

Novel Coordination Mode of Boron Tetrafluoride Anion: Structure of a BF_4^- -capped Trirhenium Cluster: $[\text{NEt}_4]^+_2[\text{Re}_3\text{H}_2(\text{CO})_9\text{BF}_4]^{2-}$

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In dichloromethane solution at room temperature, the reaction between $[\text{Re}_4\text{H}_4(\text{CO})_{12}]$ and acetone followed by addition of NEt_4BF_4 yielded $[\text{NEt}_4]^+_2[\text{Re}_3\text{H}_2(\text{CO})_9\text{BF}_4]^{2-}$ (30% yield), in which the triangular trirhenium cluster is capped by a $\mu_3\text{-FBF}_3^-$.

Organometallic compounds coordinated by weakly coordinating anions, e.g. BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , $\text{CB}_{11}\text{H}_{12}^-$ and C_{60}^- , are reactive and have attracted many studies as evidenced by two recent review articles.^{1,2} These ligands are good leaving groups; they can be easily replaced by other ligands under mild conditions; the Lewis acidity of the organometallic moieties is therefore greatly enhanced. The bonding modes for the coordination of these anions to the metal centres are as expected, e.g. BF_4^- can coordinate in the following expected bonding modes: $\mu\text{-FBF}_3^-$ (as in *cis-mer*- $[\text{IrMe}(\text{PMe}_2\text{Ph})(\text{FBF}_3)]$),³ $[\text{Ni}\{\text{CF}(\text{PEt}_3)^+(\text{CF}_2)_3\}(\text{PEt}_3)(\text{FBF}_3)]$,⁴ *mer*- $[\text{W}(\text{cis-PM}_2\text{E}_3)(\text{trans-NO})(\text{CO})_3(\text{FBF}_3)]$ ⁵ and *mer-trans*- $[\text{W}\{\text{P}(\text{C}_6\text{H}_{11})_3\}(\text{CO})_3(\text{FBF}_3)]$ ⁶; $\eta^2\text{-F}_2\text{BF}_2^-$ (as in $[\text{Cu}(\text{bipy})_2(\text{F}_2\text{BF}_2)]^+$)⁷; and $\mu\text{-}\eta^2\text{-F}_2\text{BF}_2^-$ (as in $[\text{U}(\mu\text{-}\eta^2\text{-F}_2\text{BF}_2)(\mu\text{-F})]_2$)⁸ $\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}$. However, we report here a novel coordination mode of BF_4^- in the structure of $[\text{NEt}_4]^+_2[\text{Re}_3\text{H}_2(\text{CO})_9(\mu_3\text{-FBF}_3)]^{2-}$.

$[\text{Re}_4\text{H}_4(\text{CO})_{12}]$ ⁹⁻¹³ (0.14 mmol) was reacted with acetone (14 mmol) in CH_2Cl_2 (25 ml) for 8 h at room temperature under nitrogen then NEt_4BF_4 (0.1 mmol) was added to the reaction mixture. After 30 min, the mixture was separated with silica gel TLC using $\text{CHCl}_3\text{-C}_6\text{H}_6\text{-acetone}$ (3:3:4) as eluent. A white solid product, **1**, was obtained at $R_f = 0.35$ (30% yield). Other compounds were also isolated from the reaction mixture; details will be published elsewhere. **1** was further purified by TLC separation using $\text{C}_6\text{H}_{14}\text{-CHCl}_3\text{-acetone}$ (1:2:3) as eluent. A single crystal of **1** was obtained by slow evaporation of a $\text{C}_6\text{H}_{14}\text{-CHCl}_3\text{-acetone}$ (1:2:3) solution. The ¹H NMR spectrum (400 MHz, CD_2Cl_2) indicated the presence of NEt_4^+ [δ 3.23 (16 H, q, J 7 Hz), 1.33 (24 H, t, J 7 Hz)] and hydride [δ -12.04 (2 H, s)]. The relative intensities of the protons have been carefully examined with various relaxation parameters. Three IR absorption bands [CHCl_3 , $\nu(\text{CO})$] were detected at 2045, 1982 and 1930 cm^{-1} . One UV absorption band (CHCl_3) at 283 nm ($\epsilon = 1.63 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) was detected, indicating that **1** contains no unsaturation.

From the structure of **1**⁺ (Fig. 1) and its spectral data, **1** is assigned the formula $[\text{NEt}_4]^+_2[\text{Re}_3\text{H}_2(\text{CO})_9\text{BF}_4]^{2-}$. The three rhenium atoms form an isosceles triangle, and each Re is coordinated by three mutually perpendicular carbonyl groups. All carbonyl groups coordinate linearly to Re atoms (Re-C-O angles 176–179°). The prominent feature of the anion is that one fluorine atom of BF_4^- caps the rhenium triangular face. This is the first example of a BF_4^- coordinated in a $\mu_3\text{-FBF}_3^-$ fashion. Any two rhenium atoms and the bridging fluoride form an isosceles right triangle. The Re-F(1) distances of ca. 2.14 Å are comparable to these in $(\text{CO})_5\text{Re-F-EF}_5$ (2.13 and 2.20 Å for the two crystallographically nonequivalent molecules in a unit cell, E = Re).¹⁴ However, the comparable bond distances do not indicate comparable bond strengths. It has been argued convincingly by Honeychuck and Hersch⁵ that in the organometallic compounds coordinated by weakly coordinating anions $\text{M-F}_b\text{-EF}_n$ (E = B, P, As, Sb; $n = 3, 5$) the M-F_b distance is not a good measure for the bond strength since the large span of this bond distance was found to have no obvious correlation with the bond strength. Instead, the $\text{F}_b\text{-E}$ bond distance is a much better scale. The B(1)-F(1) distance

(1.50 Å) is much larger than that in the uncoordinated BF_4^- anion (1.406 Å);¹⁵ it is also larger than the average bond distances (1.36 Å) between B(1) and the terminal fluorine atoms. This substantial lengthening of B(1)-F(1) indicates that the interaction of F(1) with the cluster is very strong and close to the upper limit for the breakdown of BF_4^- to F^- and BF_3 , as suggested by Honeychuck and Hersch.⁵ In spite of the difference in B-F bond distances, the F-B-F angles (107.0–111.4°) remain close to those of a regular tetrahedron. The Re-F(1)-B angles (ca. 126°) are close to the typical M-F-B angles (ca. 130°),^{4,5,7,16,17} which have a few exceptions found in sterically crowded complexes $\{\text{cis-mer-}[\text{IrMe}(\text{PMe}_2\text{Ph})(\text{FBF}_3)]$ ³ 160°, *mer-trans*- $[\text{W}\{\text{P}(\text{C}_6\text{H}_{11})_3\}(\text{CO})_3(\text{FBF}_3)]$ ⁶ 141°, and $[\text{Cu}(\text{PPh}_3)_3(\text{FBF}_3)]$ ¹⁸ 180°}. To fulfil the 18-electron rule for each Re centre, which is obeyed by all trirhenium clusters, the bridging fluoride must donate six electrons to the Re cluster; this is unprecedented in fluorinated organometallic compounds.

The triangular planes of Re(1)-Re(2)-Re(2a) and F(2)-F(3)-F(3a) are practically parallel (dihedral angle 0.1°), and the rhenium atoms and terminal fluorine atoms are in a staggered configuration. The three carbonyl groups

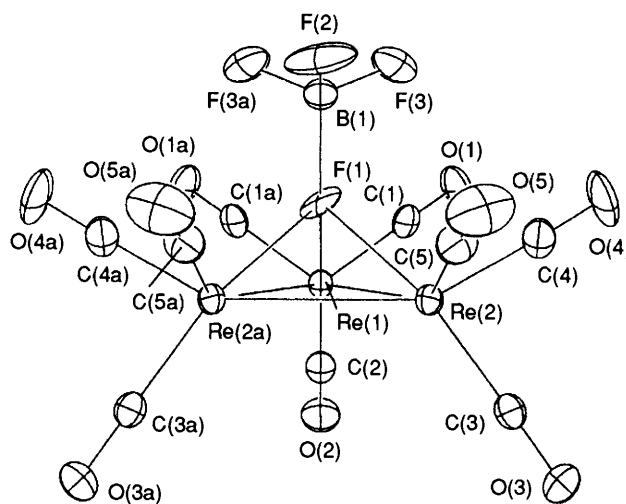


Fig. 1 ORTEP drawing of the anion of $[\text{Re}_3\text{H}_2(\text{CO})_9\text{BF}_4]^{2-}[\text{NEt}_4]^+_2$. Selected bond distances (Å): Re(1)-Re(2) 2.984(1), Re(2)-Re(2a) 3.003(1), Re(1)-F(1) 2.138(7), Re(2)-F(1) 2.146(7), F(1)-B(1) 1.503(21), F(2)-B(1) 1.395(16), F(3)-B(1) 1.338(13), Re-C(av.) 1.89, C-O(av.) 1.15. Selected bond angles (°): Re(2)-Re(1)-Re(2a) 60.4(1), Re(1)-Re(2)-Re(2a) 59.8(1), Re(1)-F(1)-Re(2) 88.3(2), Re(2)-F(1)-Re(2a) 88.8(2), Re(2)-Re(1)-F(1) 45.9(2), Re(1)-Re(2)-F(1) 45.7(2), Re(1)-F(1)-B(1) 125.0(7), Re(2)-F(1)-B(1) 127.0(4), C(2)-Re(1)-F(1) 167.8(5), C(3)-Re(2)-F(1) 167.3, F(1)-B-F(2) 107(1), F(1)-B-F(3) 110(1), F(2)-B-F(3) 111(1), F(3)-B-F(3a) 108(1), C(1)-Re(1)-C(2) 90.5(4), C(1)-Re(1)-C(1a) 91.6(6), C(3)-Re(2)-C(4), 88.9(5), C(3)-Re(2)-C(5) 87.9(5), C(4)-Re(2)-C(5) 91.2(5), Re(1)-C(1)-O(1), 178.5(9), Re(1)-C(2)-O(2) 179.6(7), Re(2)-C(3)-O(3) 179.0(6), Re-C(4)-O(4) 177.3(8), Re(2)-C(5)-O(5) 176(1).

[C(2)O(2), C(3)O(3) and C(3a)O(3a)] on one face of the Re plane are pointing nearly linearly towards F(1)[F(1)–Re–C *ca.* 167° for C = C(2), C(3) and C(3a)], which is located on the opposite face of the Re plane. This configuration allows the *trans* carbonyl groups to have the maximum π interaction with the capping fluorine.

The distances between the terminal fluorine atoms and the carbons of nearby carbonyl groups [*e.g.* F(2) and C(5), C(5a)] are in the range 3.1–3.3 Å, which is comparable to the sum of the van der Waals radii of fluorine and carbon.¹⁹ From the chemical shifts of the hydrides (δ –12.04), it is reasonable to assign them to the two symmetrical edge-bridging positions between Re(1)–Re(2) and Re(1)–Re(2a). However, the three Re–Re distances are close to each other and are *ca.* 2.99 Å which is noticeably smaller than the hydride-bridged Re–Re distances in triangular trirhenium clusters, *e.g.* [Re₃H₃(CO)₁₂] 3.241 Å,²⁰ [Re₃H₂(CO)₁₂] 3.173, 3.182 Å,²¹ [Re₃H₃(CO)₉(PPh₃)₃] 3.259 Å²² and [Re₃H₃(CO)₉{HC(PPh₂)₃}] 3.271 Å.¹³ There are precedents of shortening of hydride-bridged Re–Re bonds, *e.g.* the Re–Re bond distance in [Re₃H₃(CO)₉(μ -O)]²⁻ is 2.955 Å (av.),²³ and 2.994 Å (av.)²⁴ in [Re₃H₃(CO)₉(μ -OEt)]⁻. However, the Re(2)–Re(2a) bond does not seem to be affected by BF₄⁻ capping. On the other hand, 2.99 Å can be viewed as a typical fluorine bridged Re–Re single bond distance.

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† Crystal data for [NEt₄]⁺₂[Re₃H₂(CO)₉BF₄]²⁻, 1: C₂₅H₄₂BF₄N₂O₉Re₃, *M* = 1160.0, *P*2₁/*m*, monoclinic, *a* = 10.892(3), *b* = 16.070(3), *c* = 11.040(2) Å, β = 109.75(2)°, *Z* = 2. The diffraction intensity data were collected on a Siemens R3m/v diffractometer using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å), within the range 2.5 ≤ 2 θ ≤ 50°, 3341 independent reflections [2780 ≥ 3.0 σ (*I*)]. Absorption correction was performed. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically by full-matrix least squares. *R* = 0.0338, *R*_w = 0.0396. The two tetraethylammonium cations (not shown in Fig. 1) are disordered. Atomic coordinates, bond lengths and angles and thermal

parameters are available from the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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