New Bonding Mode for Cyanoacetylene: A Tungsten(II) Fluoride Carbonyl Complex in Which Cyanoacetylene Serves as a Four-Electron Donor Alkyne Ligand

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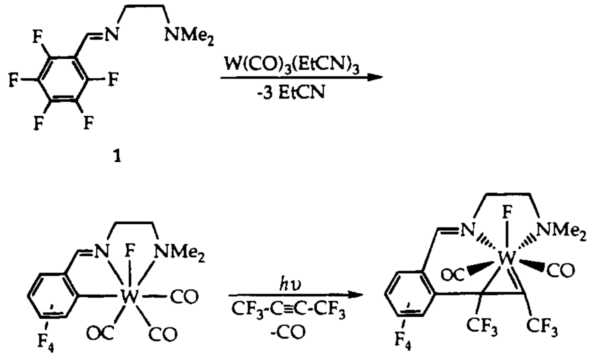
Introduction

Recently, we discovered new methods for facile transformations of strong C−F bonds into C−C bonds within the coordination sphere of a tungsten(II) metal center by sequential C−F activation and alkyne insertion.[1]



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In our continuing efforts to develop metal-based reagents for the functionalization of fluorocarbons[2] we have uncovered a new bonding mode for cyanoacetylene in which cyanoacetylene serves as a four-electron π donor ligand bound via the C≡C group.

It is surprising in light of the growing interest in organometallic polymeric magnets[3] and the reported behavior of poly(cyanoacetylene) as a semiconductor[4] that the coordination chemistry of cyanoacetylene is not well developed. Thus, the formation of organometallic complexes which may be precursors for cyanoacetylene dimerization, oligomerization, or polymerization is of interest. Several groups have demonstrated that cyanoacetylene readily inserts into metal-hydride[5] and metal−sulfur[6] bonds to afford σ-vinyl complexes. The bis(acetylide)−cobalt complex $[(\eta^5\text{-}C_5H_5)Co(PPh_3)(C{\equiv}C{-}C{\equiv}N)_2]$ has been prepared from the reaction of cyanoacetylene with $[(\eta^5\text{-}C_5H_5)Co(PPh_3)_2]$.[7] Likewise, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(C{\equiv}C{-}C{\equiv}N)]$ can be synthesized and upon reaction with $Co_2(CO)_8$ affords the bimetallic compound $[\mu\text{-}\eta^2\text{-}Fe(C{\equiv}C{-}C{\equiv}N)(\eta^5\text{-}C_5H_5)(CO)_2]$-$[Co_2(CO)_8]$ in which the Fe−C≡C−C≡N moiety is π-bound via the C≡C group to the $[Co_2(CO)_8]$ fragment.[6b] The nickel complex $[\mu\text{-}(H{-}C{\equiv}C{-}C{\equiv}N)Ni(\eta^5\text{-}C_5H_5)]_2$ has also been noted, although no structural evidence was provided to support the proposed cyanoacetylene bonding.[7]

Experimental Section

General Comments. All manipulations involving air sensitive reagents were performed under an atmosphere of purified nitrogen using standard Schlenk or glovebox techniques. Solvents were dried and distilled using standard methods. Unless noted otherwise, all chemicals were obtained from commercial sources and were used without further purification. NMR spectra were obtained using a Varian XL-300 spectrometer. Infrared spectra were recorded using a BioRad Model FTS-40 FTIR spectrometer operating with a resolution of 2.0 cm^{-1}. Solution spectra were obtained in 0.1 mm CaF_2 cells. Mineral oil mulls of solids were placed between KBr plates for spectral acquisition. All melting points were obtained in open capillary tubes and reported in °C. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Photochemical Preparation of (F_4-pia)W(CO)(F)(H−C≡C−C≡N) (4). 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**[8a] (0.16 g, 0.30 mmol) (ν_{CO} = 2020, 1934, 1900 cm^{-1}) in freshly distilled toluene (30 mL) and degassed. Cyanoacetylene (0.76 g, 1.5 mmol) (ν_{CH} = 3258 cm^{-1}, ν_{CC} = 2262 cm^{-1}, and ν_{CN} = 2067 cm^{-1}) was transferred under nitrogen by syringe to the glass bomb. The resulting bright orange solution was irradiated with a Hanovia 450 W medium-pressure Hg lamp filtered through a Pyrex cell at a distance of ca. 10 cm for 120 min. The solution changed color to a dark green. An IR spectrum of the crude product solution confirmed the reaction was complete (ν_{CN} = 2191 cm^{-1} and ν_{CO} = 1960 cm^{-1}). The reaction is accompanied with the formation of a red-brown solid believed to be 1,2-dicyanocyclobutene due to the presence of a ^{1}H NMR signal at 2.90 (s) ppm in acetone-d_6.[9] The dark green solution was filtered through Celite to remove the red-brown solid. The emerald green filtrate was purified by column chromatography using a 3 in. Florisil column and a toluene/acetone (1:1 volume) solvent mix as eluent. A yellow band eluded first and was discarded. The second fraction which is an emerald green color was collected and pumped to dryness. The resulting green residue was redissolved in 5 mL of CH_2Cl_2. Subsequent addition of hexanes (25 mL) and cooling to −10 °C afforded an emerald green powder **4** in 5% yield (8.0 mg, 0.015 mmol). Mp: 125−127 °C. Anal. Calcd for $WC_{15}H_{12}N_3OF_5{\cdot}{}^1/_4CH_2Cl_2$ (550.33 g/mol): C, 33.28; H, 2.29; N, 7.64. Found: C, 33.45; H, 2.41; N, 7.77. ^{1}H NMR (CD_2Cl_2): δ C≡C−H 13.58 s, 1H; N≡C−H 9.31 s, 1H; C=N−CH_2 4.64 tt, 1H; C=N−CH_2 4.31 dd, 1H; N−CH_2 3.17 td, 1H; N−CH_2 2.75 dm, 1H; N−CH_3 2.96 s, 3H; N−CH_3 2.00 s, 3H. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ NC−C≡C 232.77 d ($^2J_{CF}$ = 15 Hz); W−CO 224.88 d ($^2J_{CF}$ = 13 Hz); C≡C−H 187.30 d ($^2J_{CF}$ = 36 Hz); N≡C−H 167.36; N≡C−C 117.17, N−CH$_2$ 65.72; N−CH$_2$ 57.45; N−CH$_3$ 54.71; N−CH$_3$ 50.62. ^{19}F NMR (CD_2Cl_2 + $CFCl_3$): δ C−F −102.54 m, 1F; W−F −107.96 apr s, 1F; C−F −138.74 apr t, 1F; C−F −146.66 m, 1F; −157.41 apr t, 1F.

Thermal Preparation of (F_4-pia)W(CO)(F)(H−C≡C−C≡N)] (4). 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**[8a] (0.16

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Table 1. Crystallographic Data for **4**·THF

mol formula: $WF_5O_2N_3C_{19}H_{20}$
mol wt: 601.232 g/mol
space group: monoclinic, $P2_1/c$ (No. 14)
cell consts: $a = 8.173(3)$ Å, $b = 19.935(3)$ Å,
$c = 12.882(3)$ Å, $\beta = 93.24(2)°$
cell vol: 2095.39 Å^3
$Z = 4.0$
radiation: λ(Mo Kα) = 0.709 30 Å
calcd density: 1.906 g/cm^3
abs coeff (μ): 56.927 cm^{-1}
$R^a = 0.0271$
$R_w{}^a = 0.0292$

$^a R(F_o) = \Sigma(|F_o| - |F_c|/\Sigma|F_o|)$. $R_w(F_o) = [\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

g, 0.30 mmol) in freshly distilled toluene (30 mL) and degassed. Cyanoacetylene (0.76 g, 1.50 mmol) was transferred under nitrogen by syringe to the glass bomb. The resulting bright orange solution was heated to 60 °C for 8 h in an oil bath. Initial color change to a red color was observed within 30 min, and within 6 h, the solution turned an olive green color. The walls of the glass bomb become coated with a dark solid. An IR spectrum of the crude product solution confirmed the reaction was complete ($v_{CN} = 2191$ cm^{-1} and $v_{CO} = 1960$ cm^{-1}). The reaction is accompanied with the formation of the cyanoacetylene dimer (*E*)-1-butene-3-yne-1,4-dicarbonitrile as determined by the presence of ^{1}H NMR signals at δ 6.17 ppm (d, $J = 16.5$ Hz) and δ 6.52 ppm (d, $J = 16.5$ Hz) in acetone-d_6.[9] The olive green solution was filtered through Celite to remove the dark solid, and the emerald green powder **4** was isolated in 5% yield (8.0 mg, 0.015 mmol) by chromatography as described in the photochemical preparation above.

Crystallography. An emerald green prism was grown by layering a THF solution of **4** with pentanes and cooling to −10 °C. Data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation, using the ω-2θ scan technique ($4.00° < 2\theta < 50.00°$) for a crystal of dimensions 0.31 mm × 0.25 mm × 0.18 mm, mounted on a glass fiber. Details of crystal data are summarized in Table 1.

Cell constants were obtained from 25 reflections with $10° < 2\theta < 25°$. The space group was determined from systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) and subsequent least-squares refinement. Standard reflections 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 SPD/VAX package.[10]

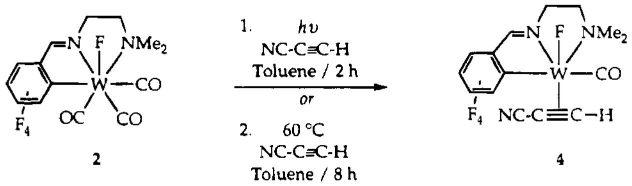
Of 4092 reflections collected at ambient temperature, 3813 were unique; 2719 of these had $I > 3\sigma(I)$ and were used in the solution and refinement (SDP PLUS software). Final refinement included all non-hydrogen atoms as anisotropic contributions and hydrogen atoms (which were located) as fixed isotropic contributions. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[11] For 271 parameters, $R = 0.0271$, $R_w = 0.0292$, and the highest peak in the final map was 0.89 e/Å^3. Atomic positional parameters for **4** are provided in Table 2.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for **4**·THF

atom	x	y	z	B^a (Å^2)
W	0.17788(3)	0.21301(1)	0.41934(2)	3.200(5)
F1	0.2769(5)	0.2531(2)	0.2956(3)	4.09(8)
F2	−0.0425(6)	0.3601(3)	0.4807(4)	6.6(1)
F3	−0.2910(8)	0.4186(3)	0.3715(5)	9.7(2)
F4	−0.4245(7)	0.3621(4)	0.1964(4)	9.7(2)
F5	−0.3033(6)	0.2444(3)	0.1270(4)	8.2(1)
O1	0.3757(8)	0.3260(3)	0.5405(4)	6.4(1)
O2	0.2779(9)	0.5487(3)	0.2750(5)	7.8(2)
N1	0.0718(7)	0.1509(3)	0.2954(4)	4.0(1)
N2	0.3844(7)	0.1386(3)	0.3898(4)	3.9(1)
N3	−0.1428(9)	0.0606(4)	0.5506(6)	7.1(2)
C1	0.3040(9)	0.2845(4)	0.4966(5)	4.5(2)
C2	0.1449(9)	0.2001(4)	0.5736(5)	4.0(2)
C3	0.0578(8)	0.1548(4)	0.5193(5)	3.8(1)
C4	−0.0533(9)	0.1024(4)	0.5378(6)	4.6(2)
C5	−0.0361(8)	0.2697(4)	0.3632(5)	4.1(2)
C6	−0.104(1)	0.3287(5)	0.3941(6)	5.1(2)
C7	−0.233(1)	0.3607(5)	0.3393(7)	6.4(2)
C8	−0.300(1)	0.3316(5)	0.2496(7)	6.3(2)
C9	−0.237(1)	0.2727(5)	0.2155(5)	5.9(2)
C10	−0.1077(9)	0.2399(4)	0.2697(5)	4.5(2)
C11	−0.0410(9)	0.1767(4)	0.2360(5)	4.7(2)
C12	0.160(1)	0.0905(4)	0.2718(6)	5.4(2)
C13	0.342(1)	0.1076(4)	0.2849(6)	5.2(2)
C14	0.549(1)	0.1715(5)	0.3862(7)	5.4(2)
C15	0.396(1)	0.0834(4)	0.4689(6)	5.0(2)
C16	0.322(2)	0.5337(6)	0.3790(8)	8.6(3)
C17	0.246(2)	0.4742(7)	0.404(1)	12.8(5)
C18	0.192(2)	0.4417(6)	0.300(1)	10.7(4)
C19	0.248(1)	0.4866(6)	0.2255(8)	8.1(3)

^{a} Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Scheme 1



Results and Discussion

As shown in Scheme 1, ambient-temperature photolysis of the known tungsten(II) fluoride **2**[8a] with 5 equiv of cyanoacetylene[12] in toluene for 120 min using a Pyrex-filtered Hg lamp generates a dark green solution with **4** as the only discernible species (v_{CO} 1960 cm^{-1} and v_{CN} 2191 cm^{-1}). The reaction is accompanied by the formation of a red-brown solid believed to be 1,2-dicyanocyclobutene due to the presence of a ^{1}H NMR signal at 2.90 (s) ppm in acetone-d_6.[9] After filtration through Celite and evaporation of the toluene solvent, the air-stable emerald green **4** is isolated in an unremarkable 5% yield following chromatography on Florisil (toluene:acetone = 1:1).

Alternatively, **4** can be prepared by treatment of **2** with 5 equiv of cyanoacetylene in toluene at 60 °C for 8 h. This route also affords **4** in only 5% yield. Interestingly, the thermal synthesis is accompanied by the formation of the cyanoacetylene dimer (*E*)-1-butene-3-yne-1,4-dicarbonitrile.[9]

The acetylenic $^{13}C\{^1H\}$ chemical shift values at δ 232.77 ($^2J_{CF} = 15$ Hz) and δ 187.30 ($^2J_{CF} = 36$ Hz) are comparable to those for other four-electron donor alkyne ligands.[13] Thus, the fluoride is *trans* to the coordinated cyanoacetylene and *cis* to the CO (δ 224.88, $^2J_{CF} = 13$ Hz). The short W—C$_{alkyne}$ bond distances of 2.036(9) Å and 2.028(9) Å and lengthened C≡C bond distance of 1.33(1) Å are consistent with a tightly bound four-electron donor alkyne (see Figure 1).[13]

The extreme downfield ^{1}H resonance exhibited at δ 13.58 ppm for the coordinated acetylene proton reflects the acidic

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(12) In toluene solution (ν_{CH} 3258 cm^{-1}, ν_{CC} 2262 cm^{-1}, and ν_{CN} 2067 cm^{-1}).

(13) For a review see: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

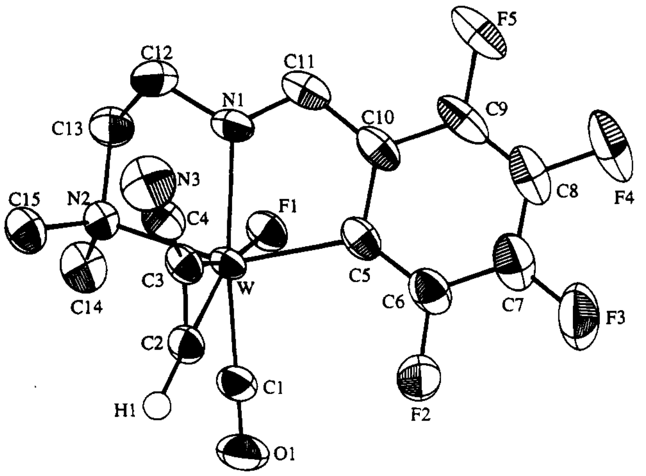

Figure 1. ORTEP representation of **4** with the THF solvate omitted. Selected bond distances (Å) are as follows: W–F1, 1.955(5); W–C2, 2.036(9); W–C3, 2.028(9); C2–C3, 1.33(1); C3–C4, 1.41(1); C4–N3, 1.13(1). Selected bond angles (deg) are as follows: F1–W–C2, 155.8(3); F1–W–C3, 165.8(3); N1–W–C1, 162.3(4); N2–W–C5, 150.1(3); C3–W–C2, 38.1(3); W–C3–C2, 71.3(6); W–C2–C3, 70.6(6); N3–C4–C3, 179(1); C4–C3–C2, 138(1); C4–C3–W, 150.4(8).

nature of the alkyne proton and is considered indicative of four-electron donation (versus free H—C≡C—C≡N at δ 6.84) by the alkyne ligand in d^4 W(II) complexes.[14] Interestingly, a survey of the packing in the unit cell illustrates that a significant amount of hydrogen bonding occurs in the solid state since the complex crystallizes as infinite chains linked between the acidic hydrogen ($\nu_{\equiv C-H\ (Nujol)}$ 3174 cm^{-1}) on the coordinated acetylene of one molecule and the basic W—F on an adjacent molecule.[15] The C2···F1 separation of 3.14 Å with a C2–H1–F1 angle of 148° is consistent with intermolecular hydrogen bonding.[16] The C2–H1···F1 interaction has a distance of 2.07 Å which is shorter than the H···F van der Waals contact separation of 2.6 Å.[17] The basicity of the fluoride was further confirmed by the ^{19}F NMR signal at δ −107.96 ppm which is slightly solvent dependent and shifts to δ −109.98 ppm upon addition of D_2O to the sample, suggesting hydrogen bonding to the fluoride.[8]

We envisioned **4** as a potential polymerization catalyst for poly(cyanoacetylene). However, treatment of a toluene solution of **4** with excess cyanoacetylene at ambient temperature merely results in slight decomposition of **4** and the production of 1,2-dicyanocyclobutene. Finally, exposure of a toluene solution of **4** to 3.5 atm of CO does not result in the substitution of the alkyne for CO, further demonstrating the strength of the W–C_{alkyne} bond.

To our knowledge this work provides the first example of cyanoacetylene functioning as a four-electron donor alkyne ligand and provides confirmation of a new mode of binding for this terminal acetylene.

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Supplementary Material Available: Full crystallographic data for **4**, including the unit cell packing diagram and tables of bond distances, bond angles, torsion angles, final positional and thermal parameters, and least-squares planes (16 pages). Ordering information is provided on any current masthead page.

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