Metal-Assisted Functionalization of Fluorocarbons: Alkyne Insertion versus Carbon Monoxide Substitution in Tungsten(II) Metallacycles

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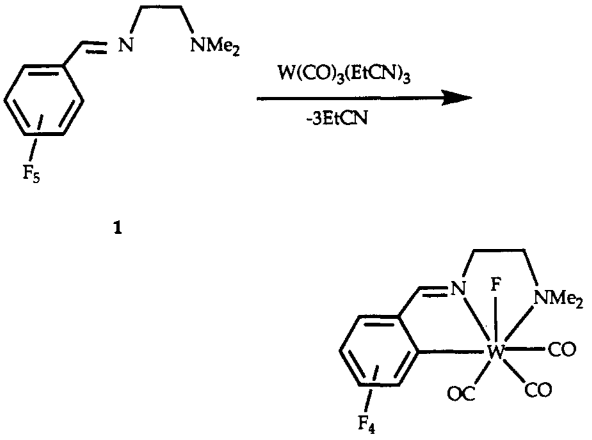
Summary: Treatment of the tungsten(II) tetrafluoroaryl metallacycle 2 with electron-deficient internal alkynes results in the formation of η^2-vinyl complexes by migratory insertion of the tetrafluoroaryl group under mild conditions. A competitive reaction involving formation of four-electron-donor alkyne complexes is favored for electron-rich alkynes. The η^2-vinyl complexes and four-electron-donor complexes are not interconvertible species, even in the presence of carbon monoxide.

Carbon–fluorine bond activation, a fundamental step in the development of metal-based catalysts for the functionalization of fluorocarbons, has been demonstrated both by our research group[1] and by others.[2] However, little is known concerning the reaction chemistry of these systems which might lead to further elaboration of the C–F bond in 1. Although pentafluoro aromatics are susceptible to attack by strong nucleophilic reagents, the usual stereochemistry is *para* to the unique group present.[3] Transition metals have been shown to alter the site of attack to the *ortho* position in suitably designed ligand systems.[4]



1

2

(1)

An alternative strategy for the functionalization of C–F bonds could involve insertion of unsaturated organics into the metal–aryl bond formed in eq 1.[5] Although metal-mediated couplings of perfluoroalkenes and -alkynes are well precedented, simple insertion reactions in which the migrating group is highly fluorinated are quite rare, presumably due to the increased strength and reduced nucleophilicity of the metal–carbon bond compared to those of hydrocarbon analogues.[6] In this work, we report that the metallacycle 2 undergoes a facile migratory insertion reaction with internal acetylenes to afford novel η^2-vinyl complexes, resulting in net replacement of a C–F bond by a C–C bond (Scheme I).

Treatment of 2 with 4.5 equiv of perfluoro-2-butyne in toluene at 80 °C for 7 h gives a maroon solution of **3** (ν_{CO} 2019, 1915 cm^{-1}), which crystallizes as an air-stable green solid η^2-vinyl product in 71% isolated yield.[7] The identification of **3** as an η^2-vinyl or metallacyclopropenyl complex was ascertained by diagnostic resonances in the $^{13}C\{^{19}F\}$ NMR spectrum (Scheme II). The carbenoid character of C_α is reflected by a large downfield chemical shift, whereas the four-coordinate carbon, C_β, has a significant upfield chemical shift. Furthermore, the fluoride was determined[8] to be *cis* to one CO (δ 221.82, $^2J_{CF}$ = 5 Hz) and *trans* to the second CO (δ 221.8, $^2J_{CF}$ = 55 Hz), leaving the inserted acetylene *cis* to the fluoride as verified crystallographically (Figure 1, left).[9] The geometry around the tungsten(II) metal center is pseudooctahedral if one considers that the η^2-vinyl ligand occupies a single coordination site. The short W–C(3) bond distance of 1.938(5) Å is consistent with a W=C double bond, and the W–C(4) bond distance of 2.196(5)

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(5) For acetylene insertion into ortho-manganated triphenyl phosphite see: Grigsby, W. J.; Lyndsay, M.; Nicholson, B. K. *Organometallics* **1993**, *12*, 397.

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(7) Anal. Calcd for **3**, $WC_{17}H_{11}N_2O_2F_{11}\cdot{}^1/_2C_7H_8$ (M_r 714.19): C, 34.48; H, 2.12; N, 3.92; F, 29.26. Found: C, 33.76; H, 2.02; N, 3.80; F, 28.54.

(8) Osterberg, C. E. Ph.D. Dissertation, University of Utah, 1990.

(9) Crystal data for **3**: $WC_{17}H_{11}N_2O_2F_{11}$, dark red, triclinic, $P\bar{1}$, a = 8.100(1) Å, b = 12.111(3) Å, c = 12.944(4) Å, α = 100.69(2)°, β = 97.92(3)°, γ = 107.97(2)°, V = 1160.79 Å^3, Z = 2.0, Mo Kα. Of 4384 reflections collected at ambient temperature (Enraf-Nonius CAD-4, $4° < 2\theta < 50°$), 4068 were unique; 3700 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. For 385 parameters, R = 0.021, R_w = 0.027, GOF = 0.80, and the highest peak in the final map was 0.48 e/Å.

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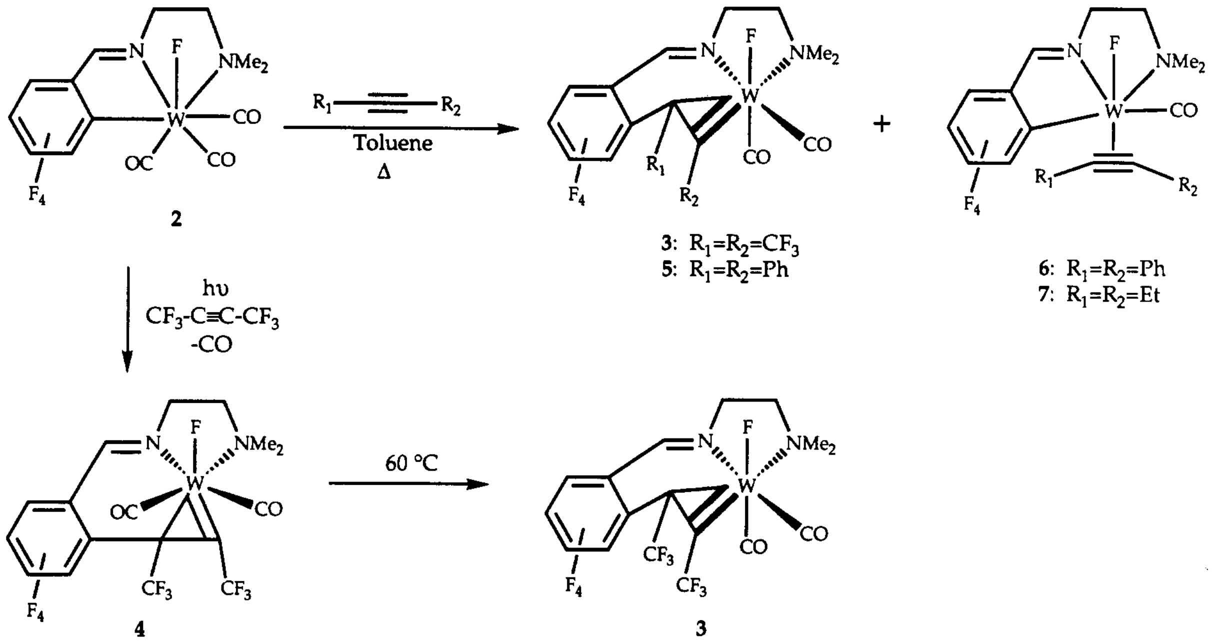
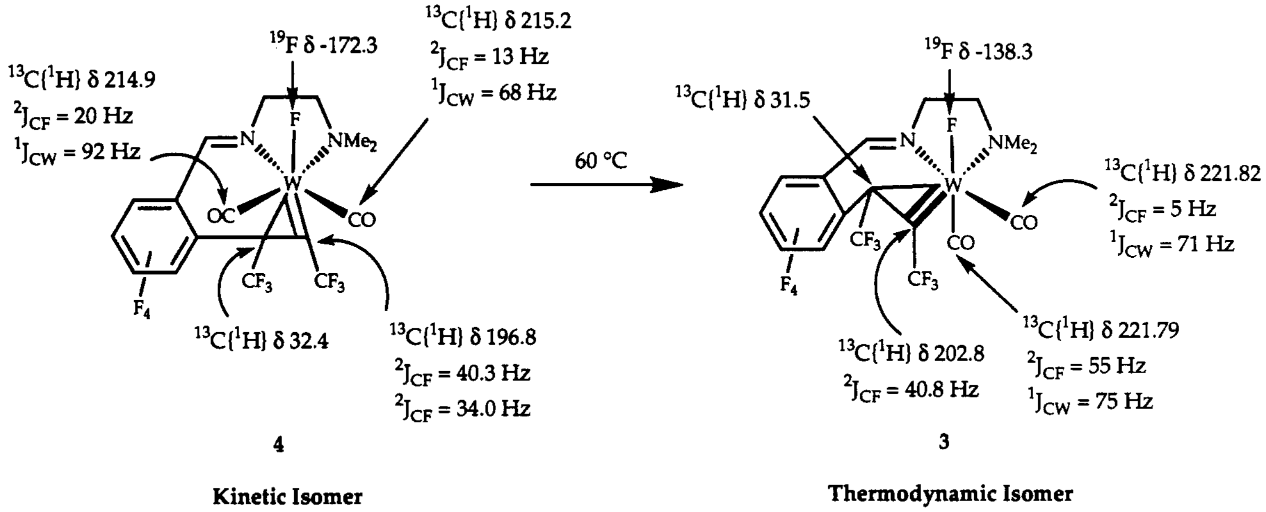
Scheme I



Scheme II



Å is in the range of a W—C single bond.[10] Furthermore, the C(3)–C(4) bond clearly exhibits partial double-bond character with a bond distance of 1.448(7) Å, justifying the η^2-vinyl structure for 3.

Ambient-temperature photolysis of 2 with 2.5 equiv of perfluoro-2-butyne in toluene for 160 min using a Pyrex-filtered Hg lamp generates a dark yellow solution with 4 as the major species (ν_{CO} 2046, 1965 cm^{-1}). Orange crystalline 4 was isolated in 50% yield following chromatography on Florisil with CH_2Cl_2 as eluent.[11] The tungsten(II) complex possesses the requisite η^2-vinyl $^{13}C\{^{19}F\}$ NMR chemical shifts at δ 196.8 and 32.4 ppm coinciding with C_α and C_β, respectively. In the $^{13}C\{^1H\}$ spectrum, C_α appears as a doublet of quartets with $^2J_{CF}$ = 40 Hz from the CF_3 group and $^2J_{CF}$ = 34 Hz from the fluoride. Notable are the reduced $^2J_{CF}$ coupling constants for the carbonyl ligands at δ 215.2 ($^2J_{CF}$ = 13 Hz) and δ 214.9 ($^2J_{CF}$ = 20 Hz), which clearly demonstrate that *both* ligands are *cis* to the fluoride. Furthermore, the kinetic η^2-vinyl product 4 is smoothly converted to the thermodynamic η^2-vinyl product 3 at 60 °C, indicating that 4 is indeed an intermediate in the formation of 3 (Scheme II). Remarkably, migration of the highly fluorinated metallacycle takes place under these mild conditions to generate the kinetic η^2-vinyl complex 4.

Less activated acetylenes also undergo this transformation. Treatment of 2 with 1.2 equiv of diphenylacetylene in toluene under reduced pressure at 60 °C for 18 h yields a dark green solution composed of two complexes, 5 (ν_{CO} 1966, 1867 cm^{-1}) and 6 (ν_{CO} 1915 cm^{-1}), in a 3:1 ratio as quantified by ^1H and ^{19}F NMR spectroscopy. The product ratios remained constant throughout the course of the reaction. The minor product was identified as the unstable four-electron donor complex 6, and the major product was recognized as the insertion product 5, which was isolated in 34% yield.[12] Analogous to 3, compound 5 is the thermodynamically stable η^2-vinyl system with resonances for the carbonyl *cis* to the fluoride at δ 224.4 ($^2J_{CF}$ = 4 Hz) and *trans* to the fluoride at δ 222.2 ($^2J_{CF}$ =

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[10] Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

[11] Anal. Calcd for 4, $WC_{17}H_{11}N_2O_2F_{11}$ (M_r 668.12): C, 30.56; H, 1.66; N, 4.19. Found: C, 30.64; H, 1.67; N, 4.13.

[12] Anal. Calcd for 5, $WC_{27}H_{21}N_2O_2F_5\cdot{}^1/_2CH_2Cl_2$ (M_r 726.76): 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.

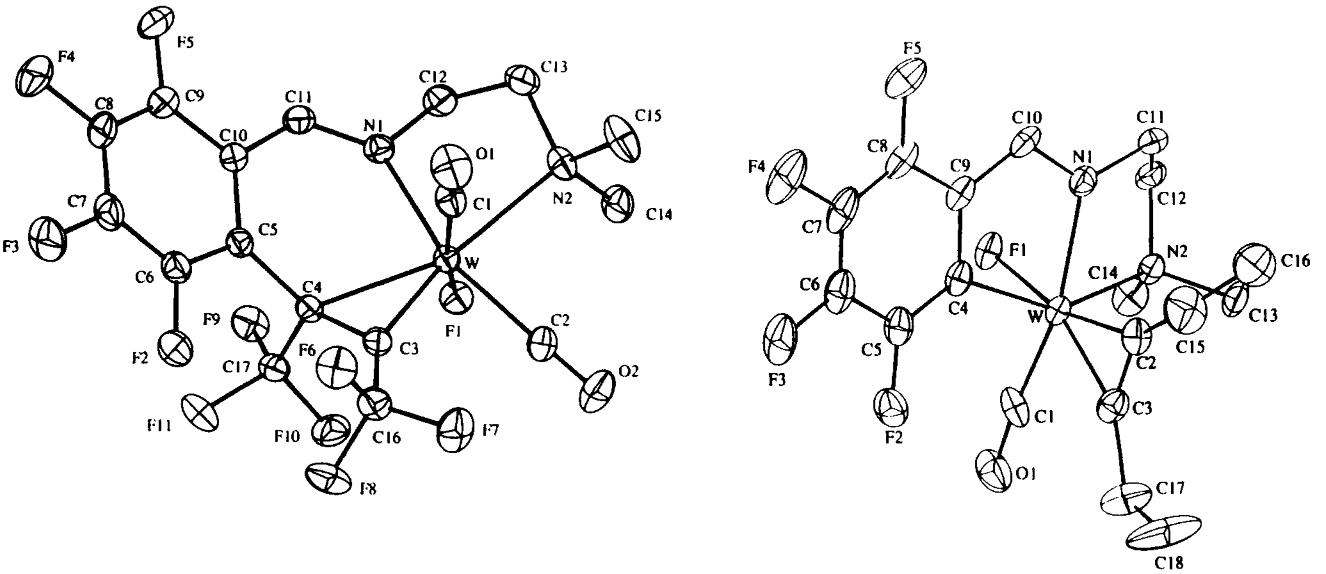

Figure 1. (Left) ORTEP representation of **3**. Selected bond distances (Å) are as follows: W–F1, 1.996(3); W–C4, 2.196(5); W–C3, 1.938(5); C3–C4, 1.448(7). Selected bond angles (deg) are as follows: F1–W–C1, 168.8(2); N1–W–C2, 160.1(2); N2–W–C3, 158.2(2); N2–W–C3, 159.1(2); C3–W–C4, 40.4(2); W–C4–C3, 60.2(3); W–C3–C4, 79.4(3). (Right) ORTEP representation of **7**. Selected bond distances (Å) are as follows: W–F1, 2.005(5); W–C2, 1.99(1); W–C3, 2.00(1); C2–C3, 1.30(2). Selected bond angles (deg) are as follows: F1–W–C2, 163.6(4); F1–W–C3, 158.4(4); N2–W–C4, 149.3(4); N1–W–C1, 161.8(5); C2–W–C3, 39.9(4); W–C3–C2, 70.8(7); W–C2–C3, 71.3(7).

56 Hz). The inserted acetylene, *cis* to the fluoride, has the essential resonances in the $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) at δ 230.1 and δ 25.7 corresponding to C_α and C_β, respectively.

The isolable four-electron donor complex **7** was obtained as an air-stable purple solid in 77% yield upon treatment of **2** with 2.2 equiv of 3-hexyne in toluene under reduced pressure at 70 °C for 51 h (ν_{CO} 1912 cm^{-1}).[13] The acetylenic $^{13}C\{^1H\}$ chemical shift values at δ 220.0 ($^2J_{CF}$ = 15 Hz) and δ 213.2 ($^2J_{CF}$ = 31 Hz) in $CDCl_3$ for **3** are comparable to those for other four-electron-donor alkyne ligands.[14] The short W–C_{alkyne} bond distances of 1.99(1) and 2.00(1) Å and lengthened C≡C bond distance of 1.30(2) Å are consistent with a tightly bound four-electron-donor alkyne (Figure 1, right).[14]

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 CO to afford the four-electron-donor alkyne complex. Interestingly, the four-electron-donor alkyne and η^2-vinyl complexes are *not* interconvertible moieties, even in the presence of carbon monoxide. The formation of four-electron-donor alkyne complexes is favored by electron-rich acetylenes, and the formation of η^2-vinyl complexes is favored by electron-deficient acetylenes.

Several groups have prepared η^2-vinyl complexes by external nucleophilic addition to four-electron-donor alkyne ligands.[14] To our knowledge this work provides the first well-defined examples of alkyne insertion into a perfluoro aromatic carbon–metal bond.

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Supplementary Material Available: Text and tables giving synthetic details and complete characterization data for all compounds and full crystallographic data for **3** and **7**, including tables of bond distances, bond angles, torsion angles, final positional and thermal parameters, and least-squares planes (43 pages). Ordering information is given on any current masthead page.

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[13] (a) Anal. Calcd for 7, $WC_{18}H_{21}N_2O_2F_5$ (M_r 576.20): C, 37.52; H, 3.67; N, 4.86; F, 16.49. Found: C, 38.87; H, 3.68; N, 4.81; F, 16.75. (b) Crystal data for 7: $WC_{18}H_{21}N_2O_2F_5$, purple, monoclinic, $P2_1/c$, a = 11.863(1) Å, b = 8.298(2) Å, c = 20.683(2) Å, β = 103.282(8)°, V = 1981.73 Å^3, Z = 4.0, Cu Kα_1. Of 3747 reflections collected at ambient temperature (Enraf-Nonius CAD-4, 4° < 2θ < 130°) 3310 were unique; 2611 of these had $I > 3\sigma(I)$. Final refinement included all non-hydrogen atoms as anisotropic and hydrogen atoms as idealized isotropic contributions. For 244 parameters, R = 0.084, R_w = 0.051, GOF = 1.3, and the highest peak in the final map was 1.1 e/Å.

[14] For an excellent review see: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.