Synthesis and reactivity of tungsten(II) carbonyl η^2-nitrile complexes: crystal structure of tetrafluoroterephthalonitrile as a four-electron donor ligand

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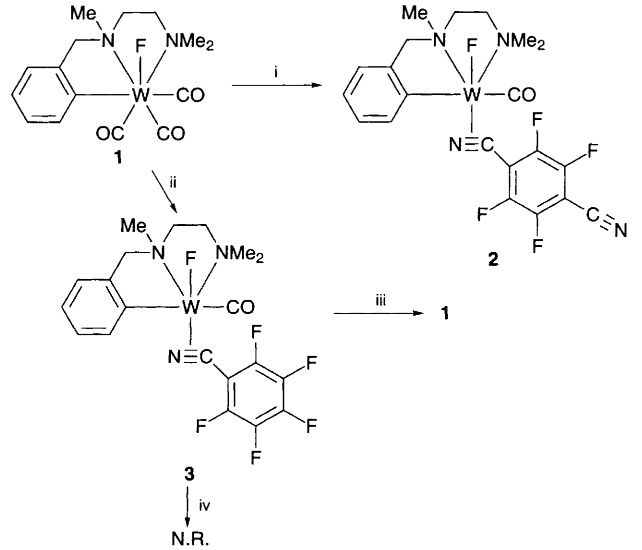
Treatment of a tungsten(II) carbonyl fluoride complex containing a tridentate monoanionic [C,N,N′] ligand with either pentafluorobenzonitrile or tetrafluoroterephthalonitrile affords tungsten(II) η^2-nitrile complexes in which the nitrile ligand functions as a four-electron donor.

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[2] are very rare but of interest as novel ligands and possible models for isoelectronic dinitrogen and other triple bonds.[1] Of the few η^2-nitrile complexes which have been structurally characterized, most are regarded as electronically saturated by considering the nitrile as a two-electron donor.[3] Recently, Etienne[4] and Harman[5] and their coworkers reported side-bound η^2-nitrile complexes in which the nitrile ligand acts as a three- and four-electron donor, respectively. In this work we report the preparation and characterization of 18e$^-$ tungsten(II) carbonyl fluoride η^2-nitrile complexes along with structural and spectroscopic evidence for the nitrile ligand acting as a four-electron donor.

As depicted in Scheme 1,† treatment of a yellow toluene solution of the tungsten(II) fluoride **1**[6] with tetrafluoroterephthalonitrile at 90 °C for 4 h affords a brilliant, ruby red solution of **2** which can be isolated as an air-stable red microcrystalline solid in 82% yield upon addition of pentane. Likewise, reaction of **1** with pentafluorobenzonitrile for 10 h in toluene at 90 °C yields **3** as an air-stable emerald green crystalline solid in 70% yield after addition of pentane.



Scheme 1 *Reagents and conditions*: i, $C_6F_4(CN)_2$-1,4, −2 CO, 90 °C, toluene, 4 h; ii, C_6F_5CN, −2 CO, 90 °C, toluene, 4 h; iii, CO (g), 90 °C, toluene, 3 h; iv, PhC≡CPh, 90 °C, toluene, 72 h; NR = no reaction

Spectroscopic† and crystallographic‡ data are consistent with an η^2-(4e)-nitrile formulation. As recently noted by Harman and coworkers,[5] η^2-(4e)-nitriles have low-field ^{13}C NMR resonances comparable to those of η^2-(4e)-alkynes (δ 190–250).[7] The $^{13}C\{^1H\}$ NMR spectra for both com- pounds **2** and **3** display a doublet in the region δ 224–226 ($^2J_{CF}$ 18 Hz) for the nitrile carbon which is *trans* to the fluoride ligand. For comparison, the free nitrile in complex **2** exhibits a ^{13}C resonance at δ 107 which is similar to shifts reported for η^1-(2e)-nitrile complexes.[3] Unlike η^2-(2e)-nitrile complexes for which weak C≡N stretches have been reported in the region 1600–1800 cm^{-1} of the IR spectrum, solid-state (KBr) IR spectra for **2** and **3** do not reveal a band which can be assigned to a C≡N stretch. However, the presence of the unbound nitrile in **2** is clearly evident in the solution IR spectrum and appears as a weak absorbance at 2246 cm^{-1}.

The nitrile complex **2** was further characterized by X-ray crystallography as it offered a unique opportunity to compare and contrast the metrical parameters of a coordinated and uncoordinated nitrile within the same complex. As illustrated in Fig. 1, the geometry around the tungsten(II) metal centre can be described as roughly octahedral if one considers that the η^2-nitrile ligand occupies a single coordination site [C(2)–W–N(1) 36.5(3)°]. In this structure, tetrafluoroterephthalonitrile is tightly bound to the tungsten(II) atom with W–N(1) [2.035(8) Å] and W–C(2) [2.039(9) Å] bonds which are virtually equal and indicate multiple metal–ligand bonding.[8] The M–C bond is quite similar to those reported for four-electron donor alkyne ligands in molybdenum(II) and tungsten(II) complexes.[7] However, the recently described η^2-(3e)-nitrile niobium(I) complex [Tp*Nb(CO)(PhC≡CMe)(PhC≡N)] possesses somewhat longer

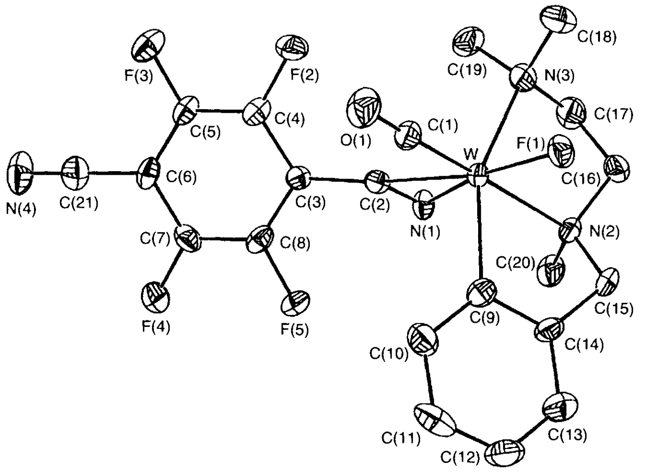


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): W–N(1) 2.035(8), W–C(2) 2.039(9), C(2)–N(1) 1.28(1), C(21)–N(4) 1.13(1), C(2)–W–N(1) 36.5(3), N(1)–C(2)–C(3) 129.7(8), C(6)–C(21)–N(4) 177.0(1), C(23)–W–F(1) 161.4(3), N(1)–W–F(1) 161.9(3), C(1)–W–N(2) 164.1(3), C(9)–W–N(3) 155.4(3).

metal–nitrogen [2.139(8) Å] and metal–carbon [2.17(1) Å] bonds.[4] The η^2-(2e)-nitrile complex [(η-C_5H_5)$_2$Mo(MeC≡N)] also exhibits significantly longer metal–nitrogen (2.22 Å) and metal–carbon (2.11 Å) bonds.[3] The coordinated nitrile of tetrafluoroterephthalonitrile in **2** [1.28(1) Å] is lengthened by 0.15 Å compared to that of the free nitrile in **2** [1.13(1) Å]. The contact carbon of the coordinated nitrile is bent with N(1)–C(2)–C(3) 129.7(8)° and is consistent with substantial sp^2 character in the ligand, a feature found in related η^2-(4e)-alkyne complexes.[7]

The majority of the known tungsten(II) and molybdenum(II) alkyne complexes possess carbonyl ligands.[7] Since the few existing η^2-(4e)-nitrile complexes do not contain carbonyl ligands it has been postulated that carbonyl and nitrile ligands are incompatible; the carbonyl ligand is a strong π acid and is believed to render the metal unsuitable for binding nitriles in an η^2-fashion.[5] Thus, the preparation and stability of **2** and **3** are of note.

As noted for other strong π-acceptor ligands, the coordinated C≡N in **2** is parallel to the W–CO axis. The orientation adopted by the nitrile allows for maximum overlap of its $\pi_\perp$ with the d_π orbital which is orthogonal to the carbonyl donor and acceptor orbitals. The monoanionic chelating nitrogen [C,N,N′] ligand system appears to support a very basic metal centre and allows for maximum overlap between the d_π orbitals on the metal and the π orbitals on the highly fluorinated nitrile ligand. Thus, in analogy to the four-electron donor alkyne ligand, the nitrile ligand seems capable of acting simultaneously as a single-faced π acid (through $\pi_\parallel$) and as a single-faced π base (through $\pi_\perp$).

The reactivity of the η^2-(4e) complex was probed with carbon monoxide and diphenylacetylene. As shown in Scheme 1, heating a toluene solution of **3** under 1.5 atm CO (g) to 90 °C for 3 h quantitatively regenerates the tungsten(II) carbonyl fluoride complex **1**. Related η^2-alkyne complexes are inert to CO under these conditions.[9] In marked contrast, no reaction takes place between **3** and excess diphenylacetylene in toluene even after 72 h at 90 °C. The latter reaction cannot be promoted even in coordinating solvents such as acetonitrile or tetrahydrofuran. The nitrile has the ability to slip from an $\eta^2 \rightarrow \eta^1$ binding mode which would enable it to allow the small CO to coordinate and ultimately displace the 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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Footnotes

† All new compounds were characterized by IR, ^{1}H, ^{13}C{^{1}H}, ^{13}C{^{19}F}, and ^{19}F NMR spectroscopic methods and satisfactory elemental analyses (C,H,N) were obtained. For ^{13}C{^{19}F} and ^{19}F NMR spectra, $CFCl_3$ was used as the external reference at δ 0.00. *Selected spectroscopic data*: **1**; IR (toluene) ν_{CO} 2004s, 1906vs, 1867s cm^{-1}. **2**: IR (toluene) ν_{CN} 2246w cm^{-1}, ν_{CO} 1930s cm^{-1}; IR (KBr) ν_{CN} 2245w cm^{-1}, ν_{CO} 1919s cm^{-1}. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 237.37 (d, $^2J_{CF}$ 11 Hz, CO), 225.83 (d, $^2J_{CF}$ 18 Hz C≡N), 176.72 (d, $^2J_{CF}$ 5 Hz, *ipso*-C), 107.49 (t, $^3J_{CF}$ 4 Hz, free N≡C). ^{19}F NMR (CD_2Cl_2): δ −47.04 (s, 1F, W–F), 130.47 (m, 2F), −134.71 (m, 2F). **3**: IR (toluene) ν_{CO} 1926s cm^{-1}; IR (KBr) ν_{CO} 1917s cm^{-1}. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 237.99 (d, $^2J_{CF}$ 11 Hz, CO), 224.94 (d, $^2J_{CF}$ 18 Hz, N≡C), 176.78 (d, $^2J_{CF}$ 5 Hz, *ipso-C*). ^{19}F NMR (CD_2Cl_2): δ −49.67 (s, 1F, W–F) −136.34 (m, 2F), −149.06 (app t, 1F), −159.21 (m, 2F).

‡ *Crystallographic data* for **2**: $C_{21}F_5H_{19}N_4OW$; orthorhombic, space group *Fdd*2 (no. 43), $a = 26.791(3)$, $b = 34.813(8)$, $c = 9.446(2)$ Å, $U = 8809.57$ Å^3, $Z = 16$ based on 1788 observations at ambient temperature (Mo-Kα, $2 < 2\theta < 50°$, $\mu = 54.177$ cm^{-1}) with $I > 2\sigma(I)$ and 288 variables to yield $R = 0.0221$, $R_w = 0.0316$. X-Ray quality crystals were grown by diffusion of pentane into a CH_2Cl_2 solution of **2**. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/133.

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