Organometallics **1997,** *16,* 246−254

Influence of π-Conflict on Structure and Reactivity. Comparative Study of η^2-Nitriles and η^2-Alkynes as Four-Electron Donor Ligands in Tungsten(II) Fluoride Carbonyl Systems

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This work describes the synthesis, structures, and reactivity studies of a series of novel η^2-nitrile and η^2-alkyne complexes in which the sidebound nitrile and alkyne ligands serve as four-electron donor ligands. In these tungsten(II) carbonyl fluoride complexes, both strong π-acceptor and π-donor ligands are extant and therefore π effects dominate the structure and reactivity manifested by these systems. The alkyne and nitrile ligands are oriented *cis* and parallel to the π-acid carbonyl ligand in these pseudooctahedral complexes. From the spectroscopic and crystallographic data it is evident that the η^2-nitrile ligand functions as a better π-acid/poorer π-base than the η^2-alkyne ligand. This results in greater electron density at the metal center for the alkyne complexes compared to the nitrile complexes and has a dramatic influence on the coordination geometry of the flexible η^3-[C,N,N′] chelate ligand system. For the nitrile complexes, the nitrile is *trans* to the fluoride and the tridentate ligand adopts a meridional geometry. To avoid π-conflicts with the fluoride ligand at the basic metal center, the tridentate ligand takes on a facial geometry in the alkyne complexes with the alkyne *cis* to the fluoride ligand. Due to steric constraints, the meridional geometry is observed for compounds containing a rigid η^3-[C,N,N′] imine chelate ligand. In contrast to the η^2-(4e)-alkyne complexes, the η^2-(4e)-nitrile ligand can be displaced by 2 equiv of carbon monoxide.

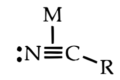
Introduction

The coordination chemistry of organonitriles is dominated by simple η^1-coordination utilizing the nitrogen lone pair, and the weak bonding is often exploited in synthetic applications where a labile ligand is required to open a coordination site on a metal.[1] As a ligand, the nitrile is appraised as both a weaker σ-donor and a weaker π-acid than CO.[1] π-Bound nitriles are very rare but of interest as novel ligands and possible models for coordination of isoelectronic dinitrogen[1,2] and other triple bonds including phosphaalkynes (P≡CR)[3] and metallocarbynes (M≡CR).[4] A search of the Cambridge Crystallographic Database[5] disclosed that compared to 828 structures deposited with the η^1-nitrile constitution **(A)** only 16 structures have been reported that contain an η^2-nitrile framework **(B)**; of these, only half are monomeric.[6,7]

$M \leftarrow :N\equiv C-R$

A

η¹-Nitrile



$:N\equiv C(M)-R$

B

η²-Nitrile

Of the few monomeric η^2-nitrile complexes which have been structurally characterized, most are regarded as electronically saturated by considering the nitrile as a two-electron donor.[8,9] Recently, Etienne[10] and Har-

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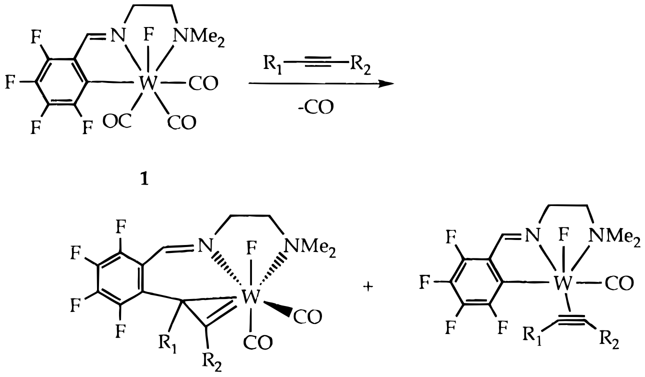
S0276-7333(96)00974-0 CCC: $14.00

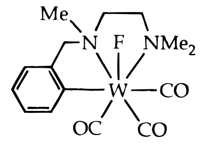
Scheme 1



man[11] reported sidebound η^2-nitrile complexes in which the nitrile ligand acts as a three- and four-electron donor, respectively.

We previously demonstrated that a rare migration reaction of a highly fluorinated ligand takes place at a tungsten(II) metal center to afford η^2-vinyl compounds (Scheme 1).[12] A competitive reaction involving the formation of four-electron donor alkyne complexes is favored for electron-rich alkynes.[13] In the course of our studies on the organometallic chemistry of the carbon−fluorine bond,[14] we have found that organonitriles do not participate in the migratory insertion pathway outlined in Scheme 1. Instead, π-bound nitrile complexes in which the nitrile accesses both of its π orbitals for bonding and serves as a four-electron donor ligand are produced.

Alkynes do not insert into the W−C_{Aryl} bond of **2**, and the flexible tridentate [C,N,N′] ligand provides an ideal framework for exploring four-electron donor alkyne and nitrile complexes.[15] The saturated ligand system supports a very basic metal center which enabled us to isolate rare examples of η^2-(4e)-nitrile tungsten(II) carbonyl fluoride complexes.[16] Given the bonding analogies frequently made between four-electron donor alkynes and nitrile ligands, we were surprised that in the alkyne adducts of **2** the η^3-[C,N,N′] ligand adopts a facial geometry with the alkyne ligand mutually *cis* to both the fluoride ligand and the carbonyl ligand as shown in **4**.[17] Since the flexible [C,N,N′] ligand takes on different geometries in these types of systems, we recognized that it could serve as a convenient handle with which to probe and elucidate the subtle differences by which the η^2-(4e)-alkyne and η^2-(4e)-nitrile ligands bind to a metal center.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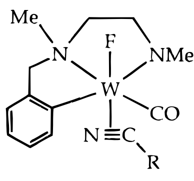
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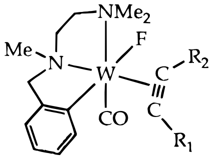
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Experimental Section

All manipulations involving air-sensitive reagents were performed under an atmosphere of purified nitrogen using standard Schlenk or glovebox techniques.[18] Solvents were purified and tungsten starting materials were prepared as previously reported.[12,13] All other chemicals were obtained from commercial sources and were used without further purification.

^1H, ^{13}C, and ^{19}F NMR spectra were obtained on Varian XL-300 spectrometers at 300, 75, and 281 MHz, respectively. All spectra obtained were referenced to residual proton peaks in the solvent. All chemical shifts are reported in δ (ppm) units with the following abbreviations: d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet, and apr = apparent. For ^{19}F NMR spectra, $CFCl_3$ was used as an external reference at δ 0.00 ppm. FTIR solution spectra were obtained in 0.1 mm CaF_2 cells. Melting points were obtained in open capillary tubes and reported in °C. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparation of (NMe-Paa)W(CO)F(N≡CC_6F_5) (7). Under a nitrogen atmosphere, a 100 mL flamed-dried glass bomb sealed with a Teflon valve and equipped with a stir bar was charged with **2** (0.32 g, 0.66 mmol) (ν_{CO} 2004, 1908, 1869 cm^{-1}),

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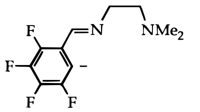
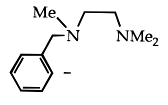
(15) Throughout the remainder of the manuscript, for convenience, F_4-Pia will refer to the ligand chelate fragment



and NMe-Paa will refer to the ligand chelate fragment



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pentafluorobenzonitrile (0.50 mL, 3.9 mmol), and 25 mL of toluene. The bomb was evacuated and heated in an oil bath at a temperature of 90 °C. During this time the reaction mixture was periodically evacuated to remove CO. Within 1 h the solution color became dark green, and IR monitoring confirmed the reaction was complete in 10 h (ν_{CO} 1926 cm^{-1}). The reaction solution was filtered through Celite, and the green filtrate was concentrated to 5 mL. Addition of 15 mL pentane and cooling to −10 °C gave crystals which were collected by filtration and washed with two 10 mL portions of pentane followed by two 10 mL portions of hexanes to remove any residual pentafluorobenzonitrile. Isolation afforded dark green crystalline **7** in 70% yield (0.29 g, 0.46 mmol). X-ray-quality crystals were grown by vapor diffusion of pentane into a 1,2-dichloroethane solution of **7**. Mp: 175−177 °C. (KBr): IR ν_{CO} 1919, 1874 (sh) cm^{-1}. Anal. Calcd for $WC_{20}F_6H_{19}N_3O$: C, 39.05; H, 3.11; N, 6.83. Found: C, 39.07; H, 3.05; N, 6.77. ^{1}H NMR (CD_2Cl_2) (δ): Ar−*H* 7.53 m, 1H; Ar−*H* 7.21 m, 1H; Ar−*H* 7.05 m, 1H; Ar−*H* 6.89 m, 1H; Ar−CH_2−N 4.86 d ($^2J_{\mathrm{HH}}$ = 13 Hz), 1H; Ar−CH_2−N 4.09 dd ($^2J_{\mathrm{HH}}$ = 13 Hz, $^4J_{\mathrm{FH}}$ = 4 Hz), 1H; N−CH_2 3.91 m, 1H; N−CH_3 3.53 s, 3H; N−CH_2 3.41 m, 1H; N−CH_2 3.01 m, 1H; N−CH_2 2.82 m, 1H; N−CH_3 2.44 d ($^4J_{\mathrm{FH}}$ = 4 Hz), 3H; N−CH_3 1.95 s, 3H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): CO 237.9 d ($^2J_{\mathrm{CF}}$ = 11 Hz); C≡N 224.9 d ($^2J_{\mathrm{CF}}$ = 18 Hz); W−*C* 176.8 d ($^2J_{\mathrm{CF}}$ = 5 Hz); Ar−C_{Quat} 149.7 s; Ar−*C*H 140.4 s; Ar−*C*H 127.2 s; Ar−*C*H 126.6 s; Ar−*C*H 124.6 s; *C*C≡N 115.5 m; Ar−CH_2−N 70.6 d ($^3J_{\mathrm{CF}}$ = 5 Hz); N−CH_2 65.4 s; N−CH_2 59.0 d ($^3J_{\mathrm{CF}}$ = 3 Hz); N−CH_3 53.7 m; N−CH_3 50.8 d ($^3J_{\mathrm{CF}}$ = 16 Hz); N−CH_3 49.5 s. ^{19}F NMR (CD_2Cl_2) (δ): W−F −49.7 s, 1F; Ar−F_{o} −136.3 m, 2F; Ar−F_{p} −149.6 m, 1F; Ar−F_{m} −159.2 m, 2F.

Preparation of (NMe-Paa)W(CO)F(4-N≡CC_6F_4C≡N) (8). As for **7**, complex **2** (0.24 g, 0.50 mmol), tetrafluoroterephthalonitrile (0.26 g, 1.3 mmol), and 20 mL of toluene were heated in an oil bath at a temperature of 90 °C. Within 30 min the solution color turned dark cherry red, and IR monitoring confirmed the reaction was complete in 4 h (ν_{CO} 1926 cm^{-1}). The reaction solution was filtered through Celite, and crystallization was achieved by reduction of the toluene solvent volume to 15 mL, followed by addition of 15 mL pentane and cooling to −10 °C. The solid was collected by filtration and washed with two 20 mL portions of pentane. Isolation afforded dark red microcrystalline **8** in 82% yield (0.26 g, 0.41 mmol). X-ray-quality crystals were grown by vapor diffusion of pentane into a CH_2Cl_2 solution of **8**. Mp: 176−178 °C (dec). IR (KBr): ν_{CO} 1919 cm^{-1}, ν_{CN} 2245 cm^{-1}. Anal. Calcd for $WC_{21}F_5H_{19}N_4O\cdot{}^1/_3C_7H_8$: C, 42.92; H, 3.34; N, 8.58. Found: C, 42.96; H, 3.39; N, 8.54. ^{1}H NMR (CD_2Cl_2) (δ): Ar−*H* 7.49 m, 1H; Ar−*H* 7.22 m, 1H; Ar−*H* 7.06 m, 1H; Ar−*H* 6.90 m, 1H; Ar−CH_2−N 4.85 d ($^2J_{\mathrm{HH}}$ = 13 Hz), 1H; Ar−CH_2−N 4.11 dd ($^2J_{\mathrm{HH}}$ = 13 Hz, $^4J_{\mathrm{FH}}$ = 4 Hz), 1H; N−CH_2 3.91 m, 1H; N−CH_3 3.55 s, 3H; N−CH_2 3.41 m, 1H; N−CH_2 3.03 m, 1H; N−CH_2 2.84 m, 1H; N−CH_3 2.44 d ($^4J_{\mathrm{FH}}$ = 4 Hz), 3H; N−CH_3 1.96 s, 3H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): W−*C*O 237.4 d ($^2J_{\mathrm{CF}}$ = 11 Hz); C≡N 225.8 d ($^2J_{\mathrm{CF}}$ = 18 Hz); W−*C* 176.7 d ($^2J_{\mathrm{CF}}$ = 5 Hz); Ar−C_{Quat} 149.7 s; Ar−*C*H 140.4 s; Ar−*C*H 127.4 s; Ar−*C*H 126.6 s; Ar−*C*H 124.6 s; C≡N 107.5 apr t ($^3J_{\mathrm{CF}}$ = 4 Hz); *C*C≡N 95.2 m; Ar−CH_2−N 70.6 d ($^3J_{\mathrm{CF}}$ = 7 Hz); N−CH_2 65.4 s; N−CH_2 59.1 d ($^3J_{\mathrm{CF}}$ = 3 Hz); N−CH_3 53.6 m; N−CH_3 50.9 d ($^3J_{\mathrm{CF}}$ = 16 Hz); N−CH_3 49.7 s. ^{19}F NMR (CD_2Cl_2) (δ): W−F −47.0 s, 1F; Ar−F_{o} −130.5 m, 2F; Ar−F_{p} −134.7 m, 2F.

Preparation of (F_4-Pia)W(CO)F(N≡CC_6H_5) (10). Under a nitrogen atmosphere, a 100 mL flamed-dried Schlenk flask equipped with a stir bar and a rubber septum was charged with **1** (0.15 g, 0.27 mmol) (ν_{CO} 2020, 1934, 1900 cm^{-1}), benzonitrile (0.31 mL, 3.0 mmol), and 30 mL of toluene. The resulting orange slurry was degassed and irradiated with a Hanovia 450 W medium-pressure Hg lamp filtered through a Pyrex cell at a distance of ca. 10 cm for 3 h under a continuous N_2 solution purge. During this time the reaction solution color changes to green. IR monitoring confirmed the reaction was complete (ν_{CO} 1925 cm^{-1}). The reaction solution was filtered through Celite, and crystallization was achieved by addition of hexanes and cooling to −10 °C. The solid was collected by filtration and washed with two 20 mL portions of hexanes to afford the flaky green solid **10** in 62% yield (0.099 g, 0.17 mmol). Mp: 136−138 °C (dec). IR (KBr): ν_{CO} 1912, 1874 (sh) cm^{-1}. Anal. Calcd for $WC_{19}F_5H_{16}N_3O$: C, 39.27; H, 2.77; N, 7.23. Found: C, 39.35; H, 2.81; N, 7.02. ^{1}H NMR (CD_2Cl_2) (δ): N═C*H* 9.17 s, 1H; Ar−H_{o} 8.12 m, 2H; Ar−$H_{\mathrm{m,p}}$ 7.61 m, 3H; N−CH_2 4.81 m, 1H; N−CH_2 4.24 m, 1H; N−CH_2 3.34 m, 1H; N−CH_3 2.89 s, 3H; N−CH_2 2.85 m, 1H; N−CH_3 1.92 s, 3H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): CO 238.5 d ($^2J_{\mathrm{CF}}$ = 11 Hz); *C*≡N 230.3 d ($^2J_{\mathrm{CF}}$ = 18 Hz); N═*C*H 165.7 s; Ar−C_{Quat} 138.2 s; Ar−*C*H 132.3 s; Ar−*C*H 131.0 s; Ar−*C*H 129.5 s; N−CH_2 66.2 s; N−CH_2 56.2 s; N−CH_3 54.6 s; N−CH_3 50.5 s. Due to extensive C−F coupling, fluorinated aryl resonances could not be resolved. ^{19}F NMR (CD_2Cl_2) (δ): W−F −60.1 s, 1F; Ar−*F* −102.4 m, 1F; Ar−*F* −140.1 m, 1F; Ar−*F* −148.0 m, 1F; Ar−*F* −157.7 s, 1F.

Preparation of (F_4-Pia)W(CO)F(N≡CC_6F_5) (11). As for **10**, complex **1** (0.14 g, 0.27 mmol), pentafluorobenzonitrile (0.36 mL, 2.9 mmol), and 30 mL of toluene were irradiated under a N_2 purge. Over the course of 4 h, the reaction solution becomes dark green, and IR monitoring confirmed the reaction was complete (ν_{CO} 1950 cm^{-1}). The reaction solution was filtered through Celite, and crystallization was achieved by addition of pentane and cooling to −10 °C. The solid was collected by filtration and washed with 15 mL of pentane to afford the dark green solid **11** in 57% yield (0.10 g, 0.15 mmol). Mp: 122−124 °C (dec). IR (KBr): ν_{CO} 1951 cm^{-1}. Anal. Calcd for $WC_{19}F_{10}H_{11}N_3O$: C, 34.00; H, 1.65; N, 6.26. Found: C, 34.01; H, 1.67; N, 5.99. ^{1}H NMR (CD_2Cl_2) (δ): N═C*H* 9.17 s, 1H; N−CH_2 4.81 m, 1H; N−CH_2 4.24 m, 1H; N−CH_2 3.34 m, 1H; N−CH_3 2.92 s, 3H; N−CH_2 2.79 m, 1H; N−CH_3 1.92 s, 3H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): CO 231.4 d ($^2J_{\mathrm{CF}}$ = 11 Hz); *C*≡N 227.4 d ($^2J_{\mathrm{CF}}$ = 17 Hz); N═*C*H 166.3 s; N−CH_2 66.1 s; N−CH_2 56.5 s; N−CH_3 54.6 d ($^3J_{\mathrm{CF}}$ = 7 Hz); N−CH_3 50.5 s. Due to extensive C-F coupling, fluorinated aryl resonances could not be resolved. ^{19}F NMR (CD_2Cl_2) (δ): W−F −55.8 s, 1F; Ar−*F* −102.3 m, 1F; Ar−F_{o} −139.2 m, 2F; Ar−*F* −140.1 m, 1F; Ar−*F* −146.6 m, 1F; Ar−F_{p} −150.6 m, 1F; Ar−*F* −156.5 m, 1F; Ar−F_{m} −161.3 m, 2F. ^{19}F NMR (CD_2Cl_2 + CH_3OH) (δ): W−F −62.8 s, 1F.

Preparation of (NMe-Paa)W(CO)F(PhC≡CPh) (13). As for **7**, complex **2** (0.25 g, 0.52 mmol), diphenylacetylene (0.28 g, 1.6 mmol), and 20 mL of toluene were heated in an oil bath at a temperature of 90 °C for 5 h (ν_{CO} 1892 cm^{-1}). The reaction solution was filtered through Celite, and crystallization was achieved by reduction of the toluene solvent volume to 5 mL, followed by addition of 15 mL of pentane and cooling to −10 °C. The solid was collected by filtration and washed sequentially with two 10 mL portions of pentane and two 10 mL portions of hexanes. Isolation gave metallic red-orange crystalline **13** in 68% yield (0.21 g, 0.35 mmol). Mp: 161−163 °C (dec). IR (KBr): ν_{CO} 1874, 1830 (sh) cm^{-1}. Anal. Calcd for $WC_{27}FH_{29}N_2O\cdot{}^1/_2C_7H_8$: C, 56.67; H, 5.15; N, 4.33. Found: C, 57.32; H, 5.15; N, 4.33. ^{1}H NMR (CD_2Cl_2) (δ): Ar−*H* 7.30 m, 10H; Ar−*H* 7.00 m, 1H; Ar−*H* 6.71 m, 3H; Ar−CH_2−N 4.49 d ($^2J_{\mathrm{HH}}$ = 14 Hz), 1H; Ar−CH_2−N 3.89 dd ($^2J_{\mathrm{HH}}$ = 14 Hz, $^4J_{\mathrm{FH}}$ = 1 Hz), 1H; N−CH_2 3.51 m, 1H; N−CH_2 3.01 m, 1H; N−CH_3 2.83 s, 3H; N−CH_3 2.81 d ($^4J_{\mathrm{FH}}$ = 4 Hz), 3H; N−CH_3 2.59 s, 3H; N−CH_2 2.45 m, 1H; N−CH_2 2.19 m, 1H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): W−*C*O 250.2 s; *C*≡CPh 207.5 s; C≡*C*Ph 204.3 s; W−*C* 189.2 d ($^2J_{\mathrm{CF}}$ = 29 Hz); Ar−C_{Quat} 142.9 s; Ar−C_{Quat} 142.7 s; Ar−C_{Quat} 140.9 s; Ar−*C*H 137.6 s; Ar−*C*H 128.6 s, 2C; Ar−*C*H 128.4 s, 2C; Ar−*C*H 128.2 s; Ar−*C*H 127.3 s, 2C; Ar−*C*H 126.9 s; Ar−*C*H 126.6 s; Ar−*C*H 125.7 s, 2C; Ar−*C*H 123.7 s; Ar−*C*H 122.5 s; Ar−CH_2−N 71.7 s; N−CH_2 61.0 d ($^3J_{\mathrm{CF}}$ = 4 Hz); N−CH_2 57.4 s; N−CH_3 50.9 s; N−CH_3 50.0 d ($^3J_{\mathrm{CF}}$ = 9 Hz); N−CH_3 48.2 d ($^3J_{\mathrm{CF}}$ = 12 Hz). ^{19}F NMR (CD_2Cl_2) (δ): W−F −139.2 br s.

Preparation of (NMe-Paa)W(CO)F(HC≡CPh) (14). As for **7**, complex **2** (0.21 g, 0.44 mmol), phenylacetylene (0.15 mL,

Table 1. Summary of Crystallographic Data of Tungsten(II) Complexes 7, 8, and 15

	7	**8**	**15**
molecular formula	$WF_6ON_3C_{20}H_{19}$	$WF_5ON_4C_{21}H_{19}$	$WSiFON_2C_{18}H_{29}$
M_r	615.234	622.254	520.379
space group	$P2_1/n$ (No. 14)	$Fdd2$ (No. 43)	$P2_1/n$ (No. 14)
cryst system	monoclinic	orthorhombic	monoclinic
cell constants	$a = 9.278(3)$ Å	$a = 26.791(3)$ Å	$a = 8.112(1)$ Å
	$b = 18.807(4)$ Å	$b = 34.813(8)$ Å	$b = 24.196(7)$ Å
	$c = 12.112(3)$ Å	$c = 9.446(2)$ Å	$c = 11.306(3)$ Å
	$\beta = 101.68(3)°$		$\beta = 108.52(2)°$
V, Å^3	2069.62	8809.57	2104.14
Z	4.0	16.0	4.0
calcd density, g cm^3	1.977	1.877	1.643
cryst dimens, mm^3	0.25 × 0.19 × 0.06	0.28 × 0.19 × 0.17	0.32 × 0.31 × 0.24
abs coeff (μ), cm^{-1}	57.766	54.177	56.787
radiation λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
no. of reflcns measd	4007	2106	4096
no. of unique reflcns:	3635	2071	3819
2θ range, deg	4.00−5.00	4.00−50.00	4.00−50.00
scan technique	$\theta/2\theta$ scan	$\theta/2\theta$ scan	$\theta/2\theta$ scan
scan width, deg	0.8000 + 0.3400(tan θ)	0.8000 + 0.3400(tan θ)	0.8000 + 0.3400(tan θ)
data collcn position	bisecting, $\omega = 0$	bisecting, $\omega = 0$	bisecting, $\omega = 0$
decay corr	none	none	none
abs corr	empirical	empirical	empirical
min % transm	55.9949	78.1621	46.2982
max % transm	99.8621	99.7918	99.7568
av % transm	84.2261	83.3791	76.7128
highest peak in final diff Fourier, e/Å^3	0.949	0.698	2.040
ignorance factor, p:	0.04	0.04	0.05
no. of observns	$I < 3.00\sigma(I) = 2367$	$I < 2.00\sigma(I) = 1788$	$I < 2.00\sigma(I) = 3044$
no. of variables	281	288	218
data to parm ratio	8.423	6.208	13.963
shift to error ratio	0.001	0.002	0.008
error in an observn	1.1701	1.3271	1.5602
R	0.0242	0.0221	0.0500
R_w	0.0319	0.0316	0.0686

1.4 mmol), and 20 mL of toluene were heated in an oil bath at a temperature of 90 °C for 3 h (ν_{CO} 1890 cm^{-1}). The reaction solution was filtered through Celite, and reduction of the toluene solvent volume to 10 mL, followed by addition of pentane and cooling to −10 °C, affords the red microcrystalline **14** in 70% yield (0.16 g, 0.31 mmol). Mp: 169−171 °C. IR (KBr): ν_{CO} 1883, 1865 cm^{-1}. Anal. Calcd for $WC_{21}FH_{25}N_2O \cdot {}^1/_2C_7H_8$: C, 51.59; H, 5.12; N, 4.91. Found: C, 51.77; H, 5.12; N, 4.91. ^{1}H NMR (CD_2Cl_2) (δ): C≡C*H* 12.49 s, 1H; Ar−*H* 8.04 m, 5H; Ar−*H* 7.60 m, 1H; Ar−*H* 7.31 m, 1H; Ar−*H* 7.22m, 1H; Ar−*H* 6.86 m, 1H; Ar−CH_2−N 5.03 d ($^2J_{HH}$ = 14 Hz), 1H; Ar−CH_2−N 4.49 dd ($^2J_{HH}$ = 14 Hz, $^4J_{FH}$ = 2 Hz), 1H; N−CH_2 4.25 m, 1H; N−CH_3 3.82 s, 3H; N−CH_2 3.67 m, 1H; N−CH_3 3.46 d ($^4J_{FH}$ = 4 Hz), 3H; N−CH_3 3.42 s, 3H; N−CH_2 3.09 m, 1H; N−CH_2 2.95 m, 1H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): W−*C*O 250.9 s; C≡*C*Ar 204.2 s; C≡*C*H 197.9 s ($^1J_{CW}$ = 66 Hz, $^1J_{CH}$ = 201 Hz); W−*C* 189.6 d ($^2J_{CF}$ = 29 Hz); Ar−C_{Quat} 142.5 s; Ar−C_{Quat} 140.7 s; Ar−*C*H 138.8 s; Ar−*C*H 128.6 s; Ar−*C*H 128.4 s, 2C; Ar−*C*H 127.9 s, 2C; Ar−*C*H 126.6 s; Ar−*C*H 123.5 s; Ar−*C*H 122.3 s; Ar−*C*H_2−N 71.5 s; N−*C*H_2 60.2 d ($^3J_{CF}$ = 4 Hz); N−*C*H_2 57.2 s; N−*C*H_3 51.5 s; N−*C*H_3 51.2 d ($^3J_{CF}$ = 9 Hz); N−*C*H_3 47.9 d ($^3J_{CF}$ = 14 Hz). ^{19}F NMR (CD_2Cl_2) (δ): W−F −136.9 br s.

Preparation of (NMe-Paa)W(CO)F(HC≡CSi(CH$_3$)$_3$) (15). As for **7**, complex **2** (0.26 g, 0.55 mmol), (trimethylsilyl)acetylene (0.25 mL, 1.8 mmol), and 20 mL of toluene were heated in an oil bath at a temperature of 90 °C for 3 h (ν_{CO} 1875 cm^{-1}). The reaction solution was filtered through Celite, and the insoluble green solid was discarded. Crystallization was achieved by reduction of the toluene solvent volume to 10 mL, followed by addition of 20 mL of pentane and cooling to −10 °C. The solid was collected by filtration and washed with two 10 mL portions of pentane to remove any residual (trimethylsilyl)acetylene. Isolation gave purple-red crystalline **15** in 46% yield (0.13 g, 0.25 mmol). X-ray-quality crystals were grown by slow vapor evaporation of CH_2Cl_2 from a CH_2Cl_2/hexamethyldisiloxane solution of **15**. Mp: 170−172 °C. IR (KBr): ν_{CO} 1860, 1829 (sh) cm^{-1}. Anal. Calcd for $WC_{18}FH_{29}N_2OSi$: C, 41.55; H, 5.62; N, 5.38. Found: C, 42.33; H, 5.63; N, 5.31. ^{1}H NMR (CD_2Cl_2) (δ): C≡C*H* 12.37 s, 1H; Ar−*H* 6.88 m, 1H; Ar−*H* 6.57 m, 1H; Ar−*H* 6.43 m, 1H; Ar−*H* 5.91m, 1H; Ar−CH_2−N 4.39 d ($^2J_{HH}$ = 14 Hz), 1H; Ar−CH_2−N 3.80 dd ($^2J_{HH}$ = 14 Hz, $^4J_{FH}$ = 2 Hz), 1H; N−CH_2 3.50 m, 1H; N−CH_3 3.08 s, 3H; N−CH_2 2.97 m, 1H; N−CH_3 2.78 d ($^4J_{FH}$ = 4 Hz), 3H; N−CH_3 2.69 s, 3H; N−CH_2 2.43 m, 1H; N−CH_2 2.25 m, 1H; Si-CH_3 0.32 s, 9H. ^{13}C{^{1}H} NMR (CD_2Cl_2) (δ): W−*C*O 252.2; C≡*C*H 211.4 s ($^1J_{CW}$ = 74 Hz, $^1J_{CH}$ = 203 Hz, $^2J_{CF}$ = 6 Hz); C≡*C*Si(CH$_3$)$_3$ 205.0 s; W−*C* 190.6 d ($^2J_{CF}$ = 29 Hz); Ar−C_{Quat} 142.4 s; Ar−*C*H 138.8 s; Ar−*C*H 126.0 s; Ar−*C*H 123.3 s; Ar−*C*H 121.9 s; Ar−*C*H_2−N 71.4 s; N−*C*H_2 60.2 d ($^3J_{CF}$ = 4 Hz); N−*C*H_2 57.3 s; N−*C*H_3 51.5 s; N−*C*H_3 51.3 d ($^3J_{CF}$ = 9 Hz); N−*C*H_3 47.9 d ($^3J_{CF}$ = 14 Hz); Si-*C*H_3 −0.77 s. ^{19}F NMR (CD_2Cl_2) (δ): W−F −137.6 br s.

Crystallography. Data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation using the $\theta-2\theta$ scan technique for a crystal mounted on a glass fiber for all structures. Cell constants were obtained from 25 reflections with 10° < 2θ < 25°, and the space groups were determined from systematic absences and subsequent least-squares refinement. Standard reflection showed no decay during data collection. Lorentz, polarization, and empirical absorption (Ψ scans) corrections were applied. The structure was solved by the standard heavy-atom techniques with the SPD/VAX package.[19] Final refinement included all non-hydrogen atoms as anisotropic contributions and hydrogens as fixed isotropic contributions. Scattering factors and

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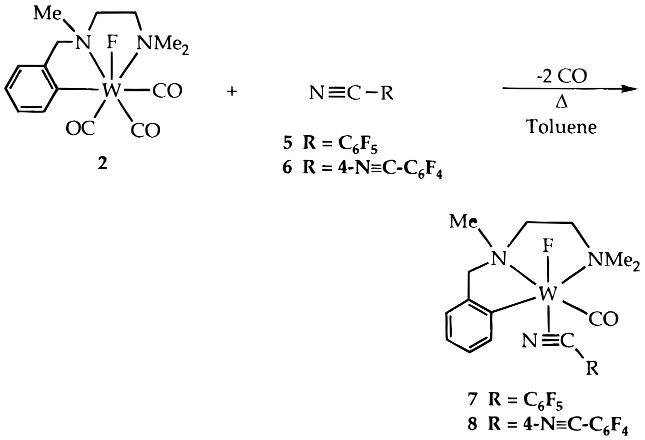
(19) Frenz, B. A. The Enraf-Nonius CAD 4 SPD-A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination. In *Computing and Crystallography*; Schenk, H., Olthof-Hazenkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft Univeristy Press: Delft, Holland, 1978; pp 64−71.

Table 2. Relevant Spectroscopic Parameters for Tungsten(II) Four-Electron Donor η^2-Nitrile and η^2-Alkyne Complexes

complex[a]	ν_{CO},[b] cm^{-1}	δ(C$_{nitrile}$), ppm	δ(C$_{alkyne}$), ppm	δ(CO), ppm	δ(W–C$_{Aryl}$), ppm	δ(W–F), ppm	λ_{max},[c] nm (ϵ, M^{-1} cm^{-1})
7	1926	224.1 d ($^2J_{CF}$ = 18 Hz)	N/A[d]	237.9 d ($^2J_{CF}$ = 11 Hz)	176.8 d ($^2J_{CF}$ = 5 Hz)	−49.7	582 (345)
8	1926	225.8 d ($^2J_{CF}$ = 18 Hz)	N/A	237.4 d ($^2J_{CF}$ = 11 Hz)	176.7 d ($^2J_{CF}$ = 5 Hz)	−47.0	598 (876)
10	1925	230.3 d ($^2J_{CF}$ = 18 Hz)	N/A	285.5 d ($^2J_{CF}$ = 11 Hz)	not resolved	−60.1	N/A
11	1951	227.4 d ($^2J_{CF}$ = 17 Hz)	N/A	231.4 d ($^2J_{CF}$ = 11 Hz)	not resolved	−55.8	N/A
13	1892	N/A	207.5, 204.3	250.2	189.2 d ($^2J_{CF}$ = 29 Hz)	−139.2	540 (379)
14	1890	N/A	204.2, 197.9	250.9	189.6 d ($^2J_{CF}$ = 29 Hz)	−136.9	540 (300)
15	1875	N/A	211.4, 205.0	252.2	190.6 d ($^2J_{CF}$ = 29 Hz)	−137.6	536 (250)

[a] NMR spectra were recorded in CD_2Cl_2. [b] Infrared spectra were recorded in toluene. [c] Electronic spectra were recorded in CH_2Cl_2. [d] N/A = not applicable.

Scheme 2



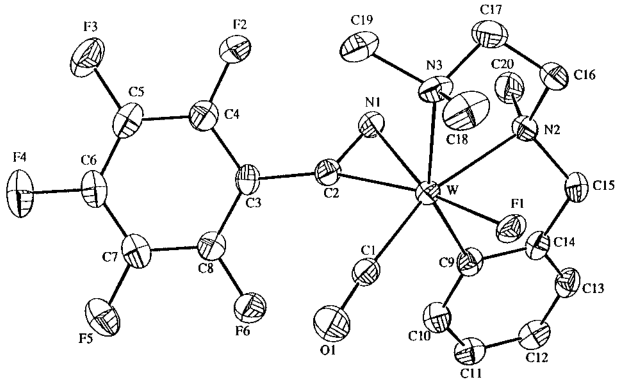


Figure 1. ORTEP representation of the tungsten(II) four-electron donor η^2-nitrilecomplex **7**.

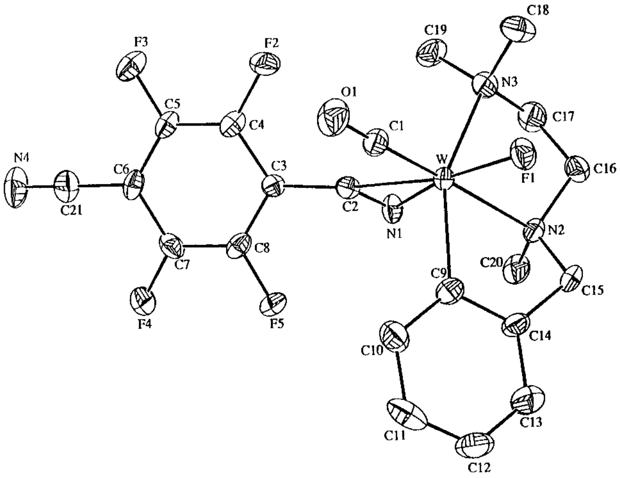


Figure 2. ORTEP representation of the tungsten(II) four-electron donor η^2-nitrile complex **8**.

$\Delta f'$ and $\Delta f''$ values were taken from the literature.[20] The lower quality of the structure for the (trimethylsilyl)acetylene adduct **15** was believed to be due to either partial twinning of the crystal or the presence of trace amounts of $Me_3SiOSiMe_3$ which could not be resolved. A summary of the crystallographic data and structure refinement is collected in Table 1.

Results

η^2-Nitrile Complexes. As depicted in Scheme 2, treatment of the tungsten(II) metallacycle **2** with a fluorinated aromatic nitrile in toluene at 90 °C under reduced pressure for 4 h affords the robust η^2-nitrile complexes **7** or **8** in high yield. Salient spectroscopic parameters for the compounds are presented in Table 2.

Benzonitrile, acrylonitrile, and aliphatic nitriles display no reactivity with the metallacycle **2**. Isonitriles show no aptitude for forming four-electron donor adducts; instead they appear to engage in CO substitution chemistry with **2** which is followed by decomposition.

Both complexes **7** and **8** display lowfield nitrile resonances at δ 224.9 ppm ($^2J_{CF}$ = 18 Hz) and at δ 225.8 ppm ($^2J_{CF}$ = 18 Hz), respectively, which suggests that the nitrile group in these compounds is serving as a four-electron donor. The lone carbonyl ligand resonates at δ 237.9 ppm ($^2J_{CF}$ = 11 Hz) for **7** and at δ 237.4 ppm ($^2J_{CF}$ = 11 Hz) for **8**. The large $^2J_{CF}$ for the nitrile contact carbon in these complexes signals that the nitrile ligand is *trans* to the metal fluoride,[13a,21] leaving the carbonyl ligand *cis* to the fluoride.[22] $^1J_{CW}$ was not observed in these systems, presumably due to the extensive fluorination. The tungsten–fluoride resonance is quite sensitive to substitution at tungsten and shifts to much lower field for the nitrile complexes (δ −49.7 ppm for **7** and δ −47.0 ppm for **8**) relative to the parent tungsten complex **2** which displays a ^{19}F NMR resonance at δ −170.4 ppm.[23]

X-ray Crystallographic Analyses of 7 and 8. The molecular structures of the η^2-nitrile complexes **7** and **8** were confirmed by X-ray crystallography and are shown in Figures 1 and 2, respectively, where the atomic

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Table 3. Selected Distances (Å) and Angles (deg) for the Tungsten(II) η^2-(4e)-Nitrile Complexes 7 and 8[a]

7		**8**	
W−F1	1.957(3)	W−F1	1.916(6)
W−N2	2.276(5)	W−N2	2.291(7)
W−N3	2.358(5)	W−N3	2.283(9)
W−C1	1.963(6)	W−C1	1.951(9)
W−C2	2.009(6)	W−C2	2.039(9)
W−N1	1.995(5)	W−N1	2.035(8)
W−C9	2.132(6)	W−C9	2.21(1)
C2−N1	1.262(7)	C2−N1	1.28(1)
		C21−N4	1.13(1)
F1−W−N	158.6(2)	F1−W−N1	161.9(3)
F1−W−C2	160.3(2)	F1−W−C2	161.4(3)
F1−W−C1	84.9(2)	F1−W−C1	87.8(3)
N3−W−C9	159.1(2)	N3−W−C9	155.4(3)
N2−W−C1	160.8(2)	N2−W−C1	164.1(3)
C2−W−N1	36.7(2)	C2−W−N1	36.5(3)
C2−N1−W	72.2(4)	C2−N1−W	71.9(5)
N1−C2−W	71.0(4)	N1−C2−W	71.6(5)
N1−C2−C3	132.3(6)	N1−C2−C3	129.7(8)
		C6−C21−N4	177.(1)
C1−W−N1−C2	−3.5	C1−W−N1−C2	0.1

[a] Number in parentheses are estimated standard deviations in the least significant digits.

numbering scheme for each compound is identified. Data collection information, selected bond distances, and selected bond angles for **7** and **8** are presented in Tables 1 and 3.

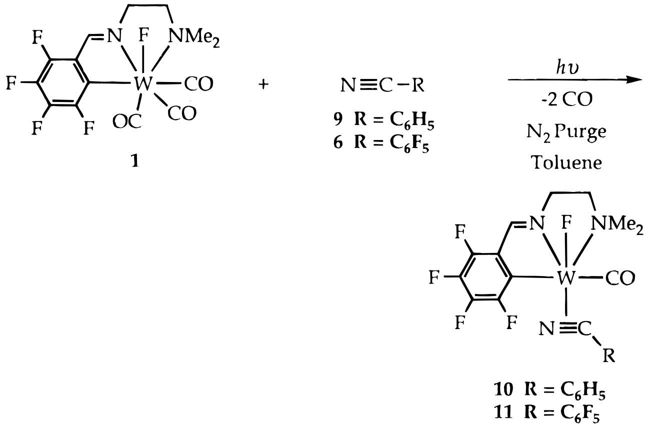
The geometry around the tungsten(II) metal center in both **7** and **8** can be described as roughly octahedral if one considers that the η^2-nitrile ligand occupies a single coordination site. A common feature present in both **7** and **8** is that the tridentate η^3-[C,N,N′] chelating ligand lies meridionally disposed about the tungsten metal center. This leaves the fluoride *trans* to the nitrile ligand. In each of these systems the nitrile unit is *cis* to the CO and essentially lies parallel to the W−CO axis (C1−W−N1−C2 = −3.5° for **7**, and C1−W−N1−C2 = 0.1° for **8**).

In both complexes, the short W-N1 (1.995(5) Å for **7** and 2.035(8) Å for **8**) and W−C2 (2.009(6) Å for **7** and 2.039(9) Å for **8**) bonds indicate multiple metal−ligand bonding.[24] Furthermore, the contact carbon of the coordinated nitrile group is bent with N1−C2−C3 = 132.3(6)° for **7** and 129.7(8)° for **8**.

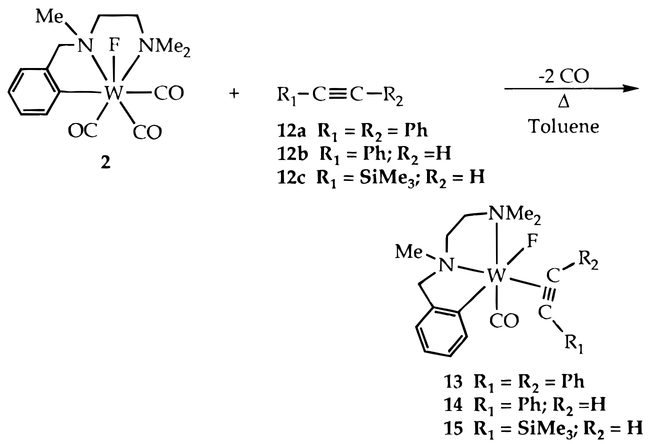
Photochemistry of Tungsten(II) Carbonyl Fluoride Complexes. Unlike the reactivity exhibited by **2**, π-bound nitrile adducts of the highly fluorinated tungsten(II) metallacycle **1** cannot be accessed via thermal methods. Reactions at elevated temperatures result in decomposition of starting materials with formation of pale blue intractable products. However, photolysis of a toluene solution of **1** (ν_{CO} 2020, 1934, 1900 cm^{-1}) in the presence of excess aromatic nitriles **9** and **6** affords the π-bound nitrile complexes **10** and **11**, respectively, in good isolated yields as illustrated in Scheme 3.

A strong nitrogen purge is necessary to reduce the facile and unproductive scavenging of carbon monoxide to regenerate **1**. As shown in Table 2, both complexes **10** and **11** were fully characterized and possess the requisite spectroscopic features consistent with their formulation as four-electron donor nitrile complexes.

Scheme 3



Scheme 4



η^2-Alkyne Complexes. The four-electron donor alkyne complexes **13**−**15** were obtained as air-stable microcrystalline solids in 46−70% isolated yields by thermal CO substitution with excess alkyne as depicted in Scheme 4. The low-field acetylenic $^{13}C\{^1H\}$ NMR chemical shift values (Table 2) possessed by complexes **13**−**15** suggest that the alkyne ligand in these compounds is serving as a four-electron donor.[25] Importantly, the large $^2J_{CF}$ of 29 Hz for the W−C$_{Aryl}$ carbon in these complexes signifies that the W−C$_{Aryl}$ carbon is *trans* to the metal fluoride,[13a,21] leaving the carbonyl and alkyne ligands *cis* to the fluoride.[22]

The ^{1}H NMR spectroscopic data for **13**−**15** and the nitrile complexes **7** and **8** are listed in Table 4 and illustrate that the geometry the η^3-[C,N,N′] chelate ligand attains in both systems is different. Consistent with extensive alkyne to metal donation is that the terminal alkyne adducts exhibit low-field chemical shifts for the acetylenic protons in the ^{1}H NMR spectra at δ 12.49 ppm for **14** and δ 12.37 ppm for **15**.[25b,26]

The ^{19}F NMR spectra for the alkyne complexes show pairwise signals of differing intensities to suggest isomeric forms for the terminal alkyne complexes **14** and **15**. This isomerization presumably results from two alkyne orientations. The major alkyne isomers (95:5

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[23] Buffin, B. P. Ph.D. Thesis, University of Utah, 1993; p 69.

[24] (a) Nugent; W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454−2458.

[25] (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288−3290. (b) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

[26] Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956−6963.

Table 4. ^{1}H NMR Spectroscopic Data for the Flexible Tridentate [C,N,N′] Ligand Present in the Tungsten(II) η^2-(4e)-Nitrile and η^2-(4e)-Alkyne Complexes[a]

complex	$N(CH_3)_2$	NCH_2	$PhCH_2N$	NCH_3
7 ($N{\equiv}CC_6F_5$)	2.44 ($^4J_{FH}$ = 4 Hz), 1.95	3.91, 3.41, 3.01, 2.82	4.86, 4.09 ($\Delta\delta$ = 0.77)	3.53
8 ($N{\equiv}CC_6F_4C{\equiv}N$)	2.44 ($^4J_{FH}$ = 3 Hz), 1.96	3.92, 3.41, 3.03, 2.84	4.85, 4.11 ($\Delta\delta$ = 0.74)	3.55
13 ($PhC{\equiv}CPh$)	2.81 ($^4J_{FH}$ = 4 Hz), 2.59	3.51, 3.01, 2.45, 2.19	4.49, 3.89 ($\Delta\delta$ = 0.60)	2.83
14 ($PhC{\equiv}CH$)	3.46 ($^4J_{FH}$ = 4 Hz), 3.42	4.25, 3.67, 3.09, 2.95	5.03, 4.49 ($\Delta\delta$ = 0.54)	3.82 ($^4J_{FH}$ = 4 Hz)
15 ($Me_3SiC{\equiv}CH$)	2.78 ($^4J_{FH}$ = 4 Hz), 2.69	3.50, 2.97, 2.43, 2.25	4.39, 3.80 ($\Delta\delta$ = 0.59)	3.08

[a] All chemical shifts are reported in ppm. [b] NMR spectra were recorded in CD_2Cl_2.

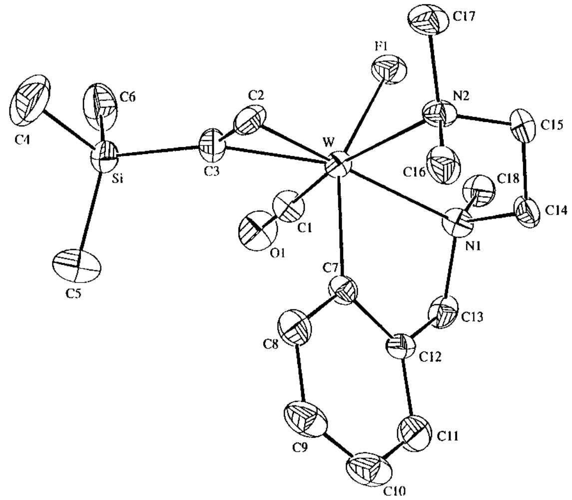
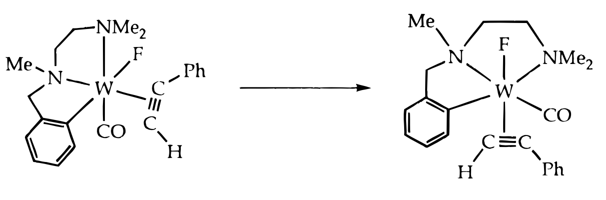


Figure 3. ORTEP representation of the tungsten(II) four-electron alkyne complex **15**.

ratio via integration) display similar W−F chemical shifts near δ −138 ppm which is only slightly downfield relative to the parent tungsten(II) fluoride complex **2**, and reflect the *cis* orientation of the fluoride and the affixed alkyne ligand. High-temperature ^{19}F NMR studies on the alkyne complexes showed no coalescence up to 100 °C, suggesting a high rotational barrier for these complexes.

Interestingly, the flexible η^3-[C,N,N′] chelate ligand in the alkyne complex **14** undergoes a slow rearrangement from a facial coordination at tungsten to a meridional arrangement (W−F, δ −80.9 ppm) in the solid state over a time period of months as evidenced by ^{19}F NMR spectroscopy (eq 1). Complimentary results were



(1)

14 **16**

obtained upon examination of the acetylenic proton for both isomers (toluene-d_8: $\equiv CH_{facial}$ δ 11.24 ppm; $\equiv CH_{meridional}$ δ 10.11 ppm) in the ^{1}H NMR spectrum. Rearrangement between the two isomeric structures is slow, and coalescence was not observed up to 100 °C.

X-ray Crystallographic Analysis of (15). The orientation of the ligands in **15** anticipated from spectral data was confirmed by the solid-state structure which is shown in Figure 3. Data collection information, selected bond distances, and selected bond angles for **15** are presented in Tables 1 and 5. The flexible η^3-[C,N,N′] monoanionic chelate ligand takes on a facial arrangement about the octahedral tungsten(II) atom with the ligand folding about the W−N1 axis with an angle of C7−W−N2 = 89.3(5)°. Consistent with the ligand arrangement predicted by spectroscopy, the fluoride ligand is *trans* to the W−C_{Aryl} linkage with F1−W−C7 = 151.9(4)° and *cis* to both the carbonyl ligand and the coordinated (trimethylsilyl)acetylene. Thus, the C_2 alkyne unit is *cis* and parallel to the W−CO axis (C1−W−C2−C3 = −3.4°). The short W−C_{Alkyne} bond distances of 1.98(2) and 2.06(1) Å are indicative of W−C multiple bond character.[24] The lengthened C≡C bond distance of 1.27(2) Å and the C2−C3−Si bond angle of 138(1)° describe the distortion of the alkyne upon coordination.

Table 5. Selected Distances (Å) and Angles (deg) for (NMe-Paa)W(CO)(F)(HC≡CSi(CH$_3$)$_3$ (15)[a]

W−F1	1.977(9)	W−C2	1.98(2)
W−N1	2.33(1)	W−C3	2.06(1)
W−N2	2.34(1)	W−C7	2.14(1)
W−C1	1.92(1)	C2−C3	1.27(2)
N1−W−C2	159.9(5)	W−C3−Si	153(1)
N1−W−C3	158.8(5)	N1−W−N2	78.0(4)
F1−W−C1	95.4(5)	W−C2−C3	75.(1)
F1−W−C2	108.8(5)	C2−W−C3	36.6(6)
F1−W−C3	110.7	C7−W−N2	89.3(5)
F1−W−C7	151.9(4)	C1−W−C2−C3	−3.4
C2−C3−Si	138.(1)		

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

Reaction Chemistry of η^2-Nitrile Complexes. Heating a toluene solution of **7** under 1.5 atm of CO (g) to 90 °C for 3 h quantitatively regenerates the tungsten(II) carbonyl fluoride complex **2**. The related η^2-alkyne complexes **13**−**15** are inert to CO under these conditions. Interestingly, no reaction takes place between **7** and excess diphenylacetylene, phenylacetylene, or (trimethylsilyl)acetylene in toluene after 72 h at 90 °C even in coordinating solvents such as acetonitrile or tetrahydrofuran. Similarly, the nitrile ligands **5** and **6** are not able to displace the coordinated alkyne ligands in complexes **13**−**15**. Reaction of **2** with a 1:1 equiv mixture of diphenylacetylene and pentafluorobenzonitrile affords exclusively the diphenylacetylene complex **13**. The nitrile and alkyne complexes resist further reaction chemistry such as [4+2] cycloadditions with various dienes.

Although nitrile replacement could not be achieved upon heating either complexes **7** or **8** in acetonitrile or benzonitrile at 90 °C for 24 h, some nitrile exchange was observed upon reaction of **7** with 2 equiv of tetrafluoroterephthalonitrile in toluene-d_8 at 90 °C for 48 h to generate a mixture of the nitrile complexes **7** and **8** in a 60:40 ratio as determined by integration of their W−F resonances. Reaction of **8** with 2 equiv of pentafluorobenzonitrile in toluene-d_8 solution for 72 h at 90 °C did not produce any of the nitrile adduct **7**, perhaps reflecting a greater thermodynamic stability of **8** relative to **7**.

Table 6. Summary of Structural and Spectroscopic Parameters of Various η^2-Nitrile and η^2-Alkyne Complexes

complex	N^a	M−C, Å	M−N(C), Å	C−N(C), Å	N(C)−C−C, deg	^{13}C NMR, ppm	ref
(NMe-Paa)W(CO)F($N{\equiv}CC_6F_5$) (**7**)	4	2.009(6)	1.995(5)	1.262(7)	132	225	this work
(NME-Paa)W(CO)F($N{\equiv}CC_6F_4C{\equiv}N$) (**8**)	4	2.039(9)	2.035(8)	1.28(1)	130	226	this work
[W(bpy)Cl(PMe_3)$_2$(Me-C≡N)]PF_6	4	2.008(4)	1.998(5)	1.267(7)	130	235	11
W(bpy)Cl_2(PMe_3)$_2$(MeC≡N)	4	1.98(1)	1.99(1)	1.27(2)	129	230	11
Tp*Nb(CO)(PhC≡CMe)(PhC≡N)^b	3	2.17(1)	2.139(8)	1.21(1)	135	174−187	10
Cp_2Mo(MeC≡N)	2	2.124(8)	2.219(7)	1.20(1)	139	171	8a,9c
(NMe-Paa)W(CO)F($Me_3SiC{\equiv}CH$) (**15**)	4	1.98(2)	2.06(1)	1.27(2)	138	211, 205	this work
(F_4-Pia)W(CO)F(EtC≡CEt)	4	1.99(1)	2.00(1)	1.30(2)	139, 138	220, 213	13a
(F_4-Pia)W(CO)F(HC≡CCN)	4	2.036(9)	2.028(9)	1.33(1)	138	233, 187	21

[a] Formal number of electrons donated by the η^2 ligand. [b] Tp* = hydridotris(3,5-dimethylpyrazolyl)borate.

Discussion

Reaction of tungsten(II) fluoride carbonyl metallacycles with alkynes or aromatic organonitriles affords η^2-alkyne or η^2-nitrile complexes, respectively. That the alkyne ligands in compounds **13**−**15** and the nitrile ligands in complexes **7**, **8**, **10**, and **11** serve as four-electron donors is suggested by both spectroscopic and structural results. All of the η^2-nitrile complexes exhibit a downfield $^{13}C\{^1H\}$ NMR chemical shift between 224 and 231 ppm for the nitrile carbon (Table 2). As summarized in Table 6, this correlates nicely with the few existing structurally and spectroscopically characterized four-electron donor η^2-(4e)-nitrile species. In contrast, three- and two-electron donor nitrile ligands have $^{13}C\{^1H\}$ NMR resonances in the δ 170−190 ppm range. The extent of the π donation (both $\pi_{\|}$ and $\pi_{\perp}$) from the nitrile ligand to the tungsten(II) metal center is indicated by the 120 ppm upfield shift of the coordinated nitrile carbon (δ 225.8 ppm) compared to the free nitrile (δ 107.7 ppm) in **8**.

The low-field ^{1}H NMR chemical shift of the acetylenic proton identifies the coordinated alkyne in both **14** (δ 12.29 ppm) and **15** (δ 12.37 ppm) as a four-electron donor ligand.[25b,26] Gated-decoupled ^{13}C NMR spectra for **14** and **15** serve to positively identify the terminal alkyne carbons while providing $^1J_{CH}$ coupling constants of 201 and 203 Hz, respectively. From the $^1J_{CH}$ values, the *s*-fractions of the coordinated acetylenes were determined to be $s = 0.40$ for **14** and $s = 0.41$ for **15** as expected for alkyne carbons with substantial sp^2 hybridization.[27,28]

The W−C and W−N distances for both **7** and **8** are virtually equal, indicate multiple metal−ligand bonding, and are similar to other structurally characterized η^2-(4e)-nitrile complexes (see Table 6). In contrast, the recently described (η^2-(3e)-nitrile)niobium(I) complex [Tp*Nb(CO)(PhC≡CMe)(PhC≡N)] possesses somewhat longer metal−nitrogen (2.13(8) Å) and metal−carbon (2.17(1) Å) bonds.[10] The η^2-(2e)-nitrile complex Cp_2Mo($CH_3C{\equiv}N$) also exhibits significantly longer metal−nitrogen (2.22 Å) and metal−carbon (2.11 Å) bonds.[8a] Coordination severely distorts the η^2-nitrile ($\Delta C{\equiv}N \approx 0.14$ Å) compared to the free nitrile (1.13 Å) of the tetrafluoroterephthalonitrile ligand in complex **8**. The nitrile aryl rings are tilted by 39.7° (**7**) and 57.8° (**8**) from the W−N1−C2 plane which indicates that conjugation between the aryl ring and the nitrile linkage is reduced upon coordination of the nitrile. By way of comparison, the alkyne complex **15** manifests a C2−C3−Si bond angle of 138° which is representative of other η^2-(4e)-alkyne complexes.[25b] The limited number of structurally characterized η^2-(3e)- and η^2-(2e)-nitrile complexes have shorter N≡C bond lengths and greater N−C−C angles (Table 6). Unlike η^2-(2e)-nitrile complexes for which weak C≡N stretches have been reported in the 1600−1800 cm^{-1} region of the IR spectrum, solid-state KBr infrared spectra for **7** and **8** do not reveal a band which can be assigned to a coordinated C≡N group.

With the exception of the Tp*W($S_2PR^*_2$)(η^2-$CH_3C{\equiv}N$)(CO) (R* = (−)-mentholate) complex recently reported by Young,[29] existing η^2-(4e)-nitrile complexes do not contain carbonyl ligands.[11] The coordinated nitrile in **7** and **8** is parallel to the W−CO axis and allows for maximum overlap of its $\pi_{\perp}$ with the vacant dπ orbital which is orthogonal to the carbonyl donor and acceptor orbitals.

Since the nitrile ligand must replace two carbonyl ligands to serve as a four-electron donor at tungsten(II), π effects dominate the synthetic and structural chemistry.[30] In the case of the electron-rich {(NMe-Paa)W(CO)F)} system, only highly fluorinated aromatic nitriles form stable complexes by lowering the π-acceptor orbitals of the nitrile ligand for better overlap with the metal d$_\pi$ orbitals. In the case of the less electron-rich {(F_4-Pia)W(CO)F} system, the benzonitrile complex **10** can be prepared and its 26 cm^{-1} lower ν_{CO} compared to the pentafluorobenzonitrile complex **11** testifies to the enhanced π-acceptor ability of the perfluorobenzonitrile ligand. After accounting for the difference due to perfluorination, the nitrile ligands appear to better π-acceptors/worse σ- and π-donors than the alkyne ligands.

A striking difference is observed in the coordination geometry of analogous nitrile (**7**, **8**) and alkyne (**13**−**15**) complexes that contain the flexible η^3-[C,N,N′] amine chelate ligand which can bind in either facial or

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(27) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectrscopy*; VCH: New York, 1993; p.95.

(28) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707−1715.

(29) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Organometallics* **1996**, *15*, 2428−2430.

(30) Complexes containing both π-acceptor and π-donor ligands are rare. For *cis*-carbonyloxo tungsten(IV) examples, see: (a) Su, F.-M.; Copper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545−3547. (b) Young, C. G.; Gable, R. W.; Mackay, M. F. *Inorg. Chem.* **1990**, *29*, 1777−1779. (c) Feng, F. G.; Luan, L.; White, P. S.; Brookhart, M. S.; Templeton, J. L.; Young, C. G. *Inorg. Chem.* **1991**, *30*, 2584−2586. For a nonclassical *cis*-carbonyl(selenido)zirconium(IV) complex, see: Howard, W. A.; Trnka, T. M.; Parkin, G. *Organometallics* **1995**, *14*, 4037−4039.

meridional orientations with little steric cost.[31] In both the solid-state (X-ray crystallography) and solution ($^2J_{CF}$), the fluoride ligand is *trans* to the nitrile. This orientation may be favored to allow for synergistic fluoride π-donation and nitrile π-back-bonding. Since the alkyne ligands are better donors, unfavorable filled−filled interactions are avoided in the observed *cis* arrangement of the fluoride and alkyne ligands.[32] The rigid tetrafluoro η^3-[C,N,N′] imine ligand system favors a meridional rather than a facial coordination mode and provides a less electron-rich metal center; these factors combine to allow both alkyne and nitrile ligands to be *trans* to the fluoride.

Thus, it is interesting that the phenylacetylene adduct **14** rearranges over time to **16** in the solid state and may reflect the fact that phenylacetylene is a poorer donor than the electron-rich (trimethylsilyl)acetylene which does not rearrange. This notion is further supported by the CO frequencies of the alkyne complexes which differ by 15 cm^{-1} as shown in Table 2.

The alkyne and nitrile complexes presented in this work are intensely colored red and green compounds, respectively. The UV−vis spectra provides some insight on the influence of the π-bonding properties of the ligand on the frontier orbitals of the {(NMe-Paa)W(CO)F} fragment. The alkyne complexes **13**−**15** display an absorption in the visible region between 535−545 nm which is red-shifted to $\lambda = 582$ nm and $\lambda = 598$ nm, respectively, for the nitrile complexes **7** and **8**. In related W(II) alkyne systems, Templeton has assigned the low-energy visible transitions to the d → d manifold.[33,34] The observed bathochromic shifts for the nitrile complexes **7** and **8** are consistent with a smaller HOMO(d_{xz})−LUMO(d_{xy}) energy gap compared to their alkyne analogs and is parallel to the trend observed for electron-rich versus electron-poor alkyne complexes[34] and by Harman for other W(II) η^2-nitrile complexes.[11]

The stability of the η^2-(4e)-nitrile and η^2-(4e)-alkyne complexes derived from the tungsten(II) metallacycle **2** is a consequence of the unique coordination environment provided by the flexible monoanionic η^3-[C,N,N′] chelating ligand. The diamine fragment lacks suitable orbitals for π-bonding, can only serve as a σ-donor, and creates a very basic metal center which can interact favorably with the low-energy π-acceptor ($\pi_{\|}$*) orbitals of π-acid ligands. In a similar vein, Looman recently exploited the π-basicity of a related tungsten(0) diamine fragment to trap the first examples of tungsten(0) η^2-aldehyde complexes.[35]

Although thermal replacement of the coordinated pentafluorobenzonitrile in **7** by alkynes was not possible, nitrile exchange was observed with tetrafluoroterephthalonitrile to afford **8**. This suggests the structure of the entering ligand is important in the reaction chemistry of the nitrile complexes. An important difference between the nitrile and alkyne systems is that the former ligand is readily displaced by carbon monoxide and the latter is not. One possible explanation for this enhanced reactivity takes advantage of the lone pair of the nitrile ligand. This allows the nitrile to slip from an $\eta^2 \rightarrow \eta^1$ binding mode which would enable a small nucleophile to coordinate and ultimately displace the weakly basic η^1-bound nitrile ligand. This new mode of reactivity suggests that four-electron donor nitriles may prove to have more diverse reaction chemistry than analogous alkynes.

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Supporting Information Available: Tables giving full crystallographic data for **7**, **8**, and **15**, including bonding distances, bond angles, and refinement data (30 pages). Ordering information is given on any current masthead page.

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[31] In related capped octahedral W(II) carbonyl complexes the flexible η^3-[C,N,N′] amine chelate usually occupies an edge with the aryl carbon capping a face. For example, see: (a) Buffin, B. P; Arif, A. M.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1432−1434. (b) Buffin, B. P.; Poss, M. J.; Arif, A. M.; Richmond, T. G. *Inorg. Chem.* **1993**, *32*, 3805−3806.

[32] For an excellent discussion on the effects of π-conflict on structure and reactivity in tungsten(IV) complexes containing both π-acceptor and π-donor ligands, see: Su, F.-M.; Bryan, J. C.; Jang, S.; Mayer, J. M. *Polyhedron* **1989**, *8*, 1261−1277. For a review on the influence of filled/filled repulsions in transition metal chemistry, see: Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.

[33] Feng, S. G.; Phillip, C. C.; Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504−3512.

[34] Templeton, J. L.; Herrick, R. S.; Morrow, J. R. *Organometallics* **1984**, *3*, 535−541.

[35] Looman, S. D.; Giese, S.; Arif, A. M.; Richmond, T. G. *Polyhedron* **1996**, *15*, 2809−2811.