol, 77% yield) of **9** as a purple powder. X-ray quality crystals were grown by slow diffusion of hexane into a $CH_2Cl_2$ solution of **9**: mp 169−171 °C; IR $\nu_{CO}$ (KBr) 1885 $cm^{-1}$. Anal. Calcd for $WC_{18}H_{21}N_2O_1F_5$: C, 38.59; H, 3.78; N, 5.00; F, 16.96. Found: C, 38.87; H, 3.68; N, 4.81; F, 16.75. $^1H$ NMR ($CDCl_3$) ($\delta$): N=C*H* 9.24 s, 1H; C=N−C$H_2$ 4.34 m, 1H; C=N−C$H_2$ 4.08 m, 1H; C≡C−C$H_2$ 3.69 m, 2H; N−C$H_2$ 3.22 m, 1H; C≡C−C$H_2$ 3.11 m, 2H; N−C$H_3$ 2.99 s, 3H; N−C$H_2$ 2.57 m, 1H; N−C$H_3$ 1.95 s, 3H; $CH_2$−C$H_3$ 1.22 t, 3H; $CH_2$−C$H_3$ 0.92 t, 3H. $^{13}C\{^1H\}$ NMR ($CDCl_3$) ($\delta$): W−*C*O 242.1 d ($^2J_{CF}$ = 11 Hz); C≡*C*−Et 219.9 d ($^2J_{CF}$ = 15 Hz); C≡*C*−Et 213.2 d ($^2J_{CF}$ = 31 Hz); N=*C*H 165.6 s; C=N−*C*$H_2$ 65.5 s; N−*C*$H_2$ 56.8 s; N−*C*$H_3$ 54.6 d ($^3J_{CF}$ = 7 Hz); N−*C*$H_3$ 49.7 s; C≡C−*C*$H_2$ 30.9 s; C≡C−*C*$H_2$ 28.1 s; $CH_2$−*C*$H_3$ 14.1 s; $CH_2$−*C*$H_3$ 13.6 s. Due to extensive C−F coupling, fluorinated aryl resonances could not be resolved. $^{19}F$ NMR ($CD_2Cl_2$) ($\delta$): Ar *F* −104.8 m, 1F; W−*F* −140.2 s, 1F; Ar *F* −141.7 m, 1F; Ar *F* −149.7 m, 1F; Ar *F* −161.7 m, 1F. $^{19}F$ NMR ($CD_2Cl_2$ + $D_2O$) ($\delta$): W−*F* −143.1 m, 1F.

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**Preparation of $(F_4\text{-Pia})W(CO)F(CH_3C{\equiv}CCH_3)$ (10).** As for **7**, complex **2** (0.29 g, 0.55 mmol), 2-butyne (0.15 mL, 1.9 mmol), and 20 mL of toluene were heated in an oil bath at a temperature of 90 °C for 2 h. Within 20 min the solution color changed to dark red, and within 40 min the solution was purple-blue. An IR spectrum of the crude product solution confirmed the reaction was complete ($\nu_{CO}$ 1914 cm$^{-1}$). The reaction solution was filtered through Celite, and the purple filtrate was collected. Crystallization was achieved by reduction of the toluene solvent volume to 10 mL, followed by addition of 5 mL of pentane and cooling to −10 °C. The solid was collected by filtration and washed with two 20 mL portions of pentane. Isolation afforded purple crystalline **10** in 72% yield (0.21 g, 0.39 mmol): mp 159−161 °C dec; IR $\nu_{CO}$ (KBr) 1902 cm$^{-1}$. Anal. Calcd for $WC_{16}F_5H_{17}N_2O\cdot{}^1/_8C_7H_8$: C, 37.28; H, 3.34; N, 5.15. Found: C, 37.57; H, 3.40; N, 5.14. Note that toluene of crystallization was observed in the NMR spectra. $^1$H NMR (−60 °C, $CD_2Cl_2$) ($\delta$): N=C−*H* 9.31 s, 1H; C=N−C*H*$_2$ 4.33 m, 1H; C=N−C*H*$_2$ 4.15 m, 1H; C≡C−C*H*$_3$ 3.09 s, 3H; N−C*H*$_2$ 3.09 m, 1H; N−C*H*$_3$ 2.90 s, 3H; N−C*H*$_2$ 2.55 m, 1H; C≡C−C*H*$_3$ 2.81 s, 3H; N−C*H*$_2$ 2.63 m, 1H; N−C*H*$_3$ 1.84 s, 3H. $^{13}$C{$^1$H} NMR (−60 °C, $CD_2Cl_2$) ($\delta$): W−*C*O 244.0 d ($^2J_{CF}$ = 10 Hz); C≡*C*−CH$_3$ 214.4 d ($^2J_{CF}$ = 15 Hz); C≡*C*−CH$_3$ 209.5 d ($^2J_{CF}$ = 32 Hz); N=*C*H 165.1 s; C=N−*C*H$_2$ 64.7 s; N−*C*H$_2$ 56.2 s; N−*C*H$_3$ 54.1 (under $CD_2Cl_2$ reference peak); N−*C*H$_3$ 48.9 s; C≡C−*C*H$_3$ 21.7 d ($^3J_{CF}$ = 3 Hz); C≡C−*C*H$_3$ 18.0 s. Due to extensive C−F coupling, fluorinated aryl resonances could not be resolved. $^{19}$F NMR (−60 °C, $CD_2Cl_2$) ($\delta$): Ar *F* −104.9 m, 1F; Ar *F* −140.4 m, 1F; W−*F* −145.7 s, 1F; Ar *F* −149.3 m, 1F; Ar *F* −160.7 m, 1F.

**Preparation of $(F_4\text{-Pia})W(CO)F(C_6H_5C{\equiv}CCH_3)$ (11).** As for **7**, complex **2** (0.24 g, 0.45 mmol), 1-phenyl-1-propyne (0.17 mL, 1.4 mmol), and 20 mL of toluene were heated in an oil bath at a temperature of 90 °C for 2 h. Within 20 min a purple color was evident and within 1 h the solution was dark blue. An IR spectrum of the crude product solution confirmed the reaction was complete ($\nu_{CO}$ 1922 cm$^{-1}$). The reaction solution was filtered through Celite, and the orange-brown insoluble matter was discarded. Crystallization was achieved by reduction of the toluene solvent volume to 10 mL, followed by addition of 15 mL of pentane and cooling to −10 °C. The solid was isolated by filtration and washed with two 20 mL portions of pentane and two 20 mL portions of hexanes. Isolation gave green-blue microcrystalline **11** in 81% yield (0.21 g, 0.36 mmol): mp 168−170 °C dec; IR $\nu_{CO}$ (KBr) 1903 cm$^{-1}$. Anal. Calcd for $WC_{21}F_5H_{19}N_2O$: C, 42.45; H, 3.22; N, 4.71. Found: C, 42.36; H, 3.24; N, 4.72. $^1$H NMR ($CD_2Cl_2$) ($\delta$): N=C−*H* 9.37 s, 1H; Ar *H* 7.30 m, 5H; C=N−C*H*$_2$ 4.20 m, 1H; C=N−C*H*$_2$ 4.10 m, 1H; C≡C−C*H*$_3$ 3.44 s, 3H; N−C*H*$_2$ 3.13 m, 1H; N−C*H*$_3$ 2.97 s, 3H; N−C*H*$_2$ 2.55 m, 1H; N−C*H*$_3$ 1.92 s, 3H. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) ($\delta$): W−*C*O 241.1 d ($^2J_{CF}$ = 11 Hz); C≡*C*−Ph 220.0 d ($^2J_{CF}$ = 14 Hz); C≡*C*−CH$_3$ 206.7 d ($^2J_{CF}$ = 34 Hz); N=*C*H 166.3 s; Ar−*C*$_{quat}$ 138.8 s; Ar *C*H 129.2 s, 2C; Ar *C*H 128.7 s; Ar *C*H 128.4 s, 2C; C=N−*C*H$_2$ 65.9 s; C=N−*C*H$_2$ 57.2 s; N−*C*H$_3$ 54.6 d ($^3J_{CF}$ = 7 Hz); N−*C*H$_3$ 50.1 s; C≡C−*C*H$_3$ 23.4 s. Due to extensive C−F coupling, fluorinated aryl resonances could not be resolved. $^{19}$F NMR ($CD_2Cl_2$) ($\delta$): Ar *F* −105.5 m, 1F; W−*F* −132.9 s, 1F; Ar *F* −141.1, 1F; Ar *F* −149.7 m, 1F; Ar *F* −161.1 m, 1F.

**Generation of $(F_4\text{-Pia})W(CO)F(C_4H_8O)$ (12).** Under a nitrogen atmosphere, a 50 mL Pyrex Schlenk flask equipped with a magnetic stir bar was charged with **2** (0.039 g, 0.073 mmol) and 25 mL of freshly distilled tetrahydrofuran. The flask was sealed with a septum equipped with a needle to maintain a strong and continuous nitrogen purge, and the reaction mixture was irradiated with a Hanovia 450 W medium-pressure Hg lamp at a distance of ca. 7 cm for 20 min. The solution changed to a dark cherry red color. An IR spectrum of the crude product solution confirmed the reaction was essentially complete ($\nu_{CO}$ 1957 and 1821 cm$^{-1}$). The tetrahydrofuran solvent was removed under reduced pressure, and the residue was redissolved in deuterated tetrahydrofuran for spectroscopic analysis $^{19}$F NMR (THF-$d_8$) ($\delta$): Ar *F* −116.6 m, 1F; Ar *F* −145.1, 1F; Ar *F* −163.4 m, 1F; Ar *F* −166.9 m, 1F; W−*F* −194.2 s, 1F.

**Preparation of *cis*-{$(Pia)W(CO)_2(F)[\eta^2\text{-}C(CF_3){=}C(CF_3)]$} (15).** Under a nitrogen atmosphere, a 100 mL glass bomb sealed with a Teflon valve and equipped with a magnetic stir bar was cooled to −196 °C and charged with perfluoro-2-butyne (1.3 g, 7.7 mmol). In a separate Schlenk flask, a slurry of **4** (1.0 g, 2.2 mmol) ($\nu_{CO}$ 2004, 1915, and 1881 cm$^{-1}$) in freshly distilled toluene (30 mL) was prepared, degassed and transferred under nitrogen by syringe to the glass bomb. The resulting bright orange solution was degassed by three freeze−pump−thaw cycles and warmed to room temperature. The reaction mixture was heated to 100 °C for 6 h in an oil bath. Initial color change to orange-brown was observed within 30 min, and within 6 h the solution turned ruby red. An IR spectrum of the crude product solution confirmed the reaction was complete ($\nu_{CO}$ 2008 and 1908 cm$^{-1}$). The solvent was removed in vacuo, and the crude solid was redissolved in a minimal amount of $CH_2Cl_2$ and filtered through a pad of Celite. The volume of the filtrate was reduced, and the product was recrystallized by the addition of hexanes ($CH_2Cl_2$:hexanes = 1:4) and cooling to −10 °C for 20 h. Isolation by vacuum filtration followed by three washings with 20 mL of toluene and drying gave 1.0 g (1.8 mmol, 79% yield) of **15** as an army green powder: mp 158−160 °C; IR $\nu_{CO}$ (KBr) 2013, 1914 cm$^{-1}$. Anal. Calcd for $WC_{17}H_{15}N_2O_2F_7\cdot{}^1/_3CH_2Cl_2$: C, 33.34; H, 2.53; N, 4.49; F, 20.29. Found: C, 33.63; H, 2.71; N, 4.42; F, 19.12. Note that $CH_2Cl_2$ of crystallization was observed in the NMR spectra. $^1$H NMR ($CD_2Cl_2$) ($\delta$): N=C−*H* 8.50 d ($^4J_{HF}$ = 1.70 Hz), 1H; Ar *H* 7.81 m, 1H; Ar *H* 7.69 m, 1H; Ar *H* 7.54 m, 1H; Ar *H* 7.45 m, 1H; C=N−C*H*$_2$ 4.66 m, 1H; C=N−C*H*$_2$ 3.87 m, 1H; N−C*H*$_3$ 3.09 s, 3H; N−C*H*$_3$ 2.92 d ($^4J_{HF}$ = 3.12 Hz), 3H; N−C*H*$_2$ 2.88 m, 1H; N−C*H*$_2$ 2.54 m, 1H. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) ($\delta$): N=*C*−H 166.4 s; W−*C* 137.2 s; Ar−*C*$_{quat}$ 136.3 s; Ar *C*H 135.5 s; Ar *C*H 134.3 s; Ar *C*H 133.9 s; Ar *C*H 128.7 s; C=N−*C*H$_2$ 62.3 s; N−*C*H$_2$ 60.1 d ($^3J_{CF}$ = 3 Hz); N−*C*H$_3$ 55.8 s; N−*C*H$_3$ 50.3 d ($^3J_{CF}$ = 14 Hz). $^{13}$C{$^{19}$F} NMR ($CD_2Cl_2$) ($\delta$): W−*C*O 223.0 d ($^2J_{CF}$ = 5 Hz); W−*C*O 222.9 ($^2J_{CF}$ = 56 Hz); W=C$_\alpha$−CF$_3$ 203.2 dq ($^2J_{CF}$ = 41 Hz); C$_\alpha$−*C*F$_3$ 131.8 q ($^1J_{CF}$ = 269 Hz); C$_\beta$−*C*F$_3$ 128.3 q ($^1J_{CF}$ = 266 Hz); W−*C*$_\beta$−CF$_3$ 37.6 dq (coupling could not be resolved). $^{19}$F NMR ($CD_2Cl_2$) ($\delta$): C$_\beta$−C*F*$_3$ −57.7 s, 3F; C$_\alpha$−C*F*$_3$ −58.9 s, 3F; W−*F* −137.5 s, 1F. $^{19}$F NMR ($CD_2Cl_2$ + $D_2O$) $\delta$ W−*F* −139.7 s, 1F.

**Preparation of *cis*-{$(Pia)W(CO)_2(F)[\eta^2\text{-}C(C_6H_5){=}C(C_6H_5)]$} (16).** Similar to **15**, complex **4** (0.35 g, 0.76 mmol), diphenylacetylene (0.35 g, 1.9 mmol), and 20 mL of freshly distilled toluene were heated to 100 °C in an oil bath. Initial color change to dark red was observed within 5 min, and within 30 min the solution color changed to dark green. IR monitoring confirmed the reaction was complete in 1.5 h ($\nu_{CO}$ 1956 and 1865 cm$^{-1}$). Crystallization of compound **16** was achieved by cooling the reaction mixture to room temperature over a time period of 2 h. Isolation by filtration followed by three washings with 20 mL of pentane (to remove unreacted alkyne) gave 0.32 g (0.52 mmol, 68% yield) of dark forest green microcrystalline **16**. X-ray quality crystals were grown by slow diffusion of pentane into a $CH_2Cl_2$ solution of **16**: mp 158−160 °C dec; IR $\nu_{CO}$ ($CH_2Cl_2$) 1957, 1861 cm$^{-1}$; $\nu_{CO}$ (KBr) 1948, 1840 cm$^{-1}$. Anal. Calcd for $WC_{27}H_{25}N_2O_2F$: C, 52.96; H, 4.12; N, 4.57. Found: C, 52.07; H, 4.14; N, 4.55. $^1$H NMR ($CD_2Cl_2$) ($\delta$): N=CH 8.43 s, 1H; Ar *H* 7.78 m, 3H; Ar *H* 7.57 m, 2H; Ar *H* 7.38 m, 4H; Ar *H* 7.02 m, 2H; Ar *H* 6.81 m, 1H; Ar *H* 6.43 m, 2H; C=N−C*H*$_2$ 4.49 m, 1H; C=N−C*H*$_2$ 3.75 m, 1H; N−C*H*$_3$ 3.16 s, 3H; N−CH$_3$ 2.90 d ($^4J_{HF}$ = 3 Hz), 3H; N−C*H*$_2$ 2.83 m, 1H; N−C*H*$_2$ 2.57 m, 1H. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) ($\delta$): W=*C*$_\alpha$ 228.4 d ($^2J_{CF}$ = 2 Hz); W−*C*O 226.8 d ($^2J_{CF}$ = 6 Hz); W−*C*O 222.9 d ($^2J_{CF}$ = 57 Hz); N=*C*H 165.9 s; C$_\alpha$−*C*$_{quat}$ 149.4 d ($^3J_{CF}$ = 4 Hz); C$_\beta$−*C*$_{quat}$ 144.5 s; Ar−*C*$_{quat}$ 143.6 s; Ar−*C*$_{quat}$ 137.2 s; Ar *C*H 135.7 s; Ar *C*H 135.4 s; Ar *C*H 134.1 s; Ar *C*H 131.7 s; Ar *C*H 130.1 s; Ar *C*H 128.9 s; Ar *C*H 128.7 s; Ar *C*H 128.3 s; Ar *C*H 127.1 s; Ar *C*H 122.6 s; C=N−CH$_2$ 62.1 s; N−*C*H$_2$ 60.3 s; N−*C*H$_3$ 55.8 s; N−*C*H$_3$ 50.3 d ($^3J_{CF}$ = 13 Hz); W−*C*$_\beta$ 43.4 s. $^{19}$F NMR ($CD_2Cl_2$) ($\delta$): W−*F* −145.3 s.

**Preparation of *cis*-{(Pia)W(CO)$_2$(F)[$\eta^2$-C(C$_6$H$_5$)=C(CH$_3$)]} (17).** As for **15**, compound **4** (0.55 g, 1.2 mmol), 1-phenyl-1-propyne (0.30 g, 2.6 mmol), and 20 mL of toluene were heated to 70 °C in an oil bath. Initial color change to dark red was observed within 1 h. IR monitoring confirmed the reaction was complete in 6 h ($\nu_{CO}$ 1947 and 1851 cm$^{-1}$). Crystallization was achieved by the addition of pentane and cooling to −10 °C for 20 h. Isolation by filtration followed by two washings with 20 mL of pentane gave 0.05 g (9.1 mmol, 16% yield) of red microcrystalline **17**. X-ray quality crystals were grown by slow diffusion of pentane into a $CH_2Cl_2$ solution of **17**: mp 181−183 °C; IR $\nu_{CO}$ ($CH_2Cl_2$) 1954, 1854 cm$^{-1}$, $\nu_{CO}$ (Nujol) 1947, 1850 cm$^{-1}$. Anal. Calcd For $WC_{22}H_{23}N_2O_2F$: C, 48.02; H, 4.21; N, 5.09. Found: C, 47.74; H, 4.27; N, 4.98. $^1$H NMR ($CD_2Cl_2$) ($\delta$): N=C*H* 8.39 s, 1H; Ar *H* 7.66 m, 1H; Ar *H* 7.53 m, 2H; Ar *H* 7.41 m, 1H; Ar *H* 7.03 m, 2H; Ar *H* 6.77 m, 1H; Ar *H* 6.39 m, 2H; $\mathrm{C{=}N{-}C}H_2$ 4.39 m, 1H; $\mathrm{C{=}N{-}C}H_2$ 3.73 m, 1H; $\mathrm{N{-}C}H_3$ 3.11 s, 3H; $\mathrm{C_\alpha{-}C}H_3$ 3.09 d ($^4J_{HF}$ = 2 Hz), 3H; $\mathrm{N{-}C}H_2$ 2.87 m, 1H; $\mathrm{N{-}C}H_3$ 2.84 d ($^3J_{HF}$ = 3 Hz), 3H; $\mathrm{N{-}C}H_2$ 2.57 m, 1H. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) ($\delta$): $\mathrm{W{=}}C_\alpha$ 237.2 s; W−*C*O 223.7 d ($^2J_{CF}$ = 5 Hz); W−*C*O 217.6 d ($^2J_{CF}$ = 58 Hz); N=*C*H 165.7 d ($^3J_{CF}$ = 3 Hz); $\mathrm{C_\beta{-}}C_{quat}$ 150.3 d ($^3J_{CF}$ = 4 Hz); $\mathrm{Ar{-}}C_{quat}$ 143.9 s; $\mathrm{Ar{-}}C_{quat}$ 137.3 s; Ar *C*H 135.3 s; Ar *C*H 134.5 s; Ar *C*H 132.9 s; Ar *C*H 128.6 s, 2C; Ar *C*H 127.3 s, 2C; Ar *C*H 126.9 s; Ar *C*H 122.4 s; $\mathrm{C{=}N{-}}C\mathrm{H_2}$ 62.1 s; $\mathrm{N{-}}C\mathrm{H_2}$ 60.1 s; $\mathrm{N{-}}C\mathrm{H_3}$ 55.7 d ($^3J_{CF}$ = 6 Hz); $\mathrm{N{-}}C\mathrm{H_3}$ 50.2 d ($^3J_{CF}$ = 8 Hz); $\mathrm{W{-}}C_\beta$ 41.9 s; $\mathrm{C_\alpha{-}}C\mathrm{H_3}$ 29.6 d ($^3J_{CF}$ = 6 Hz). $^{19}$F NMR ($CD_2Cl_2$) ($\delta$): W−*F* −160.3 s. $^{19}$F NMR ($CD_2Cl_2$ + $D_2O$) ($\delta$): W−F −162.8 s.

**Preparation of Phenyl(4′-(trifluoromethyl)phenyl)acetylene (18).** A 100 mL flame-dried Schlenk flask was charged with phenyl(tributyltin)acetylene[14] (2.9 g, 7.4 mmol), 4-iodobenzotrifluoride (2.0 g, 7.4 mmol), tetrakis(triphenylphosphine)palladium(0) (2.6 g, 30 mol %), copper iodide (0.67 g, 48 mol %), and 50 mL of DMF. The reaction mixture was degassed, placed under $N_2$, and heated in an oil bath at 85 °C for 72 h. The reaction mixture was diluted with 100 mL of $Et_2O$ and filtered through a coarse-fritted funnel. The resultant mixture was washed with saturated aqueous $NH_4Cl$ and water (2 × 200 mL). The organic layer was separated and washed with an aqueous 10% KF solution to polymerize the tin-containing byproducts. The aqueous layer was separated and extracted with $Et_2O$ (2 × 50 mL). The combined organic extracts were washed with saturated aqueous $NH_4Cl$, dried ($MgSO_4$), and concentrated. The crude product was diluted with 200 mL of hot hexane and filtered through a plug of $SiO_2$. Concentration in vacuo afforded 1.8 g of **18** (7.3 mmol, 97% yield) as a pale yellow flocculent solid: mp 104−106 °C dec; IR $\nu_{C\equiv C}$ (KBr) 2220 cm$^{-1}$. EI MS (70 eV): *m/z* 246 (M$^+$). Anal. Calcd for $C_{15}F_3H_9$: C, 73.17; H, 3.68. Found: C, 73.25; H, 3.92. $^1$H NMR ($CDCl_3$) ($\delta$): Ar *H* 7.62 m, 4H; Ar *H* 7.39 m, 5H. $^{13}$C{$^1$H} NMR ($CDCl_3$) ($\delta$): Ar *C*H 131.8 s; Ar *C*H 131.7 s; $\mathrm{CF_3{-}}C_{quat}$ 129.8 q ($^2J_{CF}$ = 32 Hz); Ar *C*H 128.8 s; Ar *C*H 128.8 s; $\mathrm{Ar{-}}C_{quat}$ 127.0 s; Ar *C*H 125.3 q ($^3J_{CF}$ = 4 Hz); $\mathrm{Ar{-}}C\mathrm{F_3}$ 123.9 q ($^1J_{CF}$ = 270 Hz); $\mathrm{Ar{-}}C_{quat}$ 122.5 s; $\mathrm{C{\equiv}}C\mathrm{{-}ArCF_3}$ 91.7 s; $\mathrm{C{\equiv}}C\mathrm{{-}Ar}$ 87.9 s. $^{19}$F NMR ($CDCl_3$) ($\delta$): $\mathrm{Ar{-}C}F_3$ −61.4.

**Preparation of *cis*-{(Pia)W(CO)$_2$(F)[$\eta^2$-C(C$_6$H$_5$)=C(4-C$_6$H$_4$CF$_3$)]} (19).** As for **15**, complex **4** (0.25 g, 0.55 mmol), **18** (0.31 g, 1.3 mmol), and 20 mL of toluene were heated to 90 °C in an oil bath. Initial color changed to dark red was observed within 1 h, and IR monitoring confirmed the reaction was complete in 4 h ($\nu_{CO}$ 1960 and 1865 cm$^{-1}$). Crystallization of compound **19** was achieved by slow cooling of the reaction mixture to room temperature over a time period of 12 h. Isolation by filtration followed by two washings with 20 mL of hexane (to remove unreacted alkyne) gave 0.11 g (0.15 mmol, 27% yield) of olive green microcrystalline **19**: mp 180−182 °C dec; IR $\nu_{CO}$ ($CH_2Cl_2$) 1964, 1867 cm$^{-1}$, $\nu_{CO}$ (KBr) 1962, 1867 cm$^{-1}$. Anal. Calcd for $WC_{28}H_{24}N_2O_2F_4\cdot{}^1/_2C_7H_8$: C, 52.08; H, 3.89; N, 3.86. Found: C, 52.09; H, 3.90; N, 3.92. Note that toluene of crystallization was observed in the NMR spectra. $^1$H NMR ($CD_2Cl_2$) ($\delta$): N=CH 8.45 d ($^4J_{HF}$ = 1 Hz), 1H; Ar *H* 7.86 m, 2H; Ar *H* 7.63 m, 4H; Ar *H* 7.39 m, 1H; Ar *H* 7.21 m, 1H; Ar *H* 7.04 m, 2H; Ar *H* 6.83 m, 1H; Ar *H* 6.42 m, 2H; $\mathrm{C{=}N{-}C}H_2$ 4.53 m, 1H; $\mathrm{C{=}N{-}C}H_2$ 3.78 m, 1H; $\mathrm{N{-}C}H_3$ 3.16 s, 3H; $\mathrm{N{-}CH_3}$ 2.91 d ($^4J_{HF}$ = 3 Hz), 3H; $\mathrm{N{-}C}H_2$ 2.85 m, 1H; $\mathrm{N{-}C}H_2$ 2.56 m, 1H. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) ($\delta$): W−*C*O 226.4 d ($^2J_{CF}$ = 6 Hz); $\mathrm{W{=}}C_\alpha$ 225.2 br s; W−*C*O 223.2 d ($^2J_{CF}$ = 57 Hz); N=*C*H 166.1 s; $\mathrm{C_\alpha{-}}C_{quat}$ 148.6 d ($^3J_{CF}$ = 4 Hz); $\mathrm{C_\beta{-}}C_{quat}$ 146.8 s; $\mathrm{Ar{-}}C_{quat}$ 144.2 s; Ar *C*H 135.7 s; Ar *C*H 134.2 s; Ar *C*H 131.5 s; Ar *C*H 129.6 s; Ar *C*H 128.8 s; Ar *C*H 127.3 s; Ar *C*H 127.2 s; Ar $C\mathrm{CF_3}$ 125.9 q ($^2J_{CF}$ = 4 Hz); Ar *C*H 123.1 s; $\mathrm{C{=}N{-}}C\mathrm{H_2}$ 62.2 s; $\mathrm{N{-}}C\mathrm{H_2}$ 60.4 s; $\mathrm{N{-}}C\mathrm{H_3}$ 55.9 s; $\mathrm{N{-}}C\mathrm{H_3}$ 50.5 d ($^3J_{CF}$ = 13 Hz); $\mathrm{W{-}}C_\beta$ 44.3 s. The $CF_3$ resonance could not be detected. $^{19}$F NMR ($CD_2Cl_2$) ($\delta$): $\mathrm{Ar{-}C}F_3$ −63.8 s, 3F; W−*F* −138.8 s, 1F.

**Preparation of *cis*-{(Pia)W(CO)$_2$(F)[$\eta^2$-C(4-C$_6$H$_4$CF$_3$)=C(C$_6$H$_5$)]} (20).** The green filtrate remaining after the isolation of **19** was collected, and the toluene solvent was removed under reduced pressure. The green residue was redissolved in a minimal amount of methylene chloride (10 mL), was filtered through a pad of Celite, and was recrystallized by the addition of 20 mL of hexanes and cooling to −10 °C for 20 h. Isolation by vacuum filtration followed by three successive washings with 20 mL of hexanes (to remove any unreacted alkyne) and drying gave 0.14 g (0.19 mmol, 34% yield) of crystalline green **20**: mp 150−152 °C dec; IR $\nu_{CO}$ ($CH_2Cl_2$) 1964, 1867 cm$^{-1}$, $\nu_{CO}$ (KBr) 1958, 1859 cm$^{-1}$. Anal. Calcd for $WC_{28}H_{24}N_2O_2F_4\cdot{}^1/_2CH_2Cl_2$: C, 47.23; H, 3.75; N, 3.86. Found: C, 46.63; H, 3.81; N, 3.56. Note that methylene chloride of crystallization was observed in the NMR spectra. $^1$H NMR ($CD_2Cl_2$) ($\delta$): N=CH 8.44 d ($^4J_{HF}$ = 2 Hz), 1H; Ar *H* 7.77 m, 3H; Ar *H* 7.59 m, 2H; Ar *H* 7.40 m, 4H; Ar *H* 6.56 m, 2H; $\mathrm{C{=}N{-}C}H_2$ 4.48 m, 1H; $\mathrm{C{=}N{-}C}H_2$ 3.78 m, 1H; $\mathrm{N{-}C}H_3$ 3.18 s, 3H; $\mathrm{N{-}CH_3}$ 2.89 d ($^4J_{HF}$ = 3 Hz), 3H; $\mathrm{N{-}C}H_2$ 2.86 m, 1H; $\mathrm{N{-}C}H_2$ 2.60 m, 1H. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) ($\delta$): $\mathrm{W{=}}C_\alpha$ 227.5 br s; W−*C*O 226.5 d ($^2J_{CF}$ = 6 Hz); W−*C*O 222.4 d ($^2J_{CF}$ = 57 Hz); N=*C*H 165.9 s; $\mathrm{C_\alpha{-}}C_{quat}$ 154.8 d ($^3J_{CF}$ = 3 Hz); $\mathrm{C_\beta{-}}C_{quat}$ 143.8 s; $\mathrm{Ar{-}}C_{quat}$ 143.2 s; $\mathrm{Ar{-}}C_{quat}$ 137.1 s; Ar *C*H 135.7 s; Ar *C*H 134.5 s; Ar *C*H 131.7 s; Ar *C*H 130.4 s; Ar *C*H 129.1 s; Ar *C*H 128.7 s; Ar *C*H 128.5 s; Ar *C*H 127.5 s; Ar $C\mathrm{CF_3}$ 123.9 q ($^2J_{CF}$ = 4 Hz); $\mathrm{C{=}N{-}}C\mathrm{H_2}$ 62.1 s; $\mathrm{N{-}}C\mathrm{H_2}$ 60.2 s; $\mathrm{N{-}}C\mathrm{H_3}$ 55.9 s; $\mathrm{N{-}}C\mathrm{H_3}$ 50.4 d ($^3J_{CF}$ = 13 Hz); $\mathrm{W{-}}C_\beta$ 42.9 s. The $CF_3$ resonance could not be detected. $^{19}$F NMR ($CD_2Cl_2$) ($\delta$): $\mathrm{Ar{-}C}F_3$ −62.9 s, 3F; W−*F* −147.9 s, 1F.

**Crystallography.** Data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer with Cu K$\alpha$ radiation (for **9** and **16**), or Mo K$\alpha$ radiation (for **17**), using the $\theta-2\theta$ scan technique for a crystal mounted on a glass fiber. Cell constants were obtained from 25 reflections with 10° < $2\theta$ < 25° and the space groups were determined from systematic absences and subsequent least-squares refinement. Standard reflections showed no decay during data collection. Lorentz, polarization, and empirical absorption ($\Psi$ scans) corrections were applied. The structure was solved by the standard heavy-atom techniques with SPD/VAX package.[15] Final refinement included all non-hydrogen atoms as anisotropic contributions and hydrogens as fixed isotropic contributions. Scattering factors, as well as $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[16] A summary of the crystallographic data and structure refinement is collected in Table 1.

## Results

**Alkyne Insertion into a Perfluoroaryl−Metal Bond.** As depicted in Scheme 1, treatment of **2** with diphenylacetylene in toluene at 60 °C for 18 h yields a

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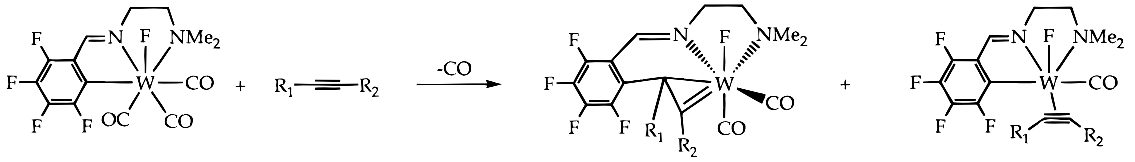
**Table 1. Summary of Crystallographic Data for Tungsten(II) Complexes 9, 16, and 17**

| | **9** | **16** | **17** |
|---|---|---|---|
| molecular formula | $WF_5O_1N_2C_{18}H_{21}$ | $WF_1O_2N_2C_{27}H_{25}$ | $WF_1Cl_2O_2N_2C_{23}H_{25}$ |
| fw, g mol$^{-1}$ | 560.223 | 612.361 | 649.229 |
| space group | $P21/c$(No. 14) | $P21/n$(No. 14) | $P\bar{1}$(No. 2) |
| crystal system | monoclinic | monoclinic | triclinic |
| cell constants | $a = 11.863(1)$ Å<br>$b = 8.298(2)$ Å<br>$c = 20.683(2)$ Å<br>$\beta = 103.282(8)°$ | $a = 12.407(1)$ Å<br>$b = 12.1689(9)$ Å<br>$c = 15.560(2)$ Å<br>$\beta = 92.638(6)°$ | $a = 10.183(1)$ Å<br>$b = 10.64(2)$ Å<br>$c = 13.185(2)$ Å<br>$\beta = 113.68(2)°$<br>$\gamma = 102.61(2)°$ |
| cell volume, Å$^3$ | 1981.73 | 2346.83 | 1212.72 |
| $Z$ | 4.0 | 4.0 | 2.0 |
| calculated density, g cm$^3$ | 1.878 | 1.733 | 1.779 |
| crystal dimensions, mm$^3$ | 0.36 × 0.15 × 0.09 | 0.22 × 0.19 × 0.12 | 0.42 × 0.36 × 0.18 |
| absorption coefficient ($\mu$), cm$^{-1}$ | 114.525 | 95.072 | 51.218 |
| radiations, Å | $\lambda$(Cu K$\alpha$) = 1.54056 | $\lambda$(Cu K$\alpha$) = 1.54056 | $\lambda$(Mo K$\alpha$) = 0.71073 |
| no. of reflections measured | 3747 | 4413 | 6154 |
| no. of unique reflections | 3310 | 3989 | 5844 |
| $2\theta$ range, deg | 4.00−130.00° | 4.00−130.00° | 4.00−56.00° |
| scan technique | $\theta/2\theta$ scan | $\theta/2\theta$ scan | $\theta/2\theta$ scan |
| scan width, deg | 0.9000 + 0.1400 (tan $\theta$) | 0.9000 + 0.1400 (tan $\theta$) | 0.8000 + 0.3400 (tan $\theta$) |
| data collection position | bisecting, $\omega = 0$ | bisecting, $\omega = 0$ | bisecting, $\omega = 0$ |
| decay correction | anisotropic | anisotropic | none |
| absorption correction | empirical | empirical | empirical |
| minimum % transmission | 78.3160 | 46.9586 | 77.9552 |
| maximum % transmission | 98.6302 | 99.9510 | 99.8572 |
| average % transmission | 87.8983 | 75.2681 | 91.9289 |
| highest peak in final difference Fourier, e/Å$^3$ | 1.08 | 0.73 | 0.87 |
| maximum $\Delta\rho$ value in Fourier map, e/Å$^3$ | 1666.5 | 1458.7 | 571.6 |
| ignorance factor, $p$ | 0.05 | 0.04 | 0.05 |
| no. of observations, $I < 3.00\ \sigma(I)$ | 2611 | 3458 | 5087 |
| no. of variables | 244 | 301 | 281 |
| data to parameter ratio | 10.701 | 11.488 | 18.103 |
| shift to error ratio | 0.013 | 0.004 | 0.001 |
| error in an observation of unit weight | 1.3381 | 1.1482 | 0.7173 |
| $R$ | 0.0426 | 0.0301 | 0.0259 |
| $R_w$ | 0.0509 | 0.0364 | 0.0297 |

**Scheme 1**



**2**

**5a** $R_1{=}R_2{=}CF_3$
**5b** $R_1{=}R_2{=}Ph$
**5c** $R_1{=}Ph;\ R_2{=}CH_3$
**5d** $R_1{=}R_2{=}CH_3$
**5e** $R_1{=}R_2{=}CH_2CH_3$

**6** $R_1{=}R_2{=}CF_3$
**7** $R_1{=}R_2{=}Ph$

**8** $R_1{=}R_2{=}Ph$
**9** $R_1{=}R_2{=}CH_2CH_3$
**10** $R_1{=}R_2{=}CH_3$
**11** $R_1{=}Ph;\ R_2{=}CH_3$

dark green solution composed of two complexes, **7** ($\nu_{CO}$ 1966, 1867 cm$^{-1}$) and **8** ($\nu_{CO}$ 1915 cm$^{-1}$), in a 3:1 ratio as quantified by $^1$H NMR spectroscopy via integration of the imine resonance for each compound and $^{19}$F NMR spectroscopy by integration of the metal-bound fluoride resonance for each compound. The product ratios remained constant throughout the course of the reaction, which suggests that the resulting complexes are not interconvertible under the reaction condition and neither compound is an intermediate in the formation of the other. The minor product was identified as the unstable four-electron donor complex **8**, and the major product was recognized as the insertion product **7**, which was isolated in 34% yield.

The identification of **7** as an $\eta^2$-vinyl, or metallacyclopropene, complex was ascertained from diagnostic resonances in the $^{13}$C{$^1$H} NMR spectrum.[17] The carbenoid character of C$_\alpha$ is reflected by a large downfield chemical shift ($\delta$ 230.1), whereas the four-coordinate carbon, C$_\beta$, has a significant upfield chemical shift that appears at $\delta$ 25.7. The fluoride was determined to be *cis* to one CO ($\delta$ 224.4, $^2J_{CF} = 5$ Hz) and *trans* to the second CO ($\delta$ 222.2, $^2J_{CF} = 56$ Hz), leaving the inserted acetylene *cis* to the fluoride. The disposition of the ligands about the tungsten(II) metal center is in agreement with the structurally characterized compound **6**.[13]

The $^{19}$F and $^1$H NMR spectra for compound **7** are essentially identical to related $\eta^2$-vinyl complexes containing the fluorinated $\eta^3$-[C,N,N′] ligand framework.[11,13] Thus, the $^1$H NMR spectrum for **7** displays four different highly coupled multiplet resonances ($\delta$ 4.65, 3.78, 2.89, and 2.68) for the methylene protons on the backbone; each resonance integrates to one proton. This nonequivalence illustrates not only the chirality of the pseudo six-coordinate tungsten(II) metal center but also the retained coordination of the ligand in solution.[13,18]

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(17) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Mann, B. E.; Taylor, B. F. *$^{13}$C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.

(18) (a) Kiplinger, J. L.; Richmond, T. G. *Polyhedron*, in press. (b) Looman, S. D.; Giese, S.; Arif, A. M.; Richmond, T. G. *Polyhedron* **1996**, *15*, 2809−2811.

**Table 2. Relevant Spectroscopic Parameters for Tungsten(II) Four-Electron Donor and $\eta^2$-Vinyl Complexes**

| complex | $\nu_{CO}$, cm$^{-1}$ (toluene) | $\delta(C_\alpha)$, ppm | $\delta$(CO), ppm | $\delta(C_\beta)$, ppm | $\delta(C_{alkyne})$, ppm | $\delta$(W−F), ppm |
|---|---|---|---|---|---|---|
| **7** | 1966, 1867 | 230.1 | 224.4 d ($^2J_{CF}$ = 5 Hz)<br>222.1 d ($^2J_{CF}$ = 56 Hz) | 25.7 | N/A | −152.9 |
| **9** | 1912 | N/A[a] | 242.1 d ($^2J_{CF}$ = 11 Hz) | N/A | 219.9 d ($^2J_{CF}$ = 15 Hz)<br>213.2 d ($^2J_{CF}$ = 31 Hz) | −140.2 |
| **10** | 1914 | N/A | 244.0 d ($^2J_{CF}$ = 10 Hz) | N/A | 214.4 d ($^2J_{CF}$ = 15 Hz)<br>209.5 d ($^2J_{CF}$ = 32 Hz) | −145.7 |
| **11** | 1922 | N/A | 241.1 d ($^2J_{CF}$ = 11 Hz) | N/A | 220.0 d ($^2J_{CF}$ = 14 Hz)<br>206.7 d ($^2J_{CF}$ = 34 Hz) | −132.9 |
| **15** | 2008, 1908 | 203.2 | 223.0 d ($^2J_{CF}$ = 5 Hz)<br>222.9 d ($^2J_{CF}$ = 56 Hz) | 37.6 | N/A | −137.5 |
| **16** | 1956, 1865 | 228.4 ($^2J_{CF}$ = 2 Hz) | 226.8 d ($^2J_{CF}$ = 6 Hz)<br>222.9 d ($^2J_{CF}$ = 57 Hz) | 43.4 | N/A | −145.3 |
| **17** | 1947, 1851 | 237.2 | 223.7 d ($^2J_{CF}$ = 5 Hz)<br>217.6 d ($^2J_{CF}$ = 58 Hz) | 41.9 | N/A | −160.3 |
| **19** | 1960, 1865 | 225.2 | 226.4 d ($^2J_{CF}$ = 6 Hz)<br>223.2 d ($^2J_{CF}$ = 57 Hz) | 44.3 | N/A | −138.8 |
| **20** | 1960, 1865 | 227.5 | 226.5 d ($^2J_{CF}$ = 6 Hz)<br>222.4 d ($^2J_{CF}$ = 57 Hz) | 42.9 | N/A | −147.9 |

[a] N/A = not applicable.

The $^{19}$F NMR spectrum for **7** shows five resonances as expected with appropriate integrations. The fluoride *ortho* to the $\eta^2$-vinyl moiety is easily identified and appears as a distinctive broad resonance at $\delta$ −126.6, and the W−F resonance is located as a singlet at $\delta$ −152.9.

**Formation of Four-Electron Donor Alkyne Coordination Complexes.** The six-coordinate, four-electron donor alkyne complexes **9**−**11** were obtained as air stable microcrystalline solids in 72−81% isolated yields upon treatment of **2** with the appropriate electron-rich internal acetylene in toluene under reduced pressure at elevated temperatures (see Scheme 1). Reaction of terminal acetylenes with **2** under similar conditions gave only intractable decomposition products. The formulation of **9**−**11** as four-electron donor alkyne complexes was determined from salient spectroscopic data which are listed in Table 2. The low-field acetylenic $^{13}C\{^1H\}$ chemical shift values exhibited by complexes **9**−**11** suggest that the alkyne ligand in these compounds is serving as a four-electron donor.[19] The lone carbonyl ligand resonates at $\delta$ 242.1 ($^2J_{CF}$ = 11 Hz) for **9**, at $\delta$ 244.0 ($^2J_{CF}$ = 10 Hz) for **10**, and at $\delta$ 241.1 ($^2J_{CF}$ = 11 Hz) for **11**. The large $^2J_{CF}$ for the alkyne contact carbons in these complexes signifies that the alkyne ligand is *trans* to the metal fluoride,[11] leaving the carbonyl ligand *cis* to the fluoride.[20]

The tungsten−fluoride resonance is quite sensitive to substitution at tungsten and shifts to much lower field for the alkyne complexes relative to the parent tungsten complex **2**, which displays a $^{19}$F NMR resonance at $\delta$ −223.4 ($CDCl_3$) for W−F.[2] Specific fluoride chemical shifts for W−F are as follows: $\delta$ −145.2 for **9**, $\delta$ −145.7 for **10**, and $\delta$ −132.4 for **11**. This denotes a significant decrease in the basicity of the fluoride ligand and indicates that the alkyne ligand functions as a voracious $\pi$ acid.

Dynamic NMR studies on the complexes revealed that a barrier to alkyne rotation exists. At −20 °C, the alkyne methyl resonances in the $^1$H NMR spectrum of **9** were observed as a pair of triplets separated by 116 Hz. Coalescence was observed at 68 °C, and a value of $\Delta G^\ddagger$ = 68.2 kJ/mol was calculated for the rotation of the alkyne ligand about the M−alkyne bond.[21] Similarly for complex **10**, a value of $\Delta G^\ddagger$ = 63.2 kJ/mol was calculated for alkyne rotation by monitoring the alkyne methyl resonances which were observed in the $^1$H NMR as a pair of singlets separated by 83 Hz at −60 °C and which coalesced at 40 °C. For complex **11**, coalescence of the W−F resonance (at −20 °C, $\Delta\nu$ = 1090 Hz) was observed at 75 °C to calculate a $\Delta G^\ddagger$ = 63.2 kJ/mol.

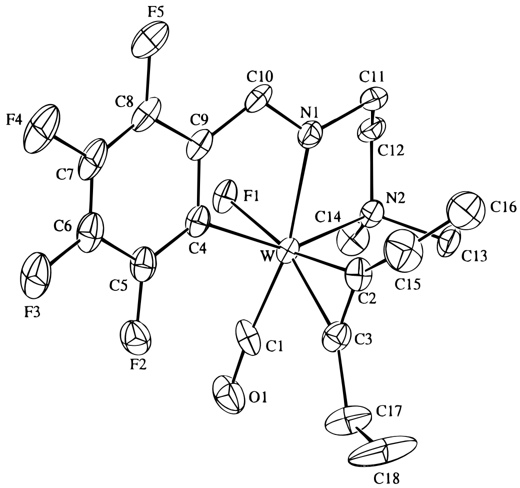

**Figure 1.** ORTEP representation of the tungsten(II) four-electron donor alkyne complex **9**.

**X-ray Crystallographic Analysis of 9.** The solid state structure of **9** is shown in Figure 1. Data collection information, selected bond distances, and bond angles for **9** are presented in Tables 1 and 3. The geometry around the tungsten(II) metal center can be viewed as roughly octahedral if one considers that the alkyne ligand with a small $C_{alkyne}$−W−$C_{alkyne}$ (C2−W−C3) bond angle of 39.9(4)° occupies a single coordination site. The rigid $\eta^3$-[C,N,N′] imine ligand lies meridionally disposed about the tungsten metal center with C4−W−N2 = 149.3(4)° and C1−W−N1 = 161.8(5)°, leaving the fluoride *trans* to the alkyne ligand with F1−W−C2 = 163.6(4)° and F1−W−C3 = 158.4(4)°. Thus, the $C_2$ alkyne

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(19) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288−3290.

(20) (a) Blake, A. J.; Cockman, R. W.; Ebsworth, E. A. V.; Holloway, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 529−530. (b) Darensbourg, D. J.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1995**, *34*, 4933−4934.

(21) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(22) For a comprehensive review on d$^4$ alkyne complexes, see: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

**Table 3. Selected Distances (Å) and Angles (deg) for ($F_4$-Pia)W(CO)(F)($CH_3CH_2C{\equiv}CCH_2CH_3$) 9**[a]

| | | | |
|---|---|---|---|
| W−F1 | 2.005(5) | W−C2 | 1.99(1) |
| W−N1 | 2.164(8) | W−C3 | 2.00(1) |
| W−N2 | 2.282(8) | W−C4 | 2.20(1) |
| W−C1 | 1.89(1) | C2−C3 | 1.30(2) |
| F1−W−N1 | 77.9(3) | C3−C2−C15 | 138.(1) |
| F1−W−N2 | 76.4(2) | N2−W−C4 | 149.3(4) |
| F1−W−C1 | 83.9(4) | W−C2−C3 | 71.3(7) |
| F1−W−C2 | 163.6(4) | C2−W−C3 | 37.9(4) |
| F1−W−C3 | 158.4(4) | W−C3−C2 | 70.8(7) |
| F1−W−C4 | 84.4(2) | C1−W−C2−C3 | 2.9 |
| C2−C3−C17 | 139.(1) | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

unit is *cis* to the CO and lies parallel to the W−CO axis (C1−W−C2−C3 = 2.9°). The short W−$C_{alkyne}$ bond distances of 1.99(1) and 2.00(1) Å are indicative of W−C multiple bond character. The lengthened C≡C bond distance of 1.30(2) Å is also consistent with a tightly bound four-electron donor alkyne.[22] Accordingly, the alkyne−ethyl substituent is bent away from the metal with C2−C3−C15 = 138(1)° and C3−C2−C17 = 139(1)° as would be expected for $sp^2$ hybridization of C2 and C3.

**Alkyne Insertion versus Carbon Monoxide Substitution: Evidence for a Two-Electron Donor Alkyne Complex Intermediate.** The reactions shown in Scheme 1 require temperatures of at least 60 °C (the same temperature required for isotopic incorporation of $^{13}CO$ into the parent compound **2**),[13] which suggests that the rate-limiting step is loss of CO. The four-electron donor alkyne and $\eta^2$-vinyl complexes are *not* interconvertible moieties, even in the presence of carbon monoxide.

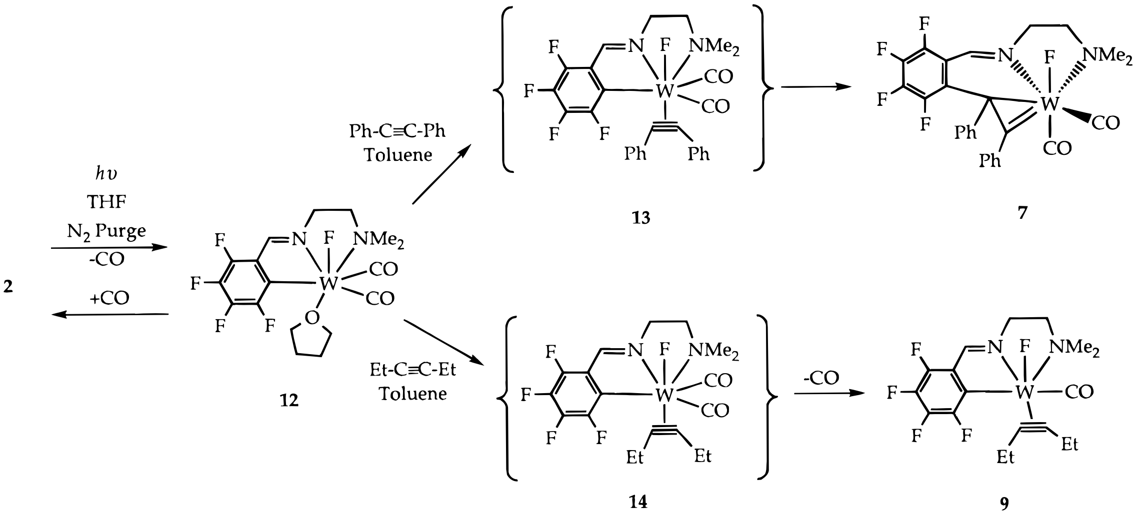
Since thermal CO loss is rate determining in the chemistry in Scheme 1, photochemical methods were employed to observe intermediates in the migration process. Room temperature photolysis (450 W Hg lamp filtered through Pyrex) of **2** in the presence of the appropriate acetylene gives **7** and **9**, but again no intermediates were detected. Photolysis of **2** in THF affords the solvato complex **12**, which could not be isolated but was characterized by $^{19}F$ NMR and IR spectroscopies.

Two very strong carbonyl stretches at 1957 and 1830 $cm^{-1}$ in THF solution signal the presence of **12**. The low-energy carbonyl two-band pattern is consistent with more electron density at the metal center and is expected upon loss of a strong $\pi$-acid carbonyl ligand and subsequent replacement by a $\sigma$-donor THF ligand. Also consistent with this formulation is the W−F resonance at $\delta$ −194.2, which is significantly downfield from that for **2** ($\delta$ −223.4, $CDCl_3$). Unfortunately, the labile complex exhibits only limited stability and rapidly decomposes in the absence of tetrahydrofuran.

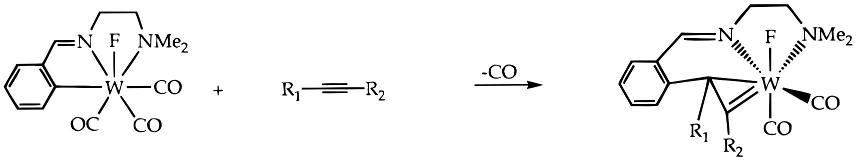
Other $\sigma$-donor solvents such as $CH_3CN$ and benzonitrile are competent ligands and displace THF to afford different adduct complexes with $\nu_{CO}$ = 1951 and 1830 $cm^{-1}$ and $\nu_{CO}$ = 1953 and 1836 $cm^{-1}$, respectively. These donor complexes were also unstable and resisted isolation, decomposing upon isolation and removal of solvent. Alternatively, the $\sigma$-bound nitrile adducts could be produced by photolysis of **2** in acetonitrile or benzonitrile solution.

As illustrated in Scheme 2, exposure of a solution of **12** to CO cleanly regenerates **2**. Reaction of **12** with diphenylacetylene and 3-hexyne *at room temperature* affords **7** and **9**, respectively. Thus, aryl migration is

**Scheme 2**



**Scheme 3**



**4**

**5a** $R_1=R_2=CF_3$
**5b** $R_1=R_2=Ph$
**5c** $R_1=Ph$; $R_2=CH_3$
**18** $R_1=4\text{-}C_6H_4\text{-}CF_3$; $R_2=Ph$

**15** $R_1=R_2=CF_3$
**16** $R_1=R_2=Ph$
**17** $R_1=Ph$; $R_2=CH_3$
**19** $R_1=Ph$; $R_2=4\text{-}C_6H_4\text{-}CF_3$
**20** $R_1=4\text{-}C_6H_4\text{-}CF_3$; $R_2=Ph$

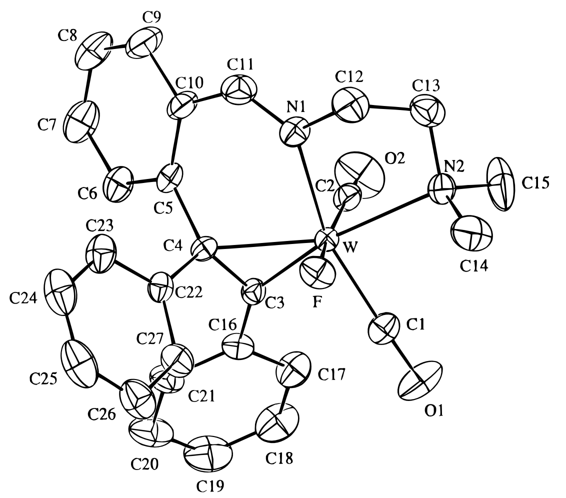


**Figure 2.** ORTEP representation of the tungsten(II) $\eta^2$-vinyl complex **16**.

fast at room temperature as is production of the four-electron donor alkyne complexes.

**Alkyne Insertion into a Nonfluorinated Aryl Carbon−Tungsten(II) Bond.** Reaction of internal electron-deficient alkynes with **4** results in exclusive $\eta^2$-vinyl complex formation as illustrated in Scheme 3. Treatment of a toluene solution of **4** with the acetylenes **5a**−**c** and **18** at elevated temperatures under reduced pressure affords the $\eta^2$-vinyl complexes **15**−**20**. As with their fluorinated congeners, the $\eta^2$-vinyl complexes **15**−**20** all display the essential spectroscopic features consistent with their assigned $\eta^2$-vinyl compositions as shown in Table 2. The $^{13}C\{^1H\}$ NMR chemical shift of $C_\alpha$ resonates at higher field as the electron demand of the alkylidene substituent increases in the series $CH_3$ < Ph < $CF_3$. Also consistent with the amount of electron density removed from the metal center by the cyclic carbene is a similar progression toward lower field strength observed in the $^{19}F$ NMR spectra for the W−F resonances with $\delta$ −137.54 for **15**, $\delta$ −145.31 for **16**, and $\delta$ −160.31 for **17**. The small $^2J_{CF}$ coupling of 2 Hz in the complex **16** is consistent with the assigned *cis* arrangement between the inserted alkyne and the metal fluoride ligand.[13]

Interestingly, electron-rich acetylenes 2-butyne and 3-hexyne display no reactivity with metallacycle **4**; reactions at elevated temperatures result in decomposition of starting materials with formation of intractable products. Likewise, terminal alkynes such as phenylacetylene and 3,3,3-trifluoropropyne do not afford any productive chemistry upon reaction with metallacycle **4**.

**X-ray Crystallographic Analyses of 16 and 17.** The molecular structures of the $\eta^2$-vinyl complexes **16** and **17** were confirmed by X-ray crystallography and are shown in Figures 2 and 3, respectively, where the atomic numbering scheme for each compound is defined. Data collection information, selected bond distances, and bond angles for **16** and **17** are presented in Tables 1 and 4.

Compounds **16** and **17** exhibit several structural features which are common[22] to $\eta^2$-vinyl complexes: (1) The orientation of the two $C_\beta$ substituents are roughly orthogonal to the $MC_\alpha C_\beta$ plane. (2) There are short $M-C_\alpha$ distances (1.976(6) and 1.966(5) Å for **16** and **17**, respectively) in the metal−carbon double-bond range. (3) The $M-C_\beta$ bond distances (2.214(6) and 2.206(5) Å) are in the metal−carbon single-bond range. (4) $C_\alpha-C_\beta$ bond distances are suggestive of double-bond character (1.454(8) and 1.435(7) Å). For both compounds **16** and **17**, comparable crystallographic data were obtained supporting their formulation as $\eta^2$-vinyl complexes. Clearly, the $C_\beta$ carbons in both compounds are approximately tetrahedral and are consistent with an $\eta^2$-vinyl composition rather than an $\eta^1$-vinyl structure where M, $C_\alpha$, $C_\beta$, and the two $C_\beta$ substituents would lie in a plane.[23] It should be noted that, in both compounds **16** and **17**, the sum of the angles around $C_\alpha$(C3) add up to 360° as expected for an $sp^2$ center.

The geometry around the tungsten(II) metal center in the $\eta^2$-vinyl compounds can be described as roughly octahedral if one considers that the $\eta^2$-vinyl moiety occupies a single coordination site. Specific $\eta^2$-vinyl

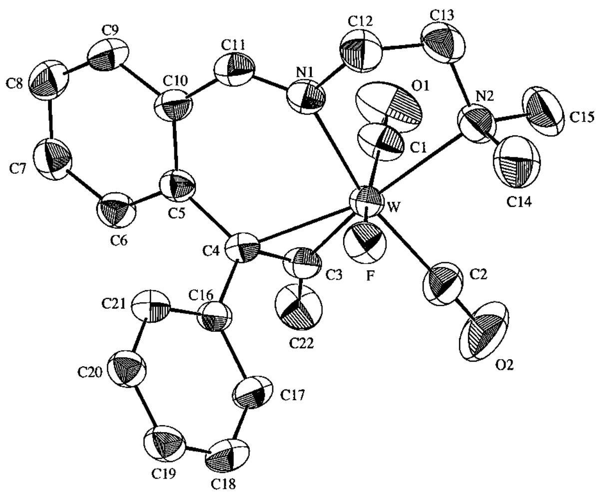


**Figure 3.** ORTEP representation of the tungsten(II) $\eta^2$-vinyl complex **17**.

**Table 4. Selected Distances (Å) and Angles (deg) for the Tungsten(II) $\eta^2$-Vinyl Complexes 16 and 17**[a]

| **16** | | **17** | |
|---|---|---|---|
| W−F | 2.002(3) | W−F | 2.044(3) |
| W−N1 | 2.185(5) | W−N1 | 2.195(4) |
| W−N2 | 2.352(5) | W−N2 | 2.344(4) |
| W−C1 | 1.957(6) | W−C1 | 1.960(6) |
| W−C2 | 1.949(6) | W−C2 | 1.976(6) |
| W−C3 | 1.976(6) | W−C3 | 1.966(5) |
| W−C4 | 2.214(6) | W−C4 | 2.206(5) |
| C3−C4 | 1.454(8) | C3−C4 | 1.435(7) |
| W−C4−C3 | 61.1(3) | W−C4−C3 | 61.1(3) |
| F−W−C1 | 93.4(2) | F−W−C1 | 168.0(2) |
| F−W−C2 | 171.6(2) | F−W−C2 | 97.1(2) |
| F−W−C3 | 111.4(2) | F−W−C3 | 116.8(2) |
| F−W−C4 | 91.2(2) | F−W−C4 | 90.1(2) |
| N1−W−N2 | 76.4(2) | N1−W−N2 | 77.5(2) |
| N1−W−C1 | 162.3(2) | N1−W−C2 | 167.8(2) |
| C3−C4−C5 | 117.0(5) | C3−C4−C5 | 117.5(4) |
| N1−W−C4 | 81.9(2) | N1−W−C4 | 84.4(2) |
| C3−C4−C22 | 119.7(5) | C3−C4−C16 | 118.9(4) |
| N2−W−C3 | 159.9(2) | N2−W−C3 | 156.9(2) |
| N2−W−C4 | 158.2(2) | N2−W−C4 | 161.3(2) |
| C5−C4−C22 | 116.4(5) | C5−C4−C16 | 114.6(4) |
| C3−W−C4 | 40.1(2) | C3−W−C4 | 39.7(2) |
| W−C3−C4 | 78.8(3) | W−C3−C4 | 79.2(3) |
| W−C3−C16 | 149.0(4) | W−C3−C22 | 148.5(4) |
| C4−C3−C16 | 132.0(5) | C4−C3−C22 | 132.3(5) |
| C16−C3−C4−C22 | 68.6 | C22−C3−C4−C16 | 72.3 |
| C16−C3−C4−C5 | −81.4 | C22−C3−C4−C5 | −72.9 |

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

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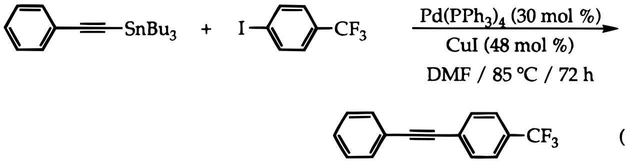
(23) (a) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Botrill, M.; Green, M.; Orpen, G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 927−939. (b) Reger, D. L. *Acc. Chem. Res.* **1988**, *21*, 229−235.

bond angles are as follows: C3−W−C4 = 40.1(2)° for **16** and C3−W−C4 = 39.7(2)° for **17**. A common feature extant in both **16** and **17** is that the rigid tridentate $\eta^3$-[C,N,N′] imine ligand adopts a meridional arrangement about the tungsten metal center. In both complexes, the inserted alkyne is approximately *cis* to the fluoride (C3−W−F = 111.4(2)° and C4−W−F = 91.2(2)° for **16**; C3−W−F = 116.8(2)° and C4−W−F = 90.1(2)° for **17**) and one carbonyl ligand (C1−W−F = 93.4(2)° for **16** and C2−W−F = 97.1(2)° for **17**) and *trans* to the second carbonyl ligand (C2−W−F = 171.6(2)° for **16** and C1−W−F = 168.0(2)° for **17**).

**Regiochemistry of the Alkyne Insertion.** As illustrated in Scheme 3, the migratory insertion reaction is regioselective for the unsymmetrical acetylene, 1-phenyl-1-propyne, with the insertion taking place at the electron-deficient, phenyl-substituted alkyne carbon (versus the electron-rich, methyl-substituted alkyne carbon).[24] To probe the regioselectivity where only electronic factors are different, the acetylene **18** was synthesized via standard Pd(0) coupling protocol in 97% yield (eq 2).[25] Elemental analysis, mass spectrometry, and $^1$H, $^{19}$F, and $^{13}$C{$^1$H} NMR data support the proposed structure.



(2)

**18**

Reaction of **18** with the metallacycle **4** in toluene solution at 90 °C for 4 h under reduced pressure affords a mixture of the isomeric $\eta^2$-vinyl complexes **19** and **20** in 56 and 44% yields, respectively, as determined using $^{19}$F NMR spectroscopy from integration of the trifluoromethyl and W−F resonances (Scheme 3).

The $\eta^2$-vinyl isomers **19** and **20** possess different solubility properties and are easily separated by crystallization. As reported in Table 2, both complexes display $^1$H, $^{19}$F, and $^{13}$C{$^1$H} NMR spectra essentially identical to those of complexes **15**−**17** as well as contain the vital spectroscopic features diagnostic for their formulation as $\eta^2$-vinyl complexes.[22] Noting the trends presented above for the $\eta^2$-vinyl complexes **15**−**17**, the NMR data for compounds **19** and **20** are consistent with the indicated regiochemistry for the alkyne insertion (Scheme 3). Compound **19** evinces an alkylidene resonance in the $^{13}$C{$^1$H} NMR at $\delta$ 225.2 and a W−F resonance in the $^{19}$F NMR at $\delta$ −138.7, whereas the alkylidene carbon in compound **20** resonates further downfield at $\delta$ 227.5 and the W−F resonates further upfield at $\delta$ −147.9, both consistent with a greater electron density on $C_\alpha$ (and less electron density at the metal center) containing the *p*-$CF_3C_6H_4$ fragment.

## Discussion

**Metal-Assisted Functionalization of Fluorocarbons.** The use of transition metal complexes to mediate ligand-based transformations on fluorinated substrates is not well developed due to the great strength of the carbon−fluorine bond.[1] The progression from compound **1** to **6** and **7** and from compound **3** to **15**−**20** is indeed unusual and exploits a rare migration reaction of a fluorinated ligand to afford robust $\eta^2$-vinyl complexes in which *net* replacement of a carbon−fluorine bond with a carbon−carbon bond has taken place. This transformation utilizes known oxidative addition chemistry in conjunction with migratory insertion of unsaturated organic compounds to sequentially activate and chemically modify carbon−fluorine bonds under mild conditions.

**$\eta^2$-Vinyl Complex versus Four-Electron Donor Alkyne Complex Formation.** Reactions of tungsten(II) fluoride carbonyl metallacycles with internal acetylenes afford a mixture of $\eta^2$-vinyl and four-electron donor alkyne complexes. Compatible with other $\eta^2$-vinyl systems, all of the $\eta^2$-vinyl complexes reported in this work exhibit a large downfield $^{13}$C{$^1$H} NMR chemical shift for the alkylidene carbon as well as a significant upfield shift for the four-coordinated carbon in the metallacyclopropenyl moiety (Table 2).[22] Similarly, the four-electron donor alkyne complexes show large downfield $^{13}$C{$^1$H} NMR chemical shifts below $\delta$ 200 that serve as a fingerprint for an alkyne donating four electrons to a metal center (Table 2).[19] Not only does this description abide by the 18-electron formalism, but these chemical shifts clearly contrast three- and two-electron donor alkyne ligands which have $^{13}$C{$^1$H} NMR resonances in the $\delta$ 140−190 and $\delta$ 90−120 ranges, respectively.

Consistent with low symmetry of the molecules, the $\eta^2$-vinyl complexes show two carbonyl resonances in the carbon spectrum. The carbonyl ligand *trans* to the fluoride ligand possesses a large $^2J_{CF}$ (∼56 Hz) and the other carbonyl, which is *cis* to the fluoride, has a small $^2J_{CF}$ (∼5 Hz).[11,13,20] Furthermore, these $\eta^2$-vinyl complexes do not manifest any dynamic behavior on the NMR time scale. This contrasts with the several $\eta^2$-vinyl systems reported by Green,[26] Templeton,[27] and Davidson[28] that undergo a variety of fluxional processes, which are attributed to a windshield-wiper motion (less than 90° rotation) of the $\eta^2$-vinyl fragment. Presumably, the steric constraint imposed by the rigid tridentate $\eta^3$-[C,N,N′] chelate ligand prevents this classical windshield-wiper motion from occurring (rotation of the $\eta^2$-vinyl ligand). Any dynamic process would require a disconnection/reconnection of the $C_\beta$ and the aromatic carbon, which is highly unlikely.

Although the $\eta^3$-[C,N,N′] chelate is rigid, the alkyne ligand in complexes **9**−**11** is dynamic and barriers to rotation of 15−17 kcal/mol were measured which are similar to other d$^4$ W(II) *cis*-$L_4M(CO)(RC{\equiv}CR)$ complexes.[22] As reported for all octahedral d$^4$ $L_4M(CO)(RC{\equiv}CR)$ complexes characterized to date, the four-electron donor alkyne complexes possess a *cis*-$M(CO)(RC{\equiv}CR)$ fragment in which the CO and alkyne ligands adopt a parallel arrangement. Alignment of the alkyne parallel to the W−CO axis uniquely positions $\pi_\perp$ to overlap the lone vacant metal d$\pi$ orbital in the octahedral geometry.

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The $\eta^2$-vinyl complexes and the four-electron donor complexes may share a common two-electron donor alkyne complex intermediate. The THF adduct **12** enables the formation of the $\eta^2$-vinyl complexes and the four-electron donor complexes presented in this work in minutes at room temperature, which supports the notion that these complexes arise from a common intermediate. Importantly, since the $\eta^2$-vinyl complexes and the four-electron donor complexes do not interconvert under the conditions used for their synthesis, neither of them is an intermediate in the formation of the other.

Organometallic $\eta^2$-vinyl complexes are of interest because a variety of catalytic chemical transformations postulate the crucial participation of vinyl intermediates stabilized by a metal center.[29] Thus, aryl migration at a tungsten(II) two-electron donor alkyne complex is significant because it provides a new avenue to access $\eta^2$-vinyl complexes. Previous synthetic approaches to $\eta^2$-vinyl complexes have involved the external attack of nucleophiles (hydrides,[26,30] thiols and thiolates,[28bc,31] isonitriles,[32] nitrogen,[33] and phosphorus[28ad,30d,32,34] reagents) on coordinated four-electron donor alkyne ligands.

**Alkyne Insertion with a Highly Fluorinated Migrating Group.** Although metal-mediated couplings of perfluoroalkenes and perfluoroalkynes are well precedented, migratory insertion reactions are quite rare presumably due to the increased strength and reduced nucleophilicity of the metal−carbon bond compared to those of hydrocarbon analogues.[1a,13,35] The diverse reactivity of the metallacycles **2** and **4** presented in this work further underscores this trend. Whereas the highly fluorinated metallacycle **2** forms the $\eta^2$-vinyl complex **7** in low yields accompanied with the generation of the four-electron donor complex **8**, the nucleophilic metallacycle **4** affords only the $\eta^2$-vinyl complex **16** in high yield. In the case of 1-phenyl-propyne, complex **2** affords only the four-electron donor alkyne complex **11**, whereas complex **4** affords only the $\eta^2$-vinyl complex **17**. The sluggish migratory aptitude of the pentafluorophenyl group has been exploited by Espinet and co-workers to isolate a rare palladium complex with mutually *cis* olefin and $C_6F_5$ groups and then to study the kinetics of the subsequent migratory insertion of the olefin into the $C_6F_5$−Pd bond.[36] Thus, it is noteworthy that the migration of the highly fluorinated metallacycle in **2** is facile at ambient temperature. Terminal acetylenes exhibit disappointing reactivity with **2** and **4**. This may be a consequence of reaction of the basic fluoride with the alkyne proton or polymerization of the alkyne. Both problems were noted in the low-yield synthesis of the four-electron donor cyanoacetylene adduct of **2**.[37]

The $\eta^2$-vinyl complexes are chemically robust toward multiple alkyne insertions into the W−$C_{aryl}$ bond. This contrasts with the alkyne reactivity of related 16-electron later transition metal complexes which readily undergo multiple insertion reactions to form large metallacycle complexes as well as novel heterocyclic ring systems upon metal extrusion.[10ab,38]

Only one regioisomer was isolated from the insertion reaction of **4** with 1-phenyl-1-propyne, albeit in low yield. Since both steric and electronic factors are different for this acetylene, we prepared the electronically unsymmetrical acetylene **18** to determine any electronic bias to the insertion process. Isomeric complexes **19** and **20** were in obtained in high yield with a 56:44 ratio favoring insertion into the more electron-rich phenyl side rather than the $CF_3$−phenyl site of the alkyne. The difference is small and suggests that there is not a great electronic bias for the nucleophilic migration process.

## Conclusion

We have demonstrated that under mild conditions oxidative addition of strong aromatic carbon−fluorine bonds in conjunction with migratory insertion of unsaturated organic compounds at a tungsten(II) metal center can be employed for the elaboration of carbon−fluorine bonds. A competitive reaction involving formation of four-electron donor alkyne complexes is favored for electron-rich alkynes. A two-electron donor alkyne complex may be a common intermediate in these transformations which could either participate in the migratory insertion reaction or lose carbon monoxide to afford the four-electron donor alkyne complex. Although these ligand-based systems are limited with respect to catalytic chemistry, they do serve as model compounds for the systematic studies of structure and reactivity directed toward catalytic activation and functionalization of carbon−fluorine bonds.

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**Supporting Information Available:** Tables giving full crystallographic data for **9**, **16**, and **17**, including bond distances, bond angles, torsional angles, final positional and general displacement parameters, and least-squares planes (57 pages). See any current masthead page for ordering information.

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