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Terminal coordination of diatomic boron monofluoride to iron

Myles J. Drance[1], Jeffrey D. Sears[2], Anthony M. Mrse[1], Curtis E. Moore[1], Arnold L. Rheingold[1], Michael L. Neidig[2], Joshua S. Figueroa[1]*

Boron monofluoride (BF) is a diatomic molecule with 10 valence electrons, isoelectronic to carbon monoxide (CO). Unlike CO, which is a stable molecule at room temperature and readily serves as both a bridging and terminal ligand to transition metals, BF is unstable below 1800°C in the gas phase, and its coordination chemistry is substantially limited. Here, we report the isolation of the iron complex $Fe(BF)(CO)_2(CNAr^{Tripp2})_2$ [Ar^{Tripp2}, 2,6-(2,4,6-(*i*-Pr)$_3C_6H_2$)$_2C_6H_3$; *i*-Pr, *iso*-propyl], featuring a terminal BF ligand. Single-crystal x-ray diffraction as well as nuclear magnetic resonance, infrared, and Mössbauer spectroscopic studies on $Fe(BF)(CO)_2(CNAr^{Tripp2})_2$ and the isoelectronic dinitrogen (N_2) and CO complexes $Fe(N_2)(CO)_2(CNAr^{Tripp2})_2$ and $Fe(CO)_3(CNAr^{Tripp2})_2$ demonstrate that the terminal BF ligand possesses particularly strong σ-donor and π-acceptor properties. Density functional theory and electron-density topology calculations support this conclusion.

Carbon monoxide (CO) is among the most widely studied ligands in organometallic chemistry. Since the original report of a CO coordination compound 150 years ago (*1*) and the discovery of the first homoleptic metal carbonyl $Ni(CO)_4$ in 1890 (*2*), the coordination chemistry of CO has occupied a central role in the development of the reactivity and electronic structure theory of transition-metal complexes (*3*, *4*). The binding of CO to transition metals has been described classically by the Dewar-Chatt-Duncanson bonding model (*5*, *6*). In the terminal coordination mode, σ-donation from the carbon-centered lone pair of CO to an empty, acceptor orbital on the metal provides a primary bonding interaction (Fig. 1A). However, this metal-CO linkage is fortified by π-backdonation interactions from filled metal-based d-orbitals to the π* orbitals of CO (Fig. 1A) (*7*). The success of CO as a ligand is derived from the polarized nature of the C–O triple bond, which renders both its σ-donor and π-acceptor functionalities energetically well matched for interaction with a transition metal (*8*). Diatomic molecules and ions that are isoelectronic and isolobal to CO—such as N_2, CN^-, and NO^+ (Fig. 1B)—are also widely known to bind transition metals (*9*). However, the less polarized nature of these diatomics substantially alters their properties as ligands. Indeed, N_2 has comparatively lower-energy σ-donor orbitals and higher-energy π* orbitals than those of CO, which limits its binding ability (*8*, *9*). In addition, the π* orbitals of CN^- are too high in energy for effective π-backdonation, and although NO^+ is a strong π-acid, it is a relatively weak σ-donor ligand (*8*, *9*).

It has long been recognized that the quintessential neutral, yet highly polarized, isoelectronic analog to CO is boron monofluoride (BF) (Fig. 1C) (*10*–*15*). Diatomic BF has been predicted to bind even more favorably to transition metals owing to a decreased HOMO/LUMO gap (HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital) relative to that of CO, leading to both more potent σ-donor and π-acceptor abilities (*16*–*19*). However, this electronic feature also renders the free BF molecule far more reactive than CO. As such, BF is not a stable molecule at room temperature. It must be prepared under low pressure at 1800° to 2000°C, and it quickly oligomerizes upon cooling (*11*, *12*, *14*). Whereas coordination to transition metals is often used as a strategy for the stabilization of highly reactive species, fluoroborylene complexes, in which BF serves as a terminal ligand, have remained long-sought synthetic targets that have eluded isolation (*14*, *20*–*24*). Here, we report the preparation and x-ray crystal structure of a terminal fluoroborylene complex of iron that possesses sufficient kinetic stability for isolation at room temperature. In addition, the iron-based molecular platform presented here allows for the direct comparison of the structural and electronic consequences of BF coordination relative to those of the neutral isoelectronic diatomic molecules CO and N_2.

To prepare a terminal fluoroborylene complex amenable to isolation, we chose to construct the BF unit directly within the coordination sphere of a kinetically stabilizing metal center. Previously, Vidovic and Aldridge reported that two equivalents of the ruthenium-based nucleophile $Na[CpRu(CO)_2]$ (Cp, cyclopentadienyl; $[C_5H_5]^-$) reacts with boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) with the formal loss of two equivalents of sodium fluoride (NaF) to produce the bridging BF complex $(\mu_2\text{-BF})[CpRu(CO)_2]_2$ (*20*). The latter is the only crystallographically characterized compound in which BF functions as a ligand to a metal center. We reasoned that a mononuclear terminal BF complex could be similarly obtained through salt elimination, if a sterically encumbered, dianionic metal–based nucleophile were used to prevent the addition of two metals to a single boron atom. Accordingly, the formally Fe(-II) species, $K_2[Fe(CO)_2(CNAr^{Tripp2})_2]$ (K_2[**1**]; Ar^{Tripp2}, 2,6-(2,4,6-(*i*-Pr)$_3C_6H_2$)$_2C_6H_3$; *i*-Pr, *iso*-propyl) (Fig. 1D), was deemed suitable for this purpose because of the presence of two encumbering *meta*-terphenyl isocyanide ligands (*25*) and its overall isolobal relationship to the well-known dianionic, iron-based nucleophile $[Fe(CO)_4]^{2-}$ (*26*).

Treatment of K_2[**1**] with 1.0 equivalent of $BF_3{\cdot}Et_2O$ in a cold diethyl ether/*n*-hexane mixture (9:1; –100°C), followed by the removal of salts and analysis by ^{1}H nuclear magnetic resonance (NMR) spectroscopy, revealed the presence of unreacted K_2[**1**] and a new diamagnetic product in a 1:1 ratio. However, treatment of K_2[**1**] with 2.0 equivalents of $BF_3{\cdot}Et_2O$ under the same conditions resulted in a distinct color change to yellow-brown from red, with ^{1}H NMR spectroscopy indicating ~90% conversion to this new product (Fig. 1D). Crystallization of the reaction mixture from *n*-hexane produced yellow single crystals, which were determined by means of x-ray crystallography to be the five-coordinate complex $Fe(BF)(CO)_2(CNAr^{Tripp2})_2$ (**2**), featuring a terminally bound fluoroborylene ligand (Fig. 2A). Analysis by means of ^{19}F NMR spectroscopy of the salts produced from the reaction revealed tetrafluoroborate ($[BF_4]^-$) ion as a by-product (figs. S11 and S12), suggesting that a second equivalent of BF_3 promotes fluoride loss during the formation of **2**. A reasonable mechanism for the formation of **2** is one that proceeds through an unobserved iron difluoroboryl intermediate (Fig. 1D, **Int**), the formation or fragmentation of which through fluoride ion elimination is aided by a second equivalent of BF_3. Accordingly, this inference allowed the synthesis to be optimized by using 2.8 equivalents of $BF_3{\cdot}Et_2O$ (Fig. 1D), which resulted in the complete conversion to **2** and allowed for its isolation as a room-temperature stable, yellow crystalline material in 82% yield.

Complex **2** is an isolobal analog to the simple, yet hypothetical, molecular species $Fe(BF)(CO)_4$, which is the most well-considered theoretical and computational model of a fluoroborylene complex (*16*–*19*). In line with this analogy, the axial ∠ C1–Fe–C2 bond angle in **2** [160.38(7)°; numbers in parentheses indicate estimated standard deviation] is in excellent agreement with the ∠ C_{ax}–Fe–C_{ax} (163.4°; ax, axial) bond angle previously predicted for $Fe(BF)(CO)_4$, as are the equatorial C_{eq}–Fe–B angles [124.6°(average) for **2** versus 123.4° for $Fe(BF)(CO)_4$; eq, equatorial] (*17*, *19*). This pronounced distortion from an ideal trigonal bipyramidal geometry results from the strong σ-donor properties of the BF ligand, which, owing to orbital mixing in C_{2v} symmetry, imparts substantial antibonding character on an otherwise nonbonding orbital directed toward the axial isocyanide ligands (*17*, *19*). In addition, the Fe–B bond distance in **2** [1.7703(25) Å] is the shortest reported for a transition metal–boron bond

[1]Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, Mail Code 0358, La Jolla, CA 92093-0358, USA. [2]Department of Chemistry, University of Rochester, Rochester, NY 14627, USA.
*Corresponding author. Email: jsfig@ucsd.edu

(fig. S28). Accordingly, this metrical parameter reflects substantial π-interactions between the BF unit and the iron center, which are in accord with the ligand's predicted strong π-acceptor properties (*17*). However, the B–F bond distance in **2** [1.2769(29) Å] is the shortest known for any structurally characterized boron-fluorine compound (figs. S29 and S30) and compares well with the equilibrium internuclear separation of free BF in the gas phase [1.262672(7) Å] (*14*).

The diamagnetism of **2** allows for an assessment of the BF unit with NMR spectroscopy. In benzene-d_6 solution, **2** gives rise to a broad ^{11}B NMR signal centered at δ_B = +56.5 parts per million (ppm) (full width at half maximum = 1820 Hz). This chemical shift is most similar to those of transition-metal aminoborylene complexes (M, B–NR_2; δ_B = +60 to 90 ppm) (*27*) and is downfield of that for the formally platinum(II) oxyboryl complex *trans*-Pt(BO)Br(PCy_3)$_2$ (δ_B = +17 ppm) that features a B–O triple bond akin to the cyanide ion ([CN]$^-$) (*28*). This difference in chemical shift signifies that π-donation from fluorine to boron in **2** is substantially diminished relative to B–O π-bonding in the oxyboryl group and is reflective of the greater electronegativity of the fluorine atom in the BF unit. Complex **2** also gives rise to a ^{19}F NMR resonance at δ_F = +1.6 ppm, which is significantly downfield relative to that found in the dinuclear bridging BF complex (μ$_2$-BF)[CpRu(CO)$_2$]$_2$ (δ_F = −185.0 ppm) (*20*) and BF_3·Et_2O (δ_F = −153 ppm). Rapid quadrupolar relaxation of the I = 3/2 ^{11}B nucleus prevented a determination of the $^1J_{BF}$ coupling constant in both the one-dimensional (1D) ^{11}B and ^{19}F NMR spectra of **2**. However, 2D ^{19}F–^{11}B heteronuclear multiple-quantum coherence NMR experiments (fig. S10) (*29*, *30*) showed maximum cross-peak signal intensity in the measurement optimized for $^1J_{BF}$ = 650 Hz. This extremely large implied coupling constant is consistent with the very short B–F bond distance observed in the x-ray structure of complex **2**. It also indicates that a high degree of boron s-orbital character is a major component of the bonding within the B–F ligand.

To further evaluate the structural and electronic effects of terminal BF coordination, the isoelectronic dinitrogen and CO complexes Fe(N$_2$)(CO)$_2$(CNAr^{Tripp2})$_2$ (**3**) and Fe(CO)$_3$(CNAr^{Tripp2})$_2$ (**4**) were prepared and characterized by means of x-ray crystallography (Fig. 2A). Complexes **3** and **4** both adopt undistorted trigonal bipyramidal coordination geometries, as indicated by near-linear axial isocyanide ∠ C1–Fe–C2 angles [179.05(14)° for **3**; 178.61(22)° for **4**]. These metrical parameters contrast with the significantly bent ∠ C1–Fe–C2 angle of complex **2** and support the notion that both CO and N_2 are weaker σ-donors than the BF ligand (*17*). Similarly, the infrared (IR) spectroscopic data of the complexes show a clear redshift of the asymmetric ν_{CN} stretch in the order **4** > **3** > **2** (Fig. 2A), further illustrating that the σ-donor ability of BF is greatest relative to CO and N_2. Accordingly, when coupled with the short Fe–B bond length in **2**, the structural and spectroscopic comparison provided by complexes **3** and **4** offers complementary support to the conclusion that BF possesses simultaneously strong σ-donor and π-acceptor characteristics. This distinct electronic character of the BF ligand is further confirmed by the Mössbauer spectroscopic data of **2**, **3**, and **4** (figs. S13 to S15). Of the series, complex **2** gives rise to the most negative isomer shift (δ = −0.15 mms^{-1}), followed by **4** then **3** (δ = −0.08 and +0.08 mms^{-1}, respectively). This trend indicates that the total bonding interactions (*31*) to the iron center are greatest for complex **2** and diminish predictably as both the σ-donor and π-acceptor abilities of CO and N_2 weaken. Furthermore, the Mössbauer quadrupolar-splitting values (ΔE_Q), which are sensitive to the iron structural environment (*31*), are nearly identical for complexes **3** and **4** (ΔE_Q = 1.94 and 2.02 mms^{-1}, respectively), whereas that of **2** varies significantly (ΔE_Q = 1.27 mms^{-1}) in a manner consistent with the solid-state structural data for the series.

With respect to the bonding interactions within the BF ligand, the IR spectrum of complex **2** shows a moderately intense band centered at 1407 cm^{-1} assignable to the ν_{BF} stretch (*32*). This band is higher in energy than that of free BF (ν_{BF} = 1374 cm^{-1}) (*33*) and the matrix-produced terminal fluoroborylene complexes Zr(BF)F_2 and Hf(BF)F_2 (ν_{BF} = 1373 and 1378 cm^{-1}, respectively) (*21*). However, it agrees well with those calculated with density functional theory methods for Fe(BF)(CO)$_4$ (ν_{BF} = 1465 cm^{-1}) (*19*) and the model complex Fe(BF)(CO)$_2$(CNAr^{Ph2})$_2$ [**2m**, ν_{BF} = 1416 cm^{-1}; Ar^{Ph2}, 2,6-(C$_6$H$_5$)$_2$C$_6$H$_3$], as well as that for the titanium terminal fluoroborylene species Ti(BF)F_2 (ν_{BF} = 1404 cm^{-1}) observed under matrix conditions (*21*). Accordingly, the low-energy nature of these experimental and calculated ν_{BF} bands provides strong indication that B–F multiple bonding is not significant in terminal fluoroborylene complexes.

Density functional theory calculations on model **2m** support this electronic structure description.

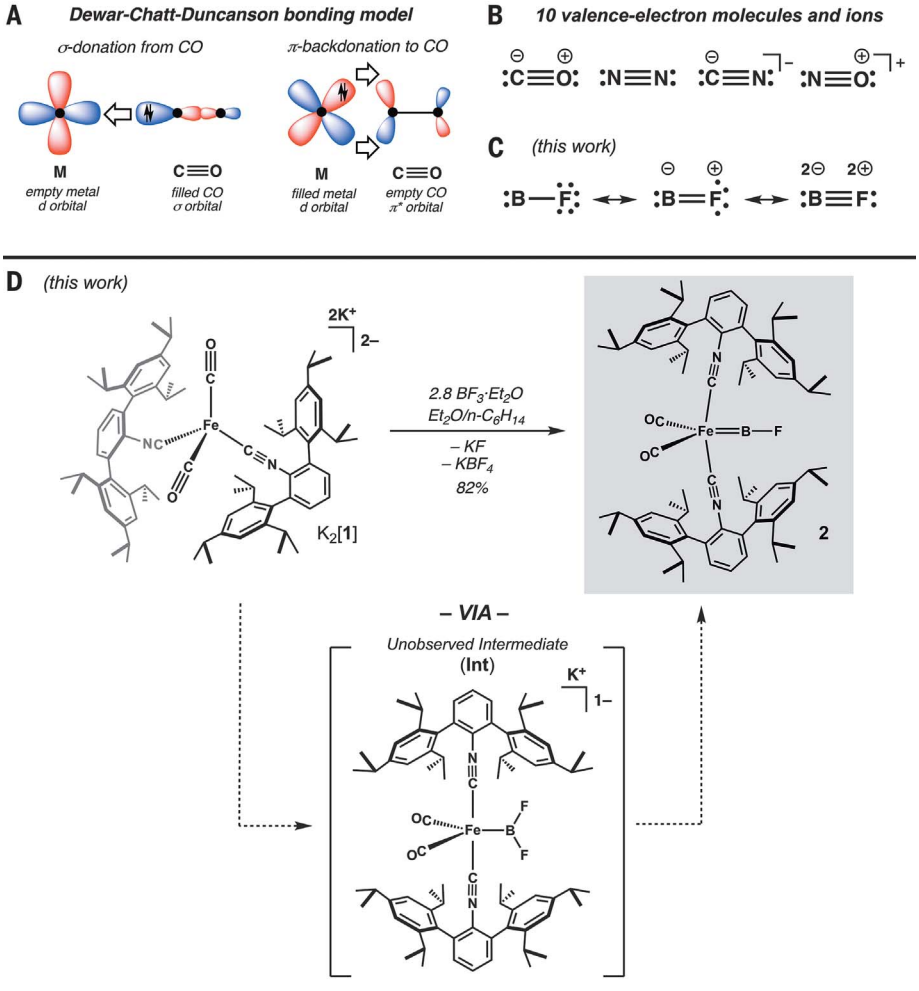

Fig. 1. End-on coordination chemistry of diatomic π-acceptor ligands. (**A**) Schematic representation of the Dewar-Chatt-Duncanson bonding model for terminal coordination of CO. (**B**) Well-known 10 valence-electron molecules and ions that function as terminal ligands to transition metals, with formal charges of each atom denoted. (**C**) Canonical resonance forms of 10 valence-electron BF. (**D**) Schematic representation of the synthetic route to the iron fluoroborylene complex **2**, including the proposed iron difluoroboryl intermediate **Int**.

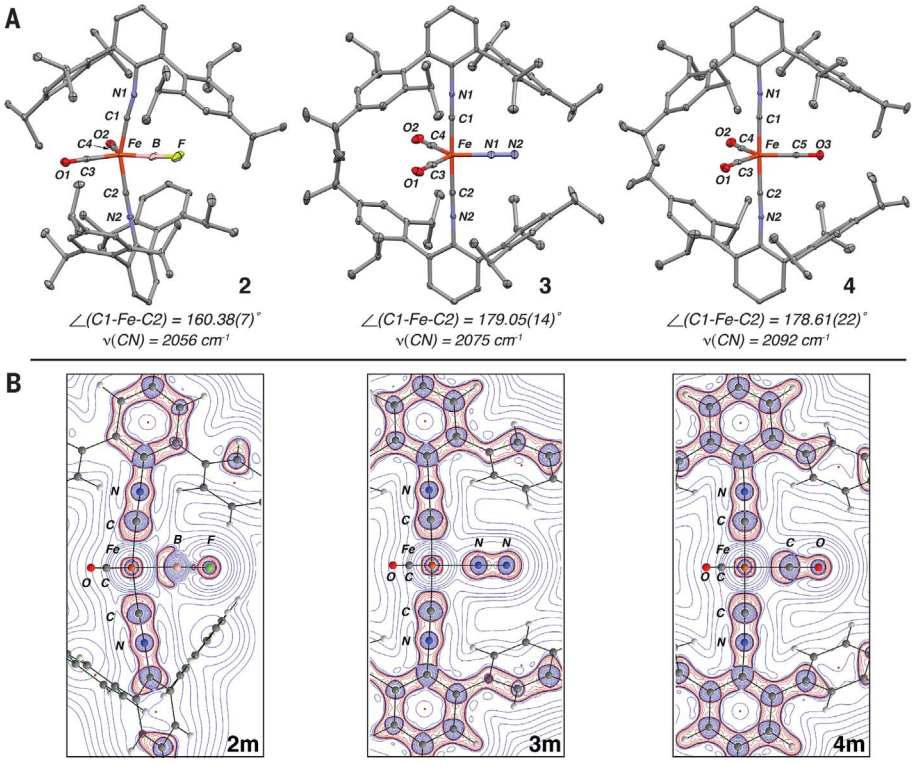

Fig. 2. Crystallographic characterization and electron-density topology calculations of isoelectronic terminal BF, N_2, and CO iron complexes. (**A**) X-ray crystal structures of the iron fluoroborylene complex **2** and the terminal N_2 and CO complexes **3** and **4**, respectively, along with metrical data for the axial C_{iso}–Fe–C_{iso} angles and IR spectroscopic data for the asymmetric ν_{CN} stretch of each complex. Hydrogen atoms from all structures and one *iso*-propyl group from **2** have been omitted for clarity. Iso, isocyanide. (**B**) Contour plots of the Laplacian of the electron-density topology ($\nabla^2\rho$) in the plane containing the iron atom; isocyanide ligands; and BF, N_2, and CO ligand for complexes **2**, **3**, and **4**, respectively. Areas of charge depletion are depicted with blue curves, and areas of charge concentration are depicted with red curves. Bond and ring critical points are denoted with green and red spheres, respectively.

Analysis of the molecular orbitals calculated for **2m** reveal that the ostensible π-bonding orbitals between the fluorine and boron atoms in the molecular *y* and *z* directions (fig. S21) are exceedingly low-lying (HOMO-63 and HOMO-64) and possess predominantly fluorine p-orbital character. As such, these components of the electronic structure of **2m** are best described as fluorine p-orbital lone pairs, rather than B–F π-bonding interactions, and indicate a nominal single bond between the B and F atoms. Natural bond orbital (NBO) analysis also indicates the presence of a B–F single bond in **2m**, yielding a Wiberg bond index of 0.8646 (*34*). Electron density topology calculations (*35*) on **2m**, and the model complexes $Fe(N_2)(CO)_2(CNAr^{Ph2})_2$ (**3m**) and $Fe(CO)_3(CNAr^{Ph2})_2$ (**4m**), most clearly illustrate the electronic differences between coordinated BF, N_2, and CO ligands. A contour plot of the Laplacian of the electron density ($\nabla^2\rho$) (Fig. 2B) for **2m** shows a significant depletion of electron density at the BF bond critical point, which is reflective of a highly polarized bonding interaction (*35*). By contrast, the Laplacian contour plots for the N_2 and CO complexes **3m** and **4m** (Fig. 2B) reveal far greater concentrations of electron density in the regions between N–N and C–O atoms, respectively, with **3m** displaying a highly symmetric electron-density distribution fully consistent with the presence of nonpolarized, multiple-bonding character (*35*). Accordingly, although BF is isoelectronic to the 10-electron diatomics CO and N_2, it lacks multiple bonding character between the boron and fluorine atoms and therefore does not possess a similar electronic structure to these ligands when complexed to a transition metal. Moreover, the totality of spectroscopic and computational results suggest that the short B–F bond distance observed for complex **2** manifests simply from a high degree of sp-hybridization of the two-coordinate boron atom, in which the diminished radial extension of the boron 2s orbital relative to its 2p orbitals results in a short BF bond (*36*).

The molecular design principles and synthetic strategy presented here outline a blueprint for the formation and stabilization of terminal BF ligands on transition metals. Given the particular electronic characteristics of terminally coordinated BF, it is anticipated that this diatomic ligand can be exploited in a general fashion to modulate the physical and chemical properties of transition-metal complexes for specific applications.

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/363/6432/1203/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S30
Tables S1 to S10
References (*37*–*70*)

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Iron's new Best Friend

Carbon monoxide (CO) is one of the most widely studied ligands in the chemistry of transition metals. One of its distinguishing features is a two-way bonding motif, in which CO donates electrons to the metal while the metal simultaneously engages in "back bonding" in the other direction. Theory has suggested that the isoelectronic boron fluoride diatomic, BF, would be even more effective at both types of bonding. However, it has been challenging to prepare the requisite compounds for comparison. Drance *et al.* now report synthesis of a terminal iron-BF complex, with donor and acceptor characteristics that compare favorably to analogous CO and N_2 complexes.

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