

## **Terminal coordination of diatomic boron monofluoride to iron**

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Recent Lit

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Vincent van der puyl

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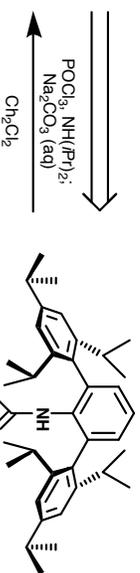
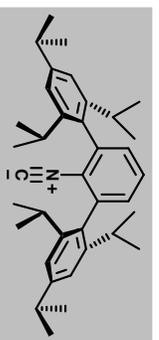
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# Terminal coordination of diatomic boron monofluoride to iron

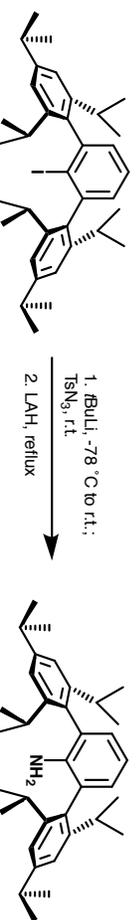
## Background: Isocyanide ligands

- Among other programs in the Figuerao group, the authors use *m*-terphenyl isocyanide ligands to study highly reactive organometallic complexes
- This includes complexes with low valent and coordinatively unsaturated metal centers
- The isocyanide moiety is isoelectronic with the –CO ligand, which has long been used as a probe to study the electronic structure and reactivity of organometallic complexes
- Furthermore, strong backbonding of the isocyanide ligand helps to stabilize electron-rich metal centers
- The bulkiness of the *m*-terphenyl isocyanide ligands enforces low coordination numbers

## Ligand synthesis

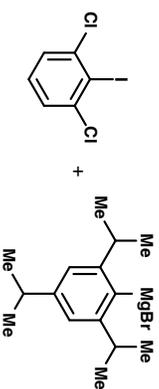


J. S. Figuerao, *et al. Inorg. Chem.* **2009**, *48*, 8362.



D. Tilley, *et al. Organometallics* **2004**, *23*, 31.

P. P. Power, *et al. Organometallics* **1996**, *15*, 958.

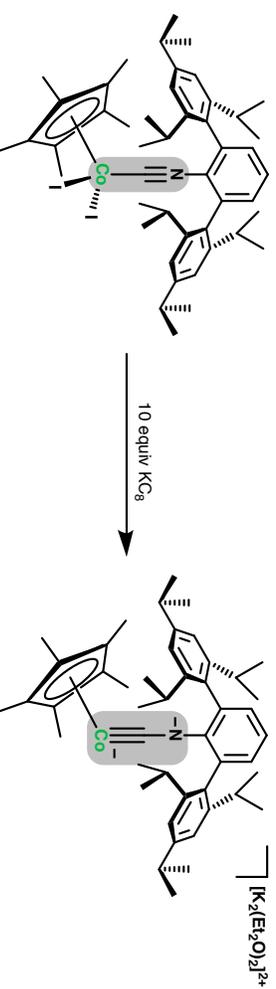


• Di-isopropyl and trimethyl analogues of CNAIrTripp<sup>2</sup> have also been used

References: For a review of M–CO chemistry, see: W. A. Herman, *J. Organomet. Chem.* **1990**, *383*, 21. For a detailed study of M<sub>n</sub>(CO)<sub>n</sub> geometry and electronic structure, see: M. Eilan, R. Hoffmann, *Inorg. Chem.* **1975**, *14*, 1058. For a review of M–CN coordination chemistry, see: W. P. Fehlhammer and M. Fritz, *Chem. Rev.* **1993**, *93*, 1243.

## Recent contributions with these ligands

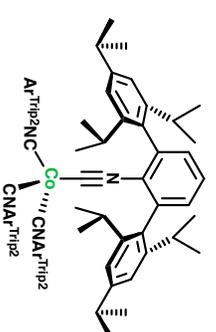
### A highly-reduced cobalt terminal carbonyne



J. S. Figuerao, *et al. J. Am. Chem. Soc.* **2018**, *140*, 8100.

- Synthesis, reactivity, and electronic structure of a highly-reduced cobalt terminal carbonyne. Omitted for clarity, the crystal structural data also indicates K<sup>+</sup> is coordinated to the C–N in addition to η<sup>5</sup>-coordination to the ligand.
- In the reduced complex, the Co–C bond distance is 1.607 Å, relatively short indicating significant multiple-bonding phenomena (previously record for a bound difluorocarbene measured at 1.740 Å).
- Cobalt is the site of nucleophilicity in reactions with prolic substrates and silyl electrophiles. The complex undergoes [2+2] cycloaddition with internal alkynes.

### Associative ligand exchange mechanism for zero-valent cobalt



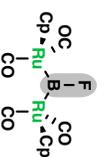
Initial Report: J. S. Figuerao, *et al. J. Am. Chem. Soc.* **2010**, *132*, 5033.  
Kinetic Study: J. S. Figuerao, *et al. Organometallics* **2019**, *38*, 1436.

- Despite the large steric profile of this zero-valent cobalt complex, kinetic data on ligand substitution (e.g. PPh<sub>3</sub> and phenylacetylene) reactions of this product proceed via associative mechanisms
- Also examined reactivity with several substrates for oxidation (TEMPO, P<sub>4</sub>, S<sub>8</sub>, and PhSSPh).
- In general, the authors conclude that the associative ligand substitution mechanism observed in this example is general for CoL<sub>4</sub> complexes.

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## Background: CO isoelectronic (and isolobal) species

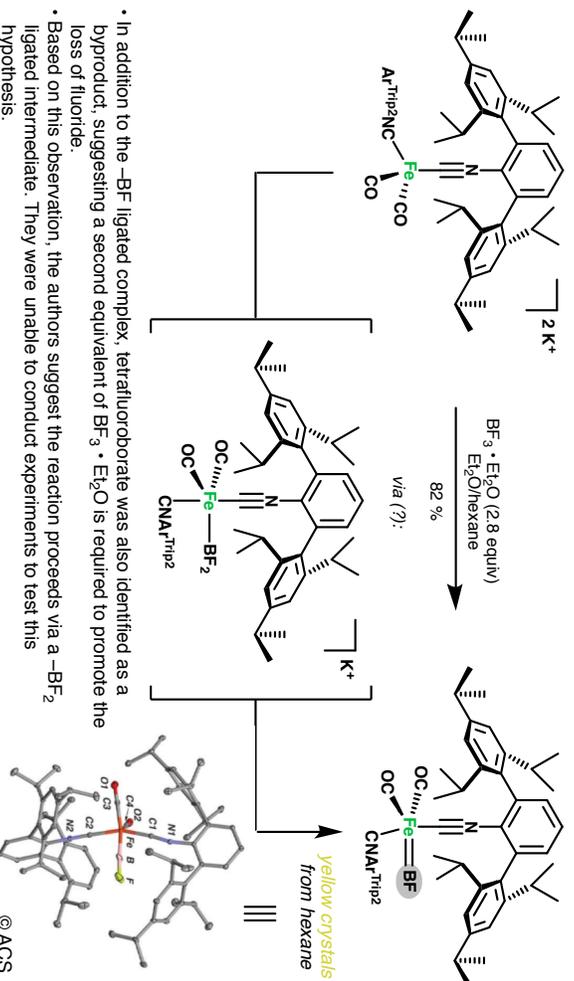
- In addition to isocyanide, CO is also isoelectronic to N<sub>2</sub>, cyanide, NO<sup>+</sup> and BF.
- Hoffmann predicted BF would bind more strongly to transition metals than CO, owing to decreased HOMO/LUMO gaps which improve  $\sigma$  donor and  $\pi$  accepting capabilities.
- Prior to a 2009 report of a BF-bridged ruthenium dinuclear complex, BF has only been observed at high temperatures or under high vacuum, highlighting the ability of transition metal catalysts to capture highly reactive species.



D. Vidovic and S. Aldridge. *Angew. Chem. Int. Ed.* **2009**, *48*, 3669.

## Results and Discussion

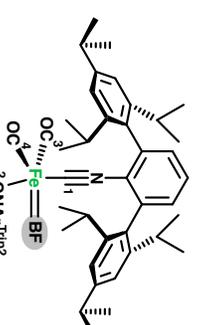
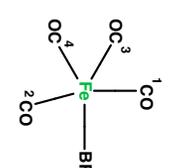
- Authors chose to assemble the BF moiety in the coordination sphere of an iron metal center. To avoid synthesis of a bridged complex as was observed in the 2009 report, they prepared the target from a highly reduced dianionic iron (-II) species.



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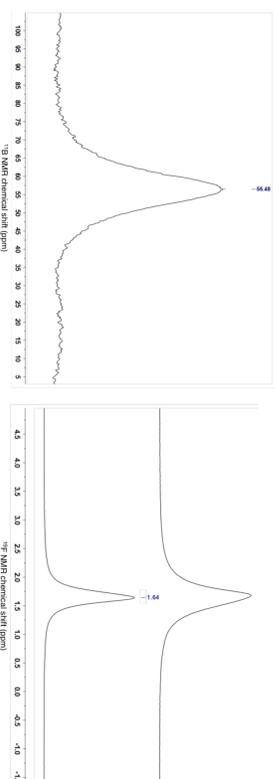
- In addition to the -BF ligated complex, tetrafluoroborate was also identified as a byproduct, suggesting a second equivalent of BF<sub>3</sub>·Et<sub>2</sub>O is required to promote the loss of fluoride.
- Based on this observation, the authors suggest the reaction proceeds via a -BF<sub>2</sub> ligated intermediate. They were unable to conduct experiments to test this hypothesis.

References: J. S. Figueroa, *et al. Science* **2019**, *363*, 1203. R. Hoffmann, *et al. Inorg. Chem.* **1998**, *37*, 1080.



Angle/Bond	Predicted	Experimental
C1-Fe-C2	163.4°	160.39°
C3/4-Fe-B	124.6°	123.4°

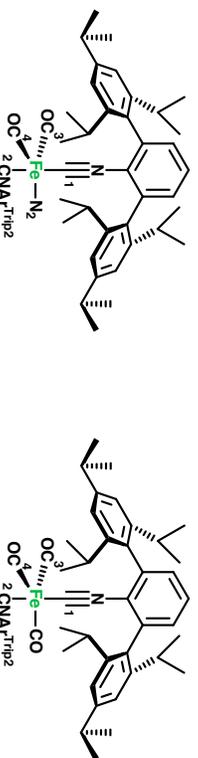
- In Hoffmann's computational study of as BF as a ligand, this heteroleptic iron complex was used as a model to predict its electronic properties relative to iron hexacarbonyl. In the current work, the authors found the Fe-BF complex they prepared is in agreement with the predicted structure of this complex in terms of geometry.
- Distortion from perfect trigonal bipyramidal is due to the strong  $\sigma$  donor properties of the BF ligand, resulting in antibonding orbital character of an orbital directed toward the axial isocyanide ligands.
- The Fe-B bond (measured at 1.7703 Å) is the shortest known metal-boron bond, indicating significant  $\pi$  character of this bond which the authors attribute to the strong  $\pi$  accepting properties of the ligand as predicted by Hoffmann
- Furthermore, the B-F bond distance (1.2769 Å) is the shortest structurally characterized and compares well with the observed free BF molecule in the gas phase, whose bond length measures at about 1.26 Å.



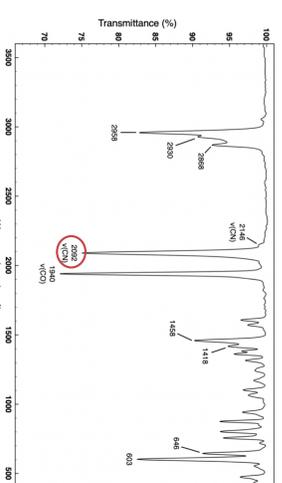
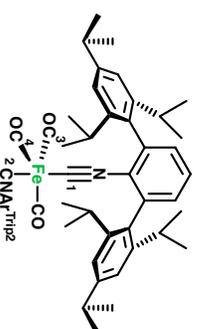
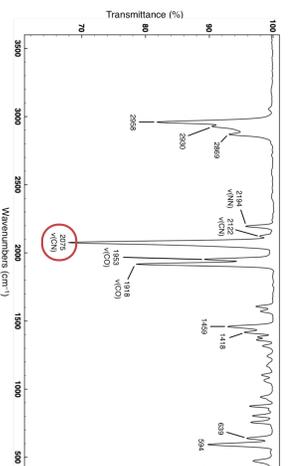
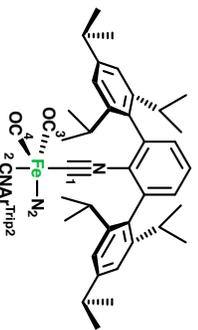
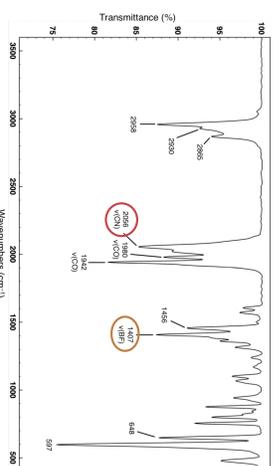
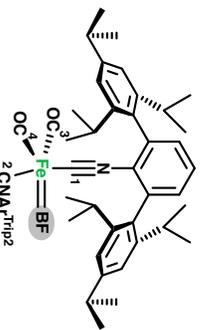
- In <sup>13</sup>B NMR, a single broad NMR signal at +56.5 ppm, comparatively downfield from known complexes bearing B-O triple bonds, indicates little  $\pi$  donation from fluorine to boron.
- <sup>19</sup>F resonance is significantly further downfield than than the Aldridge complex and extremely large <sup>19</sup>F-<sup>13</sup>B coupling constant (HMOC, not shown) indicates high contribution of the boron s-orbital to the B-F bond.

References: P. L. Timms, *Acc. Chem. Res.* **1973**, *6*, 118. A. Schneider, *et al. Science* **2010**, *328*, 345.

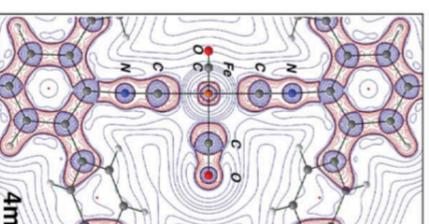
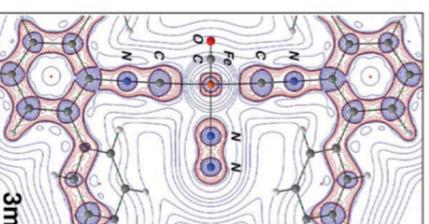
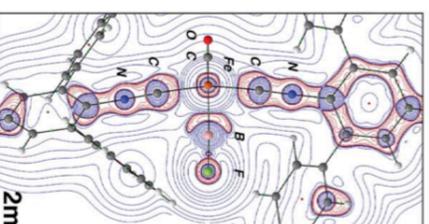
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- The authors also prepared N<sub>2</sub> and CO-ligated analogues to better understand the structural and electronic effects of the BF ligand.
- Both complexes exhibit nearly undistorted trigonal bipyramidal geometry, indicating CO and N<sub>2</sub> of their weaker donating ability compared to BF.



- Red shift of the C-N stretch in IR spectrum further supports the conclusion that BF is a stronger  $\sigma$  donor than N<sub>2</sub> or CO (circled in red).
- Highly negative isomer shift of the -BF ligated complex indicates greater number of bonding interactions at the iron center.
- B-F stretch in the IR spectrum (circled in gold) is higher in energy than in free BF, but agrees well with that calculated for the model Fe(CO)<sub>4</sub>(BF) complex and others. Combined, these data indicated there is insignificant B-F multiple bonding when coordinated to a metal.



- Molecular orbitals were calculated for the target complex. The authors found the HOMO of the B-F is best characterized as lone-pair orbitals localized on fluorine, and the B-F bond is single in character.
  - Contour plot of the laplacian of electron density indicates complexes do not have similar electronic structures.
- References:** P. Hassanzadeh and L. Andrews, *J Phys. Chem.* **1993**, *97*, 4910. H. F. Schaefer III, *et al. Inorg. Chem.* **2010**, *49*, 1046. L. Andrews, *et al. Angew. Chem. Int. Ed.* **2010**, *49*, 157.

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### Conclusions

- The authors state in their concluding paragraph that they have laid the groundwork and first principles for the formation and stabilization of BF<sub>2</sub>-ligated complexes.
- They also expect that the unique electronic structure imparted on the BF<sub>2</sub> ligand and complex in general can be exploited for novel physical properties and chemical reactivity.

### Summary

- Professor Figueroa and his students and collaborators have used sterically encumbering isocyanide ligands to synthesize and study novel, highly reactive metal complexes.
- Key to the group's success using this strategy is the isolectronic structure of isocyanides to carbonyls, which results in  $\pi$ -back-bonding that stabilizes highly reduced, low-valent metal coordination complexes.
- In the current work, the authors described a terminal-coordinated BF<sub>2</sub> ligand in an iron-isocyanide complex.
- Characterization by X-ray crystallography, NMR, and IR in combination with computational studies indicates the B-F bond is best described as a single bond with boron being doubly bonded to the iron center.
- This study is in excellent agreement with predictions made by Hoffman over 20 years ago.