

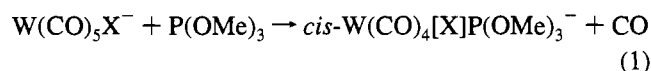
CO-Labilizing Ability of the Fluoride Ligand in Tungsten(0) Carbonyl Fluorides. X-ray Structure of [Et₄N]₃[W₂(CO)₆F₃]

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Anionic halo pentacarbonyls of the group 6 metals (M(CO)₅X⁻, M = Cr, Mo, W and X = Cl, Br, I) have long been characterized in the organometallic literature.¹ These were initially synthesized thermally from [R_nN][X] and M(CO)₆ in high-boiling solvents such as diethylene glycol dimethyl ether. Missing from this series were the fluoride analogs. Nevertheless, there are literature reports of the preparations of the PPN⁺ salts of Cr(CO)₅F⁻ and W(CO)₅F⁻ and the potassium salt of W(CO)₅F⁻ in the mid-1970s where detailed characterization is lacking.^{2,3} These derivatives were included in a comprehensive review on low-valent metal fluoride complexes by Doherty and Hoffman.⁴ Surprisingly, there was no indication of enhanced CO lability in these derivatives relative to the other halides. CO lability in the fluoride complexes is anticipated on the basis of recent studies demonstrating significant π -stabilization of unsaturated derivatives by π -donor ligands, where fluoride is reported to be a better π -donor than phenoxide.⁵ That is, the fluoride ligand is accurately defined as a *cis*-labilizing ligand.⁶ Reaction 1 has



been shown to proceed *via* CO dissociation with a first-order rate constant of $2.15 \times 10^{-2} \text{ s}^{-1}$ at 5 °C for X = OPh⁻ compared to $1.01 \times 10^{-4} \text{ s}^{-1}$ at 5 °C for X = Cl⁻.⁷ Hence, we have reinvestigated the synthesis and reactivity of the W(CO)₅F⁻ anion in order to resolve this discrepancy. By way of comparison, facile CO dissociation in the Re(I) analog, Re(CO)₅F, accounts for the formation of the structurally characterized [ReF(CO)₃]₄ derivative.⁸ Similarly, the *cis* CO ligands in *trans*-ReF(CO)₃(PPh₃)₂ have been shown to readily undergo exchange with ¹³CO in THF solution.⁹

The addition of W(CO)₅THF to 1 equiv of anhydrous Et₄NF in tetrahydrofuran resulted in the formation of a THF-insoluble solid product.¹⁰ This product, **1**, has been characterized by

infrared, ¹³C NMR, and X-ray crystallography and found to be the dinuclear complex resulting from rapid CO loss in the initially formed W(CO)₅F⁻ derivative followed by dimerization with simultaneous incorporation of an additional fluoride ligand.¹¹ Complex **1** was found to be soluble in CH₃CN but to be completely insoluble in most common organic solvents.

Crystals suitable for X-ray diffraction study were obtained from a concentrated CH₃CN solution of **1** layered with THF and toluene and allowed to stand at ambient temperature for 2 weeks.¹² The structure consists of a trianion containing two tungsten tricarbonyl fragments bridged by three fluoride ions (Figure 1).¹³ Three tetraethylammonium cations are present to balance the charge of the ditungsten anion. The geometry about each tungsten is that of a distorted octahedron with a CO ligand *trans* to each fluoride. The average W–C bond length is 1.92–[2] Å, and the average W–F distance is 2.178[9] Å. As anticipated, the average W–F distance is slightly longer than that observed in the analogously configured d⁴ tungsten complex {[W(CO)₂(PMe₂Ph)₂]₂(μ -F)₃}[BF₄], where (W–F)_{av} = 2.12(1) Å.¹⁴ The average F–W–F bond angle is rather acute, at 70.6–[3]°, the average W–F–W bond angle is 96.9 [3]°. These values compare well to those of the phenoxide-bridged analog [Et₄N]₃[W₂(CO)₆(OPh)₃],¹⁵ where the average W–C and W–O bond distances are 1.90 and 2.22 Å, respectively, with average O–W–O and W–O–W bond angles of 70.3 and 96.6°. Cocrystallized with the dimer are the decomposition product [Et₄N]₂[WF₆]¹⁶ and a molecule of THF.

The W₂(CO)₆F₃³⁻ anion reacts with carbon monoxide in solution to afford the desired pentacarbonyl tungsten derivative (**2**) (eq 2).¹⁷ This reaction takes place very rapidly and proceeds

- (1) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068.
- (2) Douglas, W.; Ruff, J. K. *J. Organomet. Chem.* **1974**, 65, 65.
- (3) Cihonski, J. L.; Levenson, R. A. *Inorg. Chem.* **1975**, 14, 1717.
- (4) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, 91, 553.
- (5) (a) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, 31, 3190. (b) Caulton, K. G. *New J. Chem.* **1994**, 18, 25.
- (6) (a) Brown, T. L.; Atwood, J. D. *J. Am. Chem. Soc.* **1976**, 98, 3160. (b) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, 100, 366.
- (7) (a) Darensbourg, D. J.; Chojnacki, J. A. Unpublished observations. (b) Allen, A. D.; Barrett, P. F. *Can. J. Chem.* **1968**, 46, 1655.
- (8) (a) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1981**, 34, 737. (b) Horn, E.; Wimmer, F. L.; Snow, M. R. *Inorg. Synth.* **1989**, 26, 81.
- (9) Hoffman, N. W.; Prokopuk, N.; Robbins, M. J.; Jones, C. M.; Doherty, N. M. *Inorg. Chem.* **1991**, 30, 4177.
- (10) The complex was prepared by photolyzing 0.5 g (1.4 mmol) of W(CO)₆ in 60 mL of THF for 35 min. This solution was then added to 1 equiv (0.21 g) of Et₄NF (obtained as a hydrate salt from Aldrich Chemicals and dried overnight at 110 °C under continuous vacuum). The reaction solution was flushed with argon for a period of 1 h to aid in the removal of liberated CO gas and hinder the formation of W(CO)₆, which is a major byproduct. W(CO)₆ was removed by washing the powder several times with hexane.

- (11) [Et₄N]₃[W₂(CO)₆F₃]: $\nu(\text{CO})$ in CH₃CN 1865 (s) and 1727 (vs) cm⁻¹; $\nu(\text{CO})$ in KBr 1868 (s) and 1722 (vs); ¹³C NMR in CD₃CN 230.8 ppm quartet, $J_{\text{C-F}} = 20.7$ Hz.
- (12) Shorter recrystallization times led to crystals of a different morphology which displayed a $\nu(\text{CO})$ infrared spectrum identical with that of the W₂(CO)₆F₃³⁻ anion but were unsuitable for X-ray diffraction. Crystal data for C₄₀H₈₄F₆N₄O₇W₂: monoclinic, *P*2₁/*n*, *a* = 16.111(12) Å, *b* = 22.93(2) Å, *c* = 15.045(9) Å, β = 115.56(5)°, *V* = 5014(6) Å³, *Z* = 4, *D*_c = 1.731 g cm⁻³, *R* = 6.74%, GOF = 1.031.
- (13) (a) [(CH₃)₄N]₃[M₂(CO)₆F₃] (M = Cr, Mo, W) derivatives have been previously reported from the reaction of (CH₃)₄NF and M(CO)₆ in refluxing ethanol.^{13b} However, the complexes were reported to be too unstable to be characterized. Nevertheless, elemental analyses for metal content were presented along with complete elemental analyses of the corresponding chloride, bromide, and iodide analogs. (b) White, J. F.; Farona, M. F. *J. Organomet. Chem.* **1972**, 37, 119.
- (14) Dawson, D. M.; Henderson, R. A.; Hills, A.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1992**, 973.
- (15) (a) Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H. *Inorg. Chem.* **1988**, 27, 3269. (b) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Johnson, C. C.; Sanchez, K. M.; Reibenspies, J. H. *Isr. J. Chem.* **1990**, 30, 369.
- (16) The complex [Et₄N]₂[WF₆] has been independently crystallized and characterized by X-ray crystallography (Reibenspies, J. H.; Klausmeyer, K. K.; Darensbourg, D. J. *Z. Kristallogr.*, in press). The average W–F bond distance in this W(IV) derivative is 1.779[6] Å. The corresponding distance in the cocrystallized sample reported herein was found to be 1.784[9] Å.
- (17) [Et₄N][W(CO)₅F]: $\nu(\text{CO})$ in CH₃CN 2060 (w), 1908 (s), and 1854 (m) cm⁻¹; ¹³C NMR in CD₃CN 200.2 ppm doublet, $J_{\text{C-F}} = 8.5$ Hz (4 CO's), and 203.3 ppm doublet, $J_{\text{C-F}} = 50.3$ Hz (1 CO).

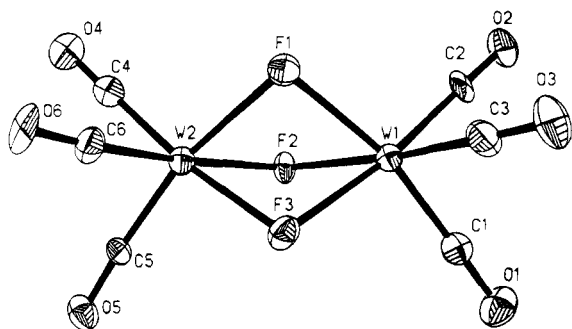
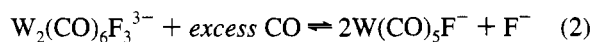


Figure 1. Thermal ellipsoid plot of the trianion, $W_2(CO)_6F_3^{3-}$. Ellipsoids are drawn with 50% probability boundaries.



to completion in CH_3CN by addition of CO to the solution. Although $[Et_4N]_3[W_2(CO)_6F_3]$ is insoluble in THF, placing an atmosphere of CO gas over a mixture of THF and complex **1** results in the slow reaction of **1** to form **2** in solution; there was no evidence in the infrared spectrum for the presence of **1** in solution. Anion **2** is very unstable in solution, reverting back to the dinuclear complex in the absence of CO, or with prolonged exposure to CO, losing the fluoride ligand to form the hexacarbonyl. This instability has thus far precluded the possibility of isolating the pentacarbonyl derivative.

Since the reverse of reaction 2 for other $W(CO)_5X^-$ derivatives has been demonstrated to undergo CO ligand substitution *via* a dissociative pathway, it is possible to conclude that CO dissociation in **2** is rapid when compared with that in the other halide complexes. The discrepancy in the previously reported lack of CO lability in $W(CO)_5F^-$ is probably due to the fact that the sample was prepared from $[PPN]F$ which contained a large quantity of methanol, where H-bonding to the fluoride ligand is possible.¹⁸ Indeed, $W-F \cdots H$ -bonding interactions have been noted in tungsten(II) fluoride carbonyl complexes.¹⁹ We have noticed that the involvement of the lone pairs of the oxygen donor in metal alkoxides in hydrogen-bonding greatly retards their ability to labilize CO ligands. The

(18) This was astutely noted by Hoffman upon repeating the synthesis of $[PPN]F$: Branan, D. M.; Hoffman, N. W.; McElroy, E. A.; Miller, N. C.; Ramage, D. L.; Schott, A. F.; Young, S. H. *Inorg. Chem.* **1987**, *26*, 2915.

(19) (a) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888. (b) Kiplinger, J. L.; Arif, A. M.; Richmond, T. G. *Inorg. Chem.* **1995**, *34*, 399. (c) Indeed, Richmond recently reviewed the ability of metal fluorides to form hydrogen bonds: Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221.

presence of hydrogen-bonding by MeOH in $M(CO)_5X^-$ derivatives leads to a shift in the $\nu(CO)$ vibrations to higher frequency. Indeed the $\nu(CO)$ E mode for the sample reported herein occurs at 1908 cm^{-1} , whereas the previously reported $\nu(CO)$ band appeared at 1915 cm^{-1} . Hence, it is possible to conclude that the fluoride ion in $W(CO)_5F^-$ is at least as CO labilizing as OPh^- and possibly more so.

It should further be noted that the CO ligands in **2** are rigid in solution at ambient temperature, as evidenced by two sharp ^{13}C resonances at 200.2 and 203.3 ppm of appropriate intensity ratio 4:1. On the other hand, the CO ligands in the trianion $W_2(CO)_6F_3^{3-}$ are undergoing rapid exchange at ambient temperature, as manifested by each ligand experiencing an average $^{13}C-^{19}F$ coupling constant (a quartet with $J_{C-F} = 20.7\text{ Hz}$)²⁰ which upon cooling of the sample to $-20\text{ }^\circ\text{C}$ starts to display inequivalent $^{13}C-^{19}F$ coupling. Unfortunately, in acetonitrile solvent, we were not able to achieve sufficiently low temperatures to completely freeze out the rotation.

Several attempts were made at synthesizing the chromium and molybdenum analogs of the dinuclear tungsten species. In each case, the addition of $M(CO)_5THF$ to Et_4NF resulted in the formation of an insoluble product. This product was insoluble even in CH_3CN and has been characterized only by solid-state infrared spectroscopy.²¹ This result indicates that a cluster, possibly $[M(CO)_3X]_4^{4-}$, has been formed, as evidenced by the large $\nu(CO)$ shifts to higher frequencies for the chromium and molybdenum compounds as compared to the dinuclear tungsten complex. Unlike the dinuclear tungsten carbonyl complex, these carbonyl derivatives were unreactive toward an atmosphere of carbon monoxide.

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Supporting Information Available: For $C_{80}H_{84}F_6N_4O_7W_3$, tables of crystal data and X-ray crystallographic refinement parameters, atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles (8 pages). See any current masthead page for ordering information.

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(20) The weighted average J_{C-F} for two *cis* and one *trans* fluorides would be anticipated to be 22.4 Hz based on the corresponding values for **2**.

(21) Solid-state $\nu(CO)$ (KBr): Mo cluster 1898 (s) and 1753 (vs), Cr cluster 1892 (s) and 1743 (vs) cm^{-1} .