Tuning secondary sphere Lewis acidity via late-stage modification of an appended borane

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ABSTRACT. To develop synthetic strategies to construct ligands containing secondary sphere acids, we demonstrate that an appended borane of low Lewis acidity (–BPin) can be upgraded to a strong Lewis acid (–BF_2). Using a pyridine-pyrazole ligand coordinated to $Mo(CO)_4$, we show that a pendent –BPin group undergoes exhaustive fluorination to –BF_3K, a precursor to a highly acidic –BF_2 unit (acceptor number ~15x greater than –BPin).

Lewis acids can enhance or promote numerous metal-based small molecule transformations and catalytic reactions including C-C and C-H bond formation,[1] CO_2 reduction,[2] oxidative addition/reductive elimination,[3] and hydride transfer.[4] Boranes represent highly tunable Lewis acids whose properties can be adjusted through modifications to the boron-adjacent substituents.

When appended to a metal's secondary coordination sphere, the acidity requirement for cooperative interactions with coordinated substrates is decreased, and preorganization of intramolecular Lewis acid/transition-metal systems can enhance these interactions.[5] Importantly, these principles present an attractive approach for catalyst development, particularly if the appended acid is selected to enable reversible acid/base binding.

Although secondary sphere acids are a promising approach to modify metal-based reactivity, their incorporation within ligand scaffolds is still underutilized in the broader design of inorganic and organometallic complexes.[6] This limitation is likely a direct consequence of available synthetic methods. Synthetic routes to append boranes are often plagued by issues regarding incompatibility of the pendent Lewis acids with reactive metal centers and/or Lewis basic ligands. A widely used method to install boranes is hydroboration of olefins (**Figure 1**, top left). However, pre-metalation hydroboration can yield irreversible intramolecular interactions, resulting in the formation of unreactive "quenched" ligand adducts,[7] which presents challenges for the synthesis of transition metal complexes featuring strong Lewis acids (**Figure 1**, top right). Due to these synthetic difficulties, many ligands containing appended boranes are limited to commercially available hydroboranes (e.g. HBBN, HBCy$_2$, HBPin) installed via post-metalation hydroboration routes.

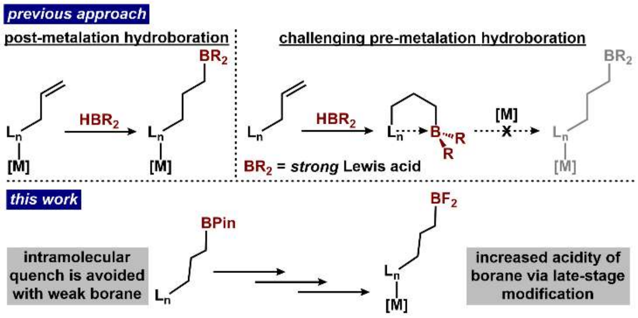


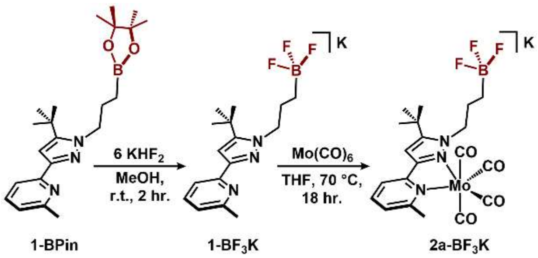
Figure 1. Top left: Frequently used post-metalation hydroboration route to append boranes to metal complexes. Top right: Limitations of common synthetic methods for borane installation. Bottom: This work, late-stage conversion of –BPin to $–BF_2$.

Altering Lewis acidity can strongly impact metal/acid cooperative reactivity[7-8] and catalytic activity/selectivity.[9] Modifying the acidity of appended boranes might appear to be a straightforward approach because boron modification strategies, such as transesterification, are described in the organic literature.[10] However, there are limited examples where the acidity of a ligand appended Lewis acid is increased. Within the context of developing modifiable appended Lewis acids, organotrifluoroborate species ($R–BF_3^-$) are attractive precursors that can be readily prepared and subsequently defluorinated to yield organodifluoroboranes ($R–BF_2$).[11] Organotrifluoroborates ($R–BF_3^-$) are bench-stable reagents used in cross-coupling reactions and prepared by addition of KHF_2 to the corresponding $R–B(OR)_2$ compound.[12] These functional groups exhibit stability toward basic reagents that are incompatible with three-coordinate boranes.[13] Although select examples have shown the viability of metal complexes containing appended $–BF_3^-$ units,[14-15] no subsequent defluorination of the $[BF_3]^-$ unit has been described. However in the absence of a metal, defluorination of $–BF_3^-$ units has been shown to generate organodifluoroboranes in-situ.[16] This approach has been leveraged to promote intramolecular Lewis acid/base adducts, to prepare boronate urea compounds,[17] as well as to enhance stereocontrol through interactions formed as a result of the in-situ generated tri-coordinate boron.[16, 18] Although $BPin/BF_3^-/BF_2$ interconversions to borane-appended metal complexes have not been explored, we propose that they may provide a new strategy to access appended boranes that are otherwise incompatible with commonly used hydroboration routes (**Figure 1**, bottom). In this manuscript, we describe the viability of this route to diversify the Lewis acidic properties of appended borane ligands.

One of the key challenges to overcome when targeting appended borane ligands is formation of intramolecular "self-quenched" ligands. To circumvent this issue, we targeted a scaffold possessing an appended borane of low Lewis acidity because we anticipated it would exhibit minimal acid/base quenching.[19] BPin reagents are versatile precursors used in synthetic chemistry and represent an ideal starting point for derivatization because they are easy to prepare, bench stable, and tolerant to chromatography.[20]

We initiated our studies using $^{3\text{-BPin}}NN^{tBu}$ (**1-BPin**),[21] a well-defined bidentate pyridine-pyrazole ligand containing an appended BPin unit. $^{3\text{-BPin}}NN^{tBu}$ (**1-BPin**) was converted to $^{3\text{-BF}_3\text{K}}NN^{tBu}$ (**1-BF₃K**) by stirring a methanol solution of **1-BPin** with excess (6 equiv.) solid KHF_2 at room temperature for two hours (**Scheme 1**). The product was isolated as a white solid in 65% yield.[22] Heteronuclear NMR spectroscopy revealed a resonance at 5.7 ppm in the $^{11}B\{^1H\}$ NMR spectrum and at -139.5 ppm in the ^{19}F NMR spectrum (25 °C, $CDCl_3$), consistent with shifts for previously reported $R\text{-}BF_3^-$ units.[14d] The negative mode ESI-MS exhibited a fragment m/z = 324, consistent with the formulation of $C_{16}H_{22}BF_3N_3$.

Scheme 1.



One anticipated hurdle of the approach to using $R\text{-}BF_3K$ precursors with metal complexes is that these compounds are activated for transmetalation to form M-R bonds.[12-13, 16] To overcome this challenge and avoid the potential for transmetalation (deborylation), we targeted a coordinatively saturated metal center ($Mo(CO)_4L_2$) . When a THF solution of **1-BF$_3$K** and excess $Mo(CO)_6$ (1.5 equiv.) was heated to 70 °C for 18 hours, a new compound formed, consistent with the formulation of ($^{3\text{-}BF_3K}NN^{tBu}$)$Mo(CO)_4$ (**2a-BF$_3$K**) (**Scheme 1**). Metalation was confirmed by ^1H NMR spectroscopy, which revealed a downfield shift of a single set of aromatic proton resonances. The $^{11}B\{^1H\}$ and ^{19}F NMR spectra (7.7 ppm and -139.3 ppm in THF, respectively) were minimally changed (<2 ppm) with respect to **1-BF$_3$K**. The carbonyl ligands were also observed via ^{13}C NMR spectroscopy in THF, where three resonances integrated 1:1:2 at 221.9, 222.0, and 203.2 ppm, respectively. Finally, solution IR spectroscopy revealed four ν_{CO} bands at 2015, 1898, 1878, and 1835 cm^{-1}. These data are consistent with a *cis*-[$M(CO)_4L$] configuration and analogous to previously reported octahedral $Mo(CO)_4$ metal centers coordinated to pyridine-pyrazole ligands.[23]

Attempts to isolate pure **2a-BF$_3$K** from the crude reaction mixture by removing solvent *in vacuo* resulted in the formation of a secondary product, as assessed by NMR and IR spectroscopy. New features in the IR spectrum revealed a ν_{CO} band at 1911 cm^{-1} and two broad overlapping signals at 1789 and 1765 cm^{-1}, consistent with a *fac*-$Mo(CO)_3$ complex.[23a] We tentatively assign the secondary product as ($^{3\text{-}BF_3K}NN^{tBu}$)$Mo(CO)_3$ (**2b-BF$_3$K***) where one of the F atoms is coordinated to the Mo center in solution (**Figure 2**). Fortunately, CO dissociation from **2a-BF$_3$K** is reversible. When a THF solution of **2a-** and **2b-BF$_3$K*** was exposed to 20 psi CO at room temperature, the mixture fully reverted to **2a-BF$_3$K** (**Figure 2**). We propose that CO dissociation may be facilitated by either a steric effect, or alternatively, formation of a new chelate of the BF_3 unit to Mo (i.e. Mo–FBF_2R). This bridging type of F-coordination to a metal center has previously been observed by the Piers group on a BF_3-appended Rh NHC complex.[14d] Mo centers have also been shown to coordinate $[BF_4]^-$ counteranions via a Mo—F—BF_3 bridging motif.[24]

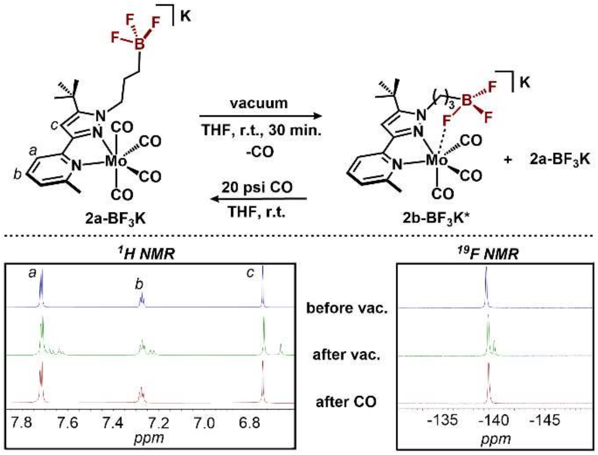


Figure 2. Reversible vacuum instability of **2a-BF$_3$K**. Top: Reaction conditions. Bottom left: ^{1}H NMR (aromatic region in THF). Bottom right: ^{19}F NMR (THF). Stacked spectra: blue (top) – crude **2a-BF$_3$K** before exposure to vacuum; green (middle) – formation of **2b-BF$_3$K*** after exposing **2a-BF$_3$K** to vacuum; blue (bottom) – after charging the **2a/2b-BF$_3$K*** mixture with 20 psi CO.

Characterization of this complex was performed on an independently synthesized sample. ($^{3\text{-}BF_3K}NN^{tBu}$)Mo(CO)$_3$(CH$_3$CN) (**2b-BF$_3$K**) was prepared by stirring a THF solution of **1-BF$_3$K** and Mo(CO)$_3$(CH$_3$CN)$_3$ at room temperature for two hours (**Figure 3**). The product was isolated as a dark red powder in 84% yield. Addition of a stoichiometric amount of 18-crown-6 enabled the growth of crystals suitable for single-crystal X-ray diffraction (XRD). Crystals of **2b-BF$_3$K(18-c-6)** reveal a primary sphere at Mo containing a coordinated CH$_3$CN ligand, rather than –BF$_3$K in the solid state. We propose that the bridging motif is only accessible in solution. The ^{1}H NMR spectrum (CD$_3$CN) of **2b-BF$_3$K*** reveals that the methylene signals of the tether connecting to the BF$_3$ unit are split (two broad multiplets integrating 1:1 for each –CH$_2$), suggesting increased asymmetry in the chain (**Figure S31**). This behavior was not observed in **2a-BF$_3$K** (**Figure S19 & 25**). Low temperature NMR studies of **2b-BF$_3$K*** showed the broad resonance in the ^{19}F NMR spectrum decoalesces into two signals, consistent with terminal versus bridging fluoride environments (**Figure S36**).

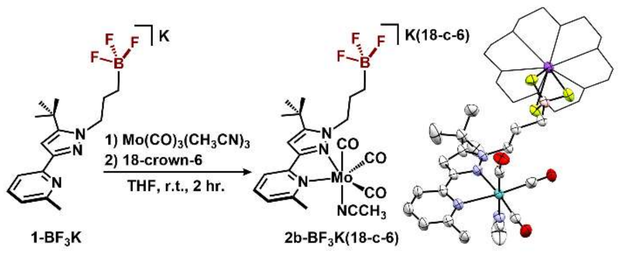


Figure 3. Synthesis and molecular structure of **2b-BF$_3$K(18-c-6)** displayed with 50% probability ellipsoids. H-atoms are omitted, and the 18-crown-6 moiety is displayed in wireframe for improved clarity.

To decouple primary and secondary sphere effects, we prepared a control complex lacking an intramolecular borane as well as a complex featuring a borane of weak Lewis acidity (**Figure 3**). Variants where the BF$_3$K unit was substituted by an inert -CH$_3$ group (**2-CH$_3$**) and weakly acidic BPin (**2-BPin**) were prepared analogously to **2a-BF$_3$K** and displayed nearly identical IR features (ν_{CO} = 2016, 1900 (BPin)/1899 (butyl), 1879, 1836 cm^{-1} in THF solution). Similar to **2a-BF$_3$K**, ^{13}C NMR spectroscopy showed three carbonyl resonances at 223.2, 221.3, and 203.9 ppm for **2-BPin** and 223.2, 221.2, and 204.0 ppm for **2-CH$_3$** (C_6D_6), consistent with identical ligand field characteristics. Single-crystal XRD also revealed comparable C≡O bond lengths ranging from 1.138(2) to 1.166(3) Å for **2-BPin** and 1.140(2)-1.164(1) Å for **2-CH$_3$**, while the boron atom in BPin was trigonal ($\sum$B = 360.0(3)°). The geometry of boron within the BPin moiety of **2-BPin** was corroborated via ^{11}B{^{1}H} NMR spectroscopy, which revealed a broad resonance at 34.2 ppm (C_6D_6), consistent with a trigonal environment. Importantly, neither **2-CH$_3$** nor **2-BPin** were unstable to vacuum. Since complexes **2** all feature identical ligand field environments, *vide supra*, we attribute differences in vacuum stability to reversible coordination with the BF$_3^-$ unit.

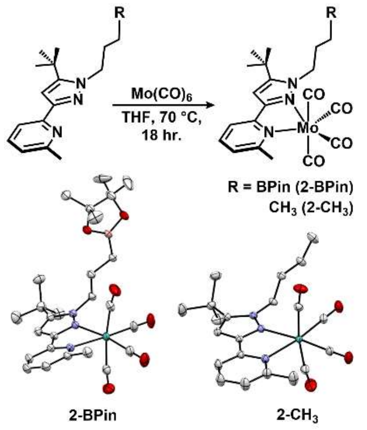


Figure 4. Synthesis and molecular structures of **2-BPin** and **2-CH$_3$** displayed with 50% probability ellipsoids. H-atoms are omitted for clarity.

To expose the acidic properties of **2a-BF$_3$K** (i.e. appended BF$_2$), we examined defluorination reactions by introducing 1 equiv. Me$_3$SiCl to **2a-BF$_3$K** (**Figure 5**).[11] Defluorination was evident in the ^{19}F NMR spectrum (THF), where one equiv. of Me$_3$SiF was observed (sextet at -156.4 ppm) in addition to a broad singlet (-144.4 ppm). The ^{11}B{^{1}H} NMR spectrum revealed a four-coordinate boron signal (10.6 ppm in THF). These data are consistent with a –BF$_2$ group coordinated to THF.[25] Isolation of the product afforded a yellow/orange crystalline solid in 41% yield, assigned as $({}^{3\text{-BF}_2\bullet\text{THF})}\text{NN}^{\text{tBu}})\text{Mo(CO)}_4$ (**2-BF$_2$•THF**). ^{1}H NMR spectroscopy provided further support for defluorination, as exhibited by the change in the splitting pattern (0.42 ppm, sextet, J = 7.3 Hz, to 0.61 ppm, broad pentet, J = 8 Hz) of the methylene unit adjacent to the –BF$_2$•THF group. Solution IR spectroscopy showed four C≡O features (ν_{CO} = 2015, 1899, 1878, 1834 cm^{-1}) with strong similarity to **2a-BF$_3$K**, indicating no interaction between the pendent –BF$_2$•THF and the carbonyl ligands. These bands are analogous with all compounds **2** possessing a tetracarbonyl Mo center.

To assess the accessibility of the **2-BF$_2$** (i.e. no THF bound), we examined variable temperature NMR spectroscopy in PhMe. At room temperature, the ^{19}F NMR spectrum exhibits a broad singlet at -115 ppm. Upon lowering the temperature to -40 °C, this resonance decoalesces to two multiplets at *ca*. -141 and -143 ppm. We propose that these results are consistent with a dynamic process between **2-BF$_2$•THF** (tetrahedral) and **2-BF$_2$** (i.e. trigonal borane), where (**2-BF$_2$•THF**) is favored at low temperature. To further examine the speciation, we obtained crystals suitable for an X-ray diffraction experiment grown at two temperatures: -25 °C and +25 °C. Crystals of **2-BF$_2$•THF** grown at -25 °C from THF/pentane confirm defluorination. The –BF$_2$ unit is coordinated to a molecule of THF and tetrahedral, consistent with the solution structure ($\sum$B = 342.3(7)°). In contrast, crystals obtained at +25 °C from slow diffusion of n-pentane into a THF solution of **2-BF$_2$•THF** revealed a structure with *no* THF bound to the borane. The isolation of these two structures from the same starting material are consistent with a temperature dependent equilibrium between **2-BF$_2$** and **2-BF$_2$•THF** where at room temperature, **2-BF$_2$** is less soluble and preferentially crystallizes.[26] Structural validation of the appended –BF$_2$ unit was confirmed by interrogating the metrical parameters surrounding boron. The CH$_2$-BF$_2$ unit is rotationally disordered, but the two moieties have essentially identical geometries. The geometry at boron is trigonal planar ($\sum$B = 360(1)° for both disordered moieties) and the nearest non-bonding boron-contacts (3.393(10) Å for B1 to an F atom, and 3.118 Å for B1B to an H atom of neighboring molecules at 1-x, +y, 3/2-z and -1/2+x, -1/2+y, +z, respectively) are consistent with an unquenched Lewis acid in the secondary sphere. Both **2-BF$_2$** and **2-BF$_2$•THF** feature C≡O bond lengths ranging from 1.085(6)-1.162(5) Å, consistent with the IR data.

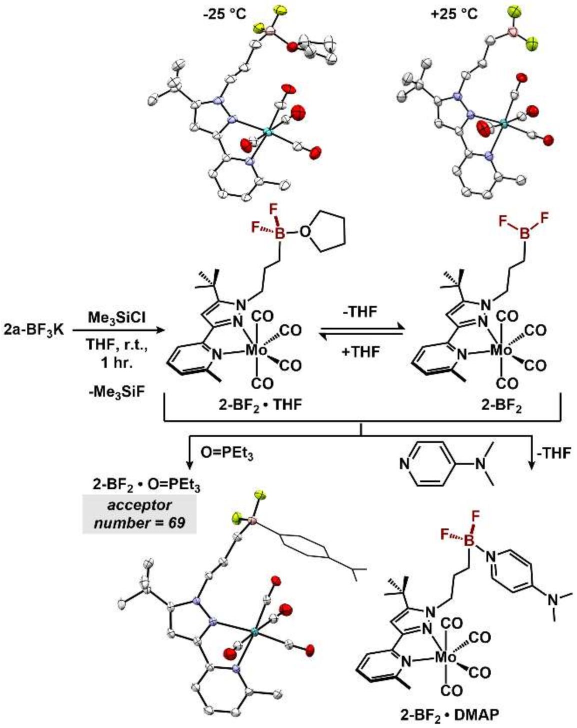


Figure 5. Synthesis and molecular structures of **2-BF₂ • THF**, **2-BF₂**, and **2-BF₂ • DMAP** displayed with 50% probability ellipsoids. H-atoms are omitted from all structures for clarity. Disorder of the CH$_2$-BF$_2$ unit in **2-BF₂** is omitted for improved clarity. The DMAP moiety of **2-BF₂ • DMAP** is displayed in wireframe for improved clarity.

For ease of handling the highly reactive –BF$_2$ complex, all manipulations were performed in THF. In non-coordinating arene solvents, even after extended (48 hr.) vacuum, the $^{11}B\{^1H\}$ NMR spectrum of **2-BF₂ • THF** still displayed a tetrahedral boron (20.8 ppm in toluene). THF resonances were also observed in the ^1H NMR spectrum at 3.79 and 1.36 ppm, slightly shifted from free THF in toluene.[27] Additional support for an adduct between RF$_2$B and THF in solution was provided by introducing a competitive base. When 1 equiv. 4-dimethylaminopyridine (DMAP) was added to a toluene solution of **2-BF₂ • THF**, the $^{11}B\{^1H\}$ NMR spectrum underwent a shift from 20.8 to 11.6 ppm, concomitant with a shift of the THF resonances in the ^1H NMR spectrum to 3.52 and

1.43 ppm, and consistent with release of THF to form ($^{3\text{-}BF_2\bullet DMAP}NN^{tBu}$)Mo(CO)$_4$ (**2-BF$_2$•DMAP**) (**Figure 5**). Crystals of the DMAP-quenched adduct confirm this assignment.

We examined differences in the Lewis acidity of **2-BPin** and **2-BF$_2$•THF** using the Gutmann-Beckett method.[28] Addition of O=PEt$_3$ to **2-BPin** afforded a minimal shift in the ^{31}P NMR spectrum (0.23 ppm), when compared to free O=PEt$_3$, corresponding to an acceptor number of 4.6 ± 0.1. In contrast, addition of O=PEt$_3$ to **2-BF$_2$•THF** exhibited a large shift (28.86 ppm), corresponding to an acceptor number of 69.0 ± 0.1. This value is comparable to BPh$_3$ (69.0) but is lower than that of other fluorinated boranes such as B(C$_6$F$_5$)$_3$ (80.9) and BF$_3$•Et$_2$O (88.1).[5, 28] Although the prepared –BF$_2$ Lewis acid has an acceptor number comparable to BPh$_3$, it features a distinctly smaller steric profile, and thus may enable cooperative M–X–BR$_2$ interactions in cases where steric clashing of substituents around boron would otherwise prevent interactions. Overall, these experiments confirm the availability of secondary sphere –BF$_2$ Lewis acids for substrate binding and moreover, establish clear enhancements of boron Lewis acidity from a synthetic path that started with a synthetically accessible, yet very weakly acidic –BPin.

In conclusion, we have adapted borane modification strategies that are more commonly used in organic literature to convert a –BPin unit to a strongly acidic, sterically unencumbered pendent borane in the secondary sphere of a Mo(CO)$_4$ complex. This –BF$_2$ Lewis acid is not a commonly used Lewis acid, and not readily accessed via traditional post-metalation hydroboration routes[29] and represents a potential entry point to systems that would benefit from highly Lewis acidic secondary coordination sphere features.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge on the ACS Publications website.

Full experimental procedures and spectroscopic characterization of all species and crystal structure data (PDF).

CCDC 2370507-2370509 & 2388499-2388501 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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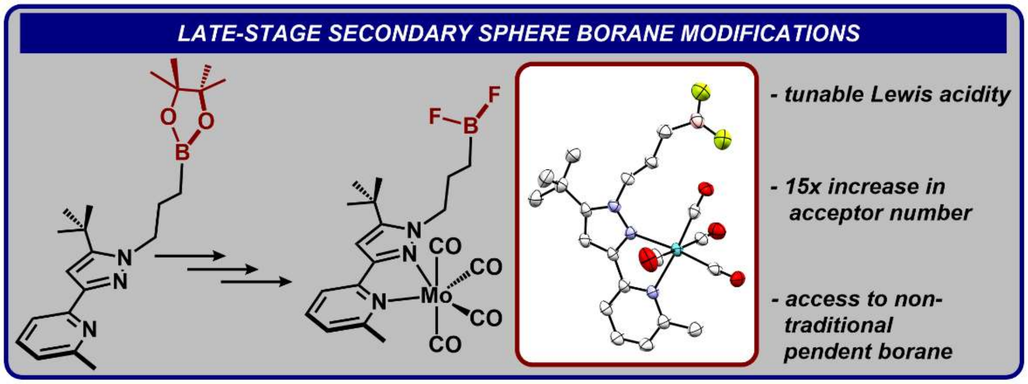
SYNOPSIS. We present a synthetic approach to enhance the Lewis acidity of a second-sphere borane. By applying boron modification strategies more commonly used in organic literature, we transformed a pendent –BPin to $–BF_2$. The $–BF_2$ moiety features a ~15x increase in acceptor number and is not accessible via standard hydroboration routes.


LATE-STAGE SECONDARY SPHERE BORANE MODIFICATIONS
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- tunable Lewis acidity
- 15x increase in acceptor number
- access to non-traditional pendent borane