Secondary Coordination Sphere Alkylation Promotes Cyclometalation

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Abstract. Diphosphines have taken on a dominant role as supporting ligands in transition metal chemistry. Here, we describe complexes of the type [Cp*Fe(diphosphine)(X)] (X = Cl, H) where for diphosphine = tetraallylphosphinoethane (tape), a Lewis-acidic secondary coordination sphere (SCS) was installed *via* allyl group hydroboration using dicyclohexylborane (HBCy$_2$). The resulting chloride complex, [Cp*Fe(P$_2$B$^{Cy}_4$)(Cl)] (P$_2$B$^{Cy}_4$ = 1,2-*bis*(di(3-cyclohexylboraneyl)propylphosphino)ethane), was treated with *n*-butyllithium (1-10 equivs.), resulting in SCS butylation, followed by cyclometalation at iron. This reactivity is contrasted with [Cp*Fe(d*n*ppe)(Cl)] (d*n*ppe = 1,2-*bis*(di-*n*-propylphosphino)ethane), whereby addition of *n*-butyllithium provides a mixture of products. Overall, transmetalation is a common elementary transformation in organometallic chemistry, and here we describe how its outcome is altered due to Lewis acid SCS incorporation.

INTRODUCTION

Ligand design is a variable that allows for control of transition metal reactivity.[1,2] While much focus has been given to modification and substitution of the atoms directly connected to a metal, there has been an increase in the number of reports that seek to modify the secondary coordination sphere (SCS) – atoms that are not directly bound to the metal, but nevertheless influence reactivity. Indeed, a surge of recent reports have capitalized on the use of purposefully incorporated SCSs for substrate activation/stabilization, metal redox modification, the selective reduction of small-molecules, and more.[3] Of the myriad functional groups available for SCS incorporation, our team and that of others, has focused on the integration of Lewis acidic boron-based SCSs (**Figure 1A**).[4] To date, such SCSs have been exploited for many different types of reactions including the cooperative stabilization (and *N-N* bond cleavage) of hydrazine (N$_2$H$_4$) and the reduction of carbon monoxide (CO).[5–7] Furthermore, a role for such Lewis acidic SCSs has been exposed in iodoarene C–I bond oxidative addition using a [Ni(diphosphine)$_2$] complex, and in producing divergent reaction pathways in the reaction of Ni(0) with organoazides.[8,9]

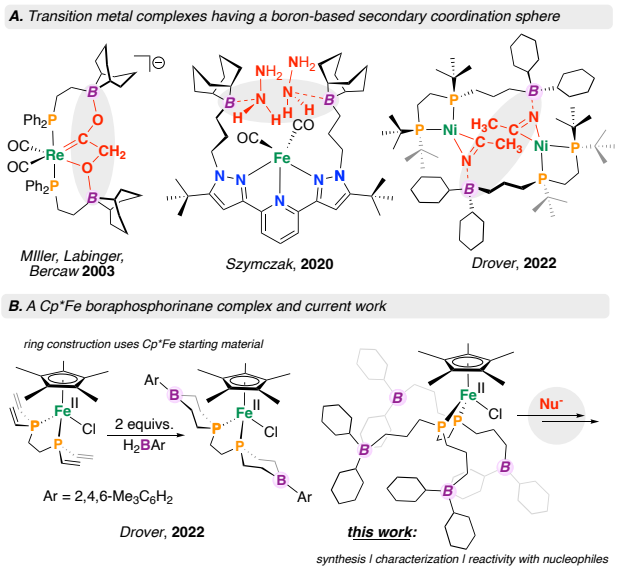


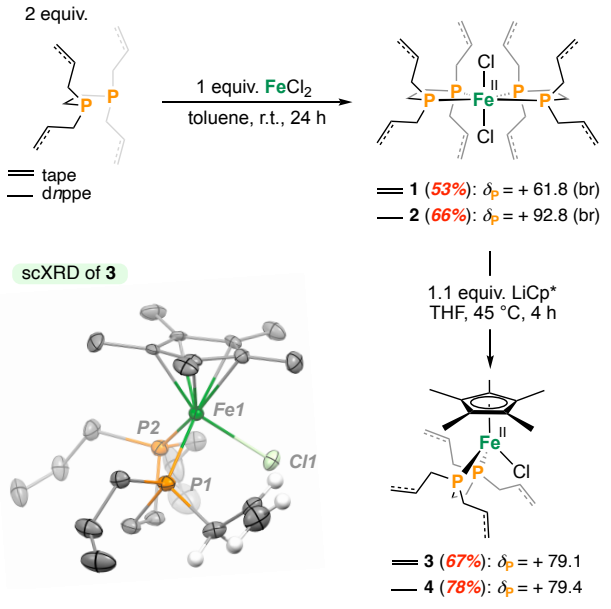
Figure 1. A collection of transition metal compounds having boron-based SCSs and the current work being explored. Nu = nucleophile.

Our group has contributed a number of diphosphine ligands where unsaturated R-groups serve as modifiable sites for the installation of Lewis-acids (boranes; –BR$_2$) *via* hydroboration.[10,11,12,13] In most cases, installation is performed post-coordination, the success of which depends on the nature of metal starting material. As an example, we previously showed that [Fe(dvpe)$_2$Cl$_2$] (dvpe = 1,2-*bis*(divinylphosphino)ethane) does not undergo productive hydroboration, instead the ligand is lost as a Lewis acid/base pair, accompanied by [FeCl$_2$(THF)$_x$].[14] It was therefore imperative to first install a Cp* (Cp* = C$_5$Me$_5^-$) ligand to prepare [Cp*Fe(dvpe)Cl], allowing for successful hydrofunctionalization (ring-closure) (**Figure 1B**). As a furtherance to our work in this area, we now disclose several complexes of the type [Cp*Fe(diphosphine)(X)] (X = Cl, H), that bear Lewis acids in their SCS. We investigate SCS effects on the reactivity of these [Fe]-complexes with conventional nucleophiles, contrasting outcomes with an "all-alkyl" ligand, d*n*ppe (d*n*ppe = 1,2-*bis*(di-*n*-propylphosphino)ethane) that affirms a role for SCS inclusion.

RESULTS AND DISCUSSION

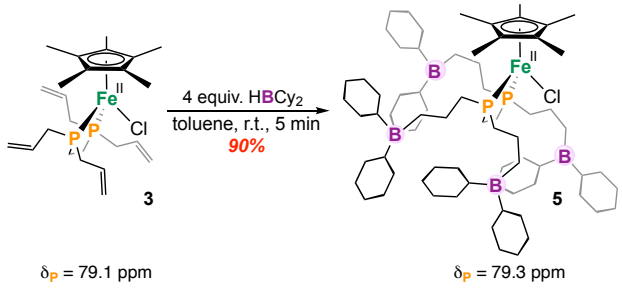
Synthesis of {[Fe]-Cl} complexes. The synthetic approach outlined herein relies upon synthesis of the known complex [Fe^{II}(tape)$_2$Cl$_2$] (**1**) (tape = tetraallylphosphinoethane),

accessed via addition of 2 equivs. tape to a toluene solution of $FeCl_2$ (**Scheme 1**).[15] Initial attempts aimed at hydroboration of **1** were unsuccessful; addition of 8 equivs. of the moderately electrophilic dicyclohexylborane ($HBCy_2$)[16] to a THF solution of **1** resulted in an immediate color change from clear green to cloudy with concomitant formation of uncoordinated $P_2B^{Cy}{}_4$ (δ_P = 15.5 ppm),[11] resulting from ligand dissociation. In order to prevent ligand dissociation (and formation of free $FeCl_2(THF)_x$), the half-sandwich complex [Cp*Fe(tape)Cl] (Cp* = $C_5Me_5^-$) (**3**) was synthesized by addition of 1.1 equivs. LiCp* to a THF solution of **1** at 45 °C for 4 h. Workup gave **3** as dark purple crystals (**Scheme 1**). The $^{31}P\{^1H\}$ NMR spectrum of **3** featured a single peak at δ_P = 79.1 ppm; the ^1H NMR spectrum showed characteristic C_s-symmetric allyl signals at δ_H = 6.18 and 5.73 ppm, which correspond to the allyl C(sp^2)H groups on both the front and back allyl arms (with respect to the chloride ligand). A cluster of other allyl signals from 5.14 > δ_H > 4.90 ppm were also observed for the remaining C(sp^2)H protons.[8,13,17] "All-alkyl" analogues **2** and **4** using d*n*ppe (d*n*ppe = 1,2-*bis*(di-*n*-propylphosphino)ethane) were also synthesized following similar procedures to that of **1** and **3** (**Scheme 1**). Single-crystal X-ray diffraction (scXRD) was used to confirm and structurally authenticate the identities of compounds **2**, **3**, and **4**. For both **2** and **4**, the solid-state structures show a classic three-legged piano stool complex (see **Scheme 1** for **3**). Throughout this study, **4** was used as a negative control with respect to reactivity, as a comparator devoid of a Lewis acid SCS.



Scheme 1. Synthesis of Fe(II) compounds **1-4**. Inset shows the crystal structure of **3** with ellipsoids drawn at 50% probability; hydrogen atoms on one allyl moiety are shown.

We next sought to install a Lewis-acidic SCS around iron(II)-chloride **3**. As such, 4 equivs. $HBCy_2$ was added to a toluene solution of **3**.[16] After 5 min, ^1H NMR spectroscopic data was acquired, indicating an absence of allyl signals in the region of δ_H = 6 - 4 ppm, confirming four-fold hydroboration of **3** to afford [Cp*Fe($P_2B^{Cy}{}_4$)Cl] (**5**) ($P_2B^{Cy}{}_4$ = 1,2-*bis*(di(3-dicyclohexylboranyl)propylphosphino)ethane) (**Scheme 2**). The $^{31}P\{^1H\}$ NMR spectrum showed a near-identical signal at δ_P = 79.3 ppm (*c.f.*, δ_P = 79.1 ppm for **3**). The $^{11}B\{^1H\}$ spectrum showed a broad signature at δ_B = + 85 ppm ($\Delta_{1/2}$ = 1306 Hz), indicative of sp^2-hybridized SCS boranes.[11] With complex **5** in-hand, we next sought to examine reactivity to determine the effect (if any) of the borane SCS on [Fe]-based reactivity.

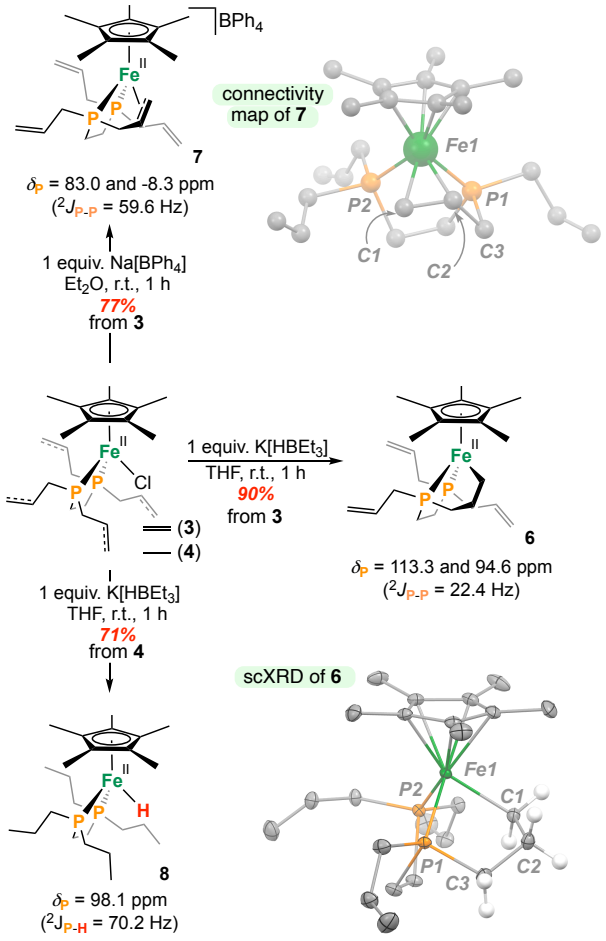


Scheme 2. Hydroboration of **3** using $HBCy_2$ to form the tetraboranyl complex **5**.

Synthesis of {[Fe]—H} complexes. Previously, we showed that for a related Rh(I) octaboranyl system, ([$Rh(P_2B^{Cy}{}_4)_2]^+$), hydride transfer could occur either at the SCS (forming a {H–BR_3} fragment) or rhodium, owing to similar values in hydricity (ΔG_{H^-}).[17] We accordingly sought to access the reactivity of our iron(II)-chloride complexes with hydride transfer reagents. To begin, exposure of **3** to 1 equiv. K[$HBEt_3$] in THF resulted in a marked color change from purple to orange. A new set of peaks was observed in the $^{31}P\{^1H\}$ NMR spectrum: two doublets at δ_P = 113.3 and 94.6 ppm ($^2J_{P\text{-}P}$ = 22.4 Hz), indicating loss of C_s-symmetry (chemically distinct phosphorus atoms). Analysis of the ^1H NMR spectrum showed an upfield shifted signal at δ_H = -0.05 ppm (1H), suggesting the presence of an α-proton connected to Fe. Indeed, α-protons on other [Cp*Fe(diphosphine)(alkyl)] complexes are known to display similarly upfield-shifted resonances (*e.g.*, [Cp*Fe(dmpe)CH_3] (dmpe = 1,2-*bis*(dimethylphosphino)ethane) where the CH_3 group appears at δ_H = -0.10 ppm in C_6D_6).[18] On the basis of this NMR spectroscopic data, this compound was assigned as [Cp*Fe(κ^3-CPP$^{allyl}{}_2$)] (**6**) (**Scheme 3**). Crystals of **6** were grown from a saturated pentane solution at -35 °C and analyzed by scXRD (**Scheme 3**). The solid-state structure confirmed that one of the allyl moieties on the tape ligand had been activated, presumably through a transient (and unobserved) [Fe]–H intermediate. The formation of **6** indicates that the allyl moieties on **3** are prone to migratory insertion. Promiscuity of the tape ligand is further showcased by halide abstraction from **3**, which gives the η^2-alkene complex, **7** – $^{31}P\{^1H\}$ NMR signatures at δ_P = + 83.0 and - 8.3 ppm ($^2J_{P\text{-}P}$ = 59.6 Hz) in addition to a connectivity map provided by X-ray crystallography, buttress this assignment (**Scheme 3**).[19]

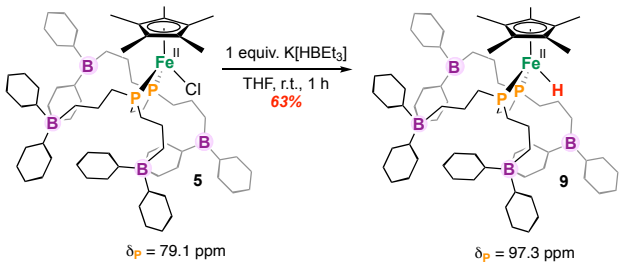
By contrast to compound **3**, exposure of **4** to 1 equiv. K[$HBEt_3$] results in successful formation of [Cp*Fe(d*n*ppe)(H)] (**8**) (**Scheme 3**). Complex **8** was characterized by a characteristic triplet at δ_H = -17.9 ppm ($^2J_{H\text{-}P}$ =

70.2 Hz) in its ^{1}H NMR spectrum, a $^{31}P\{^{1}H\}$ signal at δ_P = + 98.1 ppm (*c.f.*, δ_P = + 79.4 ppm for **4**), and an IR stretch of ν([Fe]–H) = 1865 cm^{-1}.



Scheme 3. Formation of **6**-**8**. Inset shows a connectivity map for compound **7** with hydrogen atoms omitted and a crystal structure of **8** shown with ellipsoids drawn at 50% probability; hydrogen atoms omitted except for the P-CH_2-CH_2-CH_2-Fe linker.

Consistent with complex **4**, reaction of complex **5** with 1 equiv. K[HBEt3] results in an immediate color change from purple to yellow, giving [FeCp*($P_2B^{Cy}_4$)H] (**9**). Analysis of the ^{1}H NMR spectrum revealed a triplet at δ_H = -17.7 ppm ($^{2}J_{H\text{-}P}$ = 70.2 Hz), indicating successful [Fe]–H formation. The $^{31}P\{^{1}H\}$ NMR spectrum contained a singlet at δ_P = + 97.3 ppm, and the $^{11}B\{^{1}H\}$ NMR spectrum showed a characteristic signal at δ_B = + 84 ppm ($\Delta_{1/2}$ = 920 Hz) for the sp^2-hybridized boranes. Given the weakly donating hydride ability for {CpFe(L_n)H} compounds e.g., ΔG_{H^-} = 61.7 kcal mol^{-1} in CH_3CN for [CpFe(CO)$_2$H] (Cp = $C_5H_5^-$)[20] *cf.* [$HBEt_3$]$^-$ (26 kcal mol^{-1}), it stands to reason that Fe, rather than B, serves as the thermodynamic site of hydride transfer.



Scheme 4. Generation of [FeCp*($P_2B^{Cy}_4$)H] (**9**).

Reactivity with *n*-butyllithium and methyllithium. Transition metal alkyl compounds are often accessed by salt metathesis, with the corresponding halide undergoing exchange. This is a common method for methyl group installation – to prepare [Cp*Fe(dmpe)(CH_3)], for example.[18] In cases where such alkyl groups have β-hydrogens, elimination can occur producing an alkene as well as a transition metal hydride ([M]—H) species.[21] Indeed, it has been shown that [Cp*Fe(dppe)(Cl)] (dppe = 1,2-*bis*(diphenylphosphino)ethane) reacts with (^{n}Bu)MgCl to give both [Cp*Fe(dppe)(^{n}Bu)] and [Cp*Fe(dppe)(H)] in a 93:7 ratio at -10 °C; heating to 98 °C results in near-quantitative conversion to [Cp*Fe(dppe)(H)].[22]

We next wondered whether the electron-accepting pendant boranyl groups would play a role on treatment with a conventional alkylating reagent e.g., by conferring protection to the "[Fe]—Cl" unit or by serving as an acceptor from a generated "[Fe]—alkyl" compound. In a previous report, we showed that [Rh($P_2B^{Cy}_4$)$_2$]$^+$ underwent alkylation at boron and not rhodium – even in the presence of ≥ 8 equivalents of *n*-butyllithium.[17] We thus turned our attention to the reactivity of boranyl compound **5** with *n*-butyllithium (^{n}BuLi), which in theory could provide an alternative route to generate the [Fe]—H **9**. Conversely, addition of 1-10 equivs. ^{n}BuLi to a THF solution of **5** resulted in a new C_1-symmetric complex that showed neither characteristic resonances attributable to an iron hydride ([Fe]–H e.g., compound **9**, *vide supra*) nor an iron-butyl ([Fe]–(CH_2)$_3$$CH_3$) compound (**Figure 2**).

Careful titration of compound **5** and acquisition of $^{31}P\{^{1}H\}$ NMR spectra showed formation of two sets of doublets centered at δ_P = 118.2 and 93.7 ppm ($^{2}J_{P\text{-}P}$ = 31.8 Hz). Upon addition of excess ^{n}BuLi (> 4 equivs.), no further changes were observed (**Figure 2**). Moreover, by ^{1}H NMR spectroscopy, a cluster of upfield-shifted signals at 0.1 < δ_H < -0.1 ppm were witnessed for the quaternary *n*-propyl C<u>H</u>$_2$ and cyclohexyl C<u>H</u> groups of {(-^{n}Pr)(Cy)$_2$B(^{n}Bu)}$^-$, while the $^{11}B\{^{1}H\}$ NMR spectrum showed characteristic sharp peaks indicative of sp^3-hybridized borates, [BR_4]$^-$ (see ESI). To explain the results from this titration with ^{n}BuLi, two key pieces of evidence were considered: 1) the $^{31}P\{^{1}H\}$ NMR chemical shifts of the newly formed complex (δ_P = 118.2 and 93.7 ppm ($^{2}J_{P\text{-}P}$ = 31.8 Hz)) were similar to those of complex **6** (*vide supra*, for **6**: δ_P = 113.3 and 94.6 ppm ($^{2}J_{P\text{-}P}$ = 22.4 Hz)) and, 2) lithium tetraalkylborates (Li[BR_4]) are known to serve as sources of "R^- ", allowing for transmetalation at a transition metal center (**Figure 2**).[23–25] Together, these points suggest that upon addition of ^{n}BuLi to **5**, one of the

(Pr)BCy_2 (Pr = propyl linker to P) groups is alkylated to form [Cy_2B(Pr)(^{n}Bu)]$^-$, rearranging to cyclometalate [Fe], giving [**10**]$^{3-}$, with concomitant release of LiCl and $Cy_2B(^n$Bu) (**Figures 2** and **3**).

The cyclometalation outcome described above is not limited to ^{n}BuLi as the alkylating reagent. Indeed, treatment of **5** with excess CH_3Li also affords a near-identical cyclometalated product (δ_P = 118.4 and 94.6 ppm ($^2J_{P,P}$ = 32.1 Hz)), and not the expected ([Fe]–CH_3) compound.

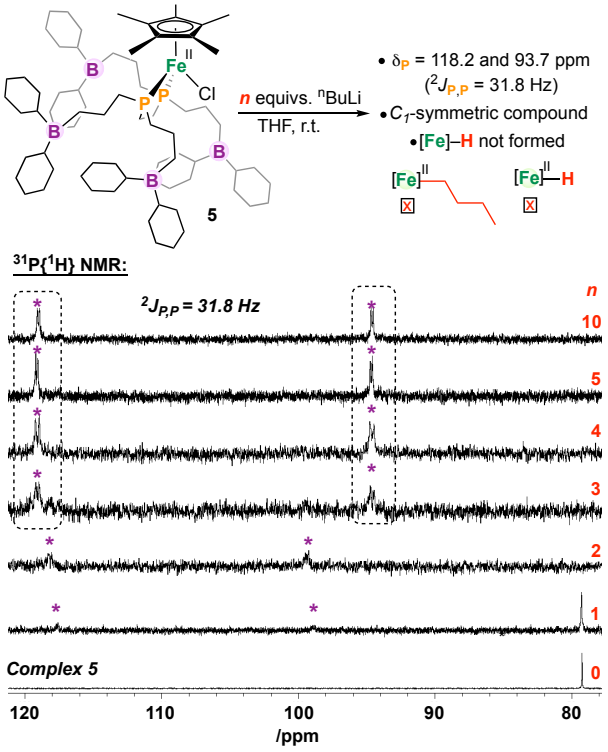


Figure 2. Reaction of **5** with *n* equivs. ^{n}BuLi. Inset shows stacked $^{31}P\{^1H\}$ NMR spectra (202.5 MHz, 298 K).

To corroborate our hypothesis of a borane-encouraged transmetalation event, we next sought to independently prepare [**10**]$^{3-}$ from precursor [Cp*Fe(κ^3-CCP_2^{BCy2})] (**10**). Beginning with **6**, three-fold hydroboration with $HBCy_2$ produced **10**, confirmed by an absence of allyl signals in the ^1H NMR spectrum and a slight shift in the $^{31}P\{^1H\}$ spectrum (δ_P = 117.3 and 98.6 ppm ($^2J_{P\text{-}P}$ = 28.3 Hz)) (**Figure 3**). For **10**, the $^{11}B\{^1H\}$ NMR spectrum showed the expected broad signature for sp^2-hybridized boranes in the SCS (δ_B = 83.4 ppm, $\Delta_{1/2}$ = 1031 Hz). Upon addition of 3 equivs. ^{n}BuLi to **10**, the $^{31}P\{^1H\}$ NMR signals shifted slightly from the starting triboranyl complex **10** (from δ_P = 117.3 and 98.6 ppm ($^2J_{P\text{-}P}$ = 28.3 Hz) to δ_P = 118.2 and 93.7 ppm ($^2J_{P\text{-}P}$ = 31.8 Hz)), revealing a perfect match of $^{31}P\{^1H\}$ NMR signals between [**10**]$^{3-}$ and the product from titration of **5** with ^{n}BuLi (**Figure 3**). These data show that upon addition of ^{n}BuLi to **5**, the site of alkylation is the electrophilic borane in the SCS, which then reacts at [Fe], giving [**10**]$^{3-}$ instead of an [Fe]–H complex. These findings illustrate that SCS boron groups undoubtedly influence reactivity at iron(II), even in a transformation as "simple" as salt metathesis.

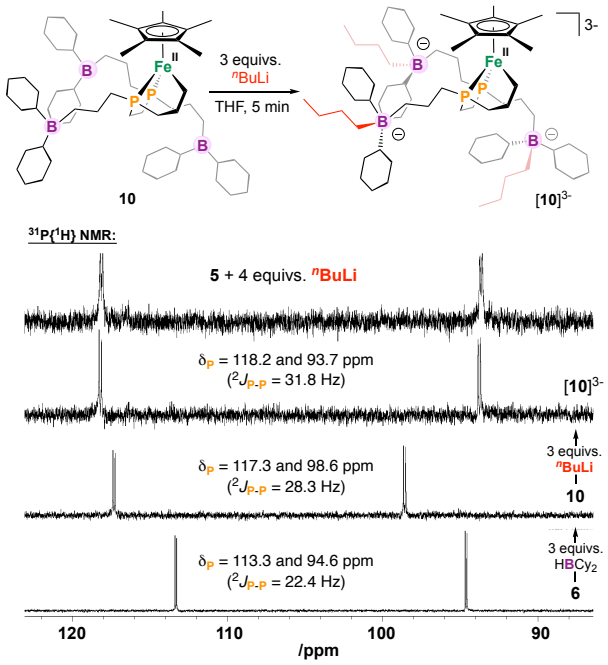
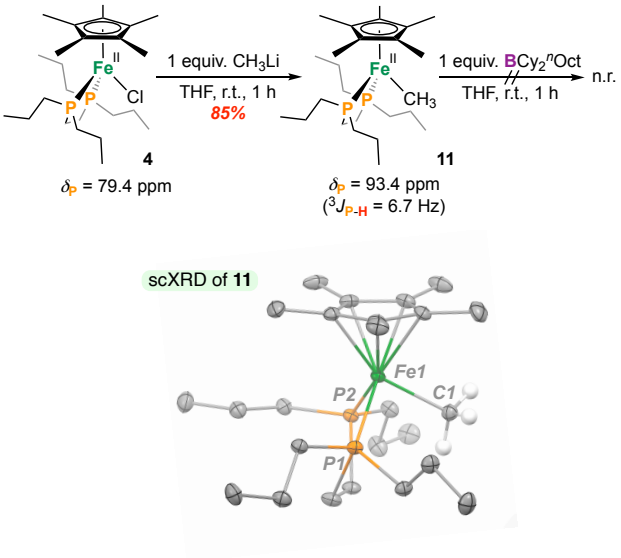


Figure 3. Reactivity of **6** with $HBCy_2$ to give **10** and alkylation with ^{n}BuLi to give [**10**]$^{3-}$. **B)** Overlayed $^{31}P\{^1H\}$ NMR spectra (202.5 MHz, 298 K) of **6**, **10**, [**10**]$^{3-}$, and **5** + 5 equivs. ^{n}BuLi.

To further illustrate the difference of SCS borane incorporation, the "all-alkyl" compound **4** was exposed to 1 equiv. ^{n}BuLi and monitored by NMR spectroscopy. The $^{31}P\{^1H\}$ spectrum showed the formation of several products (see ESI) - none of these signals correspond to [Cp*Fe(d*n*ppe)(H)] (**8**). Notably, broad resonances from 20.9 > δ_H > -17.6 ppm were also observed, indicating that at least one (or more) of the products from this reaction is paramagnetic.

Further highlighting the relevance of borane SCS incorporation, we elected to react the model compound [Cp*Fe(d*n*ppe)Cl] (**4**) with excess CH_3Li. By contrast to **5**, clean alkylation of iron was concluded, giving an orange solution of [Cp*Fe(d*n*ppe)CH_3] (**11**) with diagnostic signatures at δ_H = -0.94 (t; 3H; Fe-$\underline{CH_3}$, $^3J_{H\text{-}P}$ = 6.7 Hz) and δ_P = 93.4 ppm. The X-ray structure of **11** is provided in **Scheme 5**. To probe the likelihood of methyl transfer to an electrophilic borane (which would be the case if alkylation first occurred at [Fe] followed by B-abstraction), an intermolecular reaction with the model sp^2-hybridized borane, $BCy_2{}^n$Oct, was performed, resulting in null reactivity. Altogether, this suggests that boron, rather than iron, is the primary site of alkylation, and that transmetalation only occurs once the SCS has been attacked with exogenous nucleophile.



Scheme 5. Generation of compound **11** and null reactivity with $BCy_2{}^nOct$.

CONCLUSION

Collectively, these data show that installing a Lewis-acidic SCS around {Cp*Fe} tunes reactivity toward cyclometalation. This is exemplified by preparation of a series of new [Cp*Fe(diphosphine)(X)] (diphosphine = tape, d*n*ppe, $P_2B^{Cy}{}_4$; X = Cl, H) complexes, contrasting the differential behaviour between *n*-boranyl and *n*-alkyl variants. For the tetraboranyl complex **5**, only one reaction product was observed upon addition of ^{n}BuLi, whereas for the "all-alkyl" complex **4**, many products resulted under identical reaction conditions. These findings have implications for ligand design, wherein a functional SCS can be installed to induce new reaction outcomes.

EXPERIMENTAL DATA

General Considerations. All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents in a solvent purification system supplied by PPT, LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective moisture removal. d_6-benzene was dried over molecular sieves and degassed by three freeze-pump-thaw cycles. Reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

Physical methods. ^{1}H NMR spectra are reported in parts per million (ppm) and are referenced to residual solvent e.g., ^{1}H(C_6D_6): δ 7.16; ^{13}C(C_6D_6): 128.06; coupling constants are reported in Hz. ^{13}C{^{1}H}, ^{11}B{^{1}H}, and ^{31}P{^{1}H} NMR spectra were performed as proton-decoupled experiments and are reported in ppm. Compound **1** was prepared according to a literature procedure.[15]

Preparation of Compounds.

[Fe^{II}(d*n*ppe)$_2$Cl$_2$] (**2**; $C_{28}H_{64}Cl_2FeP_2$, M_W = 652 g/mol): In the glovebox, $FeCl_2$ (35 mg, 0.28 mmol) was suspended in approximately 4 mL of toluene in a 20 mL scintillation vial equipped with a stir bar. Next, 1,2-*bis*-(di-*n*-propylphosphino)ethane (d*n*ppe) (146 mg, 0.56 mmol, 2 equiv.) was added and the reaction mixture stirred for 24 h. The resulting green solution was filtered through Celite® and reduced to half of its original volume. Approximately 8 mL of hexane was layered onto the solution. Recrystallization at -35 °C overnight gave the titled compound as green crystals (120 mg, 66 %). **^{1}H NMR (500 MHz, C_6D_6, 298 K):** δ_H = 2.38-2.11 (br. m, 20H; multiple overlapping C$\underline{H}_2$ signals), 1.65 (br. m; 20H; multiple overlapping C$\underline{H}_2$ signals), 0.99 (br. m; 24H; C$\underline{H}_3$). **^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K):** δ_C = 28.2 (br), 21.4 (br), 19.4 (br), 16.9 (br. s; $CH_2CH_2\underline{C}H_3$). **^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 298 K):** δ_P = + 92.8 (br). Anal. Calcd for $C_{28}H_{64}Cl_2FeP_2$ (652): C, 51.62; H, 9.90. Found: C, 51.63; 9.94.

[Cp*Fe^{II}(tape)Cl] (**3**; $C_{24}H_{39}ClFeP_2$, M_W = 481 g/mol): In the glovebox, **1** (180 mg, 0.28 mmol) was weighed into a 100 mL thick-walled reaction vessel equipped with a stir bar. Approximately 20 mL of THF was added. To this solution was added a 10 mL solution of LiCp* (44 mg, 0.31 mmol, 1.1 equiv.) in THF. The reaction mixture was stirred for 4 h at 45 °C. The solution became gradually darker over time. The solvent was removed *in-vacuo*, and the product was extracted with 3 x 2 mL portions of pentane and filtered through Celite®. The solvent was reduced to a quarter of its original volume. Recrystallization at -35 °C overnight gave **3** as dark purple crystals (90 mg, 67%). **^{1}H NMR (500 MHz, C_6D_6, 298 K):** δ_H = 6.14 (m, 2H; C$\underline{H}$(allyl)), 5.69 (m, 2H; C$\underline{H}$(allyl)), 5.14-4.90 (m, 8H (two sets); C$\underline{H}_2$(allyl)), 3.01 (m, 4H; P-C$\underline{H}_2$), 2.92 (m, 2H; P-C$\underline{H}_2$-C$\underline{H}_2$ linker), 2.32 (m, 2H; P-C$\underline{H}_2$-C$\underline{H}_2$ linker), 1.57 (s, 15H; Cp*$\underline{H}$), 1.36 (m, 4H; P-C$\underline{H}_2$),. **^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K):** δ_C = 134.6 (m; $\underline{C}$H(allyl)), 133.1 (m; $\underline{C}$H(allyl)), 117.1-116.9 (dm; P-$\underline{C}$H$_2$(allyl)), 83.2 (s; Cp*(aromatic)), 34.5 (m; P-$\underline{C}$H$_2$-$\underline{C}$H$_2$ linker), 32.4 (m; P-$\underline{C}$H$_2$), 23.1 (m; P-$\underline{C}$H$_2$), 11.1 (s; $\underline{C}$H$_3$-Cp*). **^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 298 K):** δ_P = + 79.1. Anal. Calcd for $C_{24}H_{39}ClFeP_2$ (481): C, 59.95; H, 8.18. Found: C, 59.73; H, 8.21.

[Cp*Fe^{II}(d*n*ppe)Cl] (**4**; $C_{24}H_{47}ClFeP_2$, M_W = 489 g/mol): In the glovebox, **2** (110 mg, 0.17 mmol) was weighed into a 100 mL thick-walled reaction vessel equipped with a stir bar. Approximately 20 mL of THF was added. To this solution was added LiCp* (27 mg, 0.19 mmol, 1.1 equiv.) suspended in 10 mL of THF. The reaction was stirred for 4 h at 45 °C. The solution became gradually darker over time. The solvent was removed *in-vacuo*, and the product was extracted with 3 x 2 mL portions of pentane and filtered through Celite®. The solvent was reduced to a quarter of its original volume. Recrystallization at -35 °C overnight gave the titled compound as dark purple crystals (65 mg, 78%). **^{1}H NMR (500 MHz, C_6D_6, 298 K):** δ_H = 2.13-2.05 (m; 6H; multiple overlapping C$\underline{H}_2$ signals), 1.88 (m; 2H; C$\underline{H}_2$), 1.65 (s,

15H, Cp*-C$\underline{H}_3$), 1.43-1.24 (m; 12H; multiple overlapping C$\underline{H}_2$ signals), 1.05 (t; 6H; P-CH$_2$-CH$_2$-C$\underline{H}_3$), 0.89 (t; 6H; P-CH$_2$-CH$_2$-C$\underline{H}_3$). **^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 298 K):** δ_C = 82.1 (s; Cp*(aromatic)), 31.8 (m; $\underline{C}$H$_2$), 29.2 (m; $\underline{C}$H$_2$), 23.5 (m; $\underline{C}$H$_2$), 19.3 (m; $\underline{C}$H$_2$), 18.5 (m; $\underline{C}$H$_2$), 16.8 (m; overlapping $\underline{C}$H$_3$ signals), 11.3 (s; $\underline{C}$H$_3$-Cp*). **^{31}P{^{1}H} NMR (202.5 MHz, C$_6$D$_6$, 298 K):** δ_P = + 79.4.

[Cp*Fe^{II}(P$_2$B$^{Cy}_4$)Cl]; (**5**; C$_{72}$H$_{131}$B$_4$ClFeP$_2$, M$_W$ = 1193 g/mol): In the glovebox, **3** (35 mg, 0.07 mmol) and HBCy$_2$ (50 mg, 0.28 mmol, 4 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of toluene was added, and the solution was allowed to stir for 30 min at room temperature. The resulting dark purple solution was filtered through Celite® and the solvent was removed *in-vacuo* to give the titled compound as a purple oil (78 mg, 90%). **^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K):** δ_H = 2.42-2.13 (m, 6H; multiple P-C$\underline{H}_2$ signals), 1.79 (s, 15H; Cp*-C$\underline{H}_3$ (located by ^{1}H-^{13}C HSQC)), 2.00-1.15 (multiple overlapping C(sp^3)–H resonances). **^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 298 K):** δ_C = 81.8 (s; Cp*(aromatic)), 35.9 (m), 35.7 (m), 34.6 (m), 33.3 (m), 31.6 (m), 28.2-26.5 (multiple overlapping C(sp^3)-H resonances), 22.7 (m), 20.6 (m), 19.7 (m), 11.1 (s; Cp*-$\underline{C}$H$_3$). **^{31}P{^{1}H} NMR (202.5 MHz, C$_6$D$_6$, 298 K):** δ_P = + 79.3. **^{11}B{^{1}H} NMR (160.5 MHz, C$_6$D$_6$, 298 K):** δ_B = + 85 ($\Delta_{1/2}$ = 1306 Hz).

[Cp*Fe^{II}(κ^3-CPP$^{allyl}_3$)] (**6**; C$_{24}$H$_{40}$FeP$_2$, M$_W$ = 446 g/mol): In the glovebox, **3** (15 mg, 0.03 mmol) was suspended in approximately 4 mL of THF in a 20 mL scintillation vial equipped with a stir bar. Next, K[HBEt$_3$] was added (1 equiv., 1.0 M THF). The reaction was stirred for 1 hour. After this, the solvent was removed *in vacuo*, the orange powder extracted into pentane and filtered through Celite®. Recrystallization at -35 °C overnight gave **6** as orange crystals (13 mg, 93%). **^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K):** δ_H = 5.88-5.76 (br. m, 3H; C$\underline{H}$(allyl)), 4.99-4.92 (br. m; 6H; C$\underline{H}_2$(allyl)), 2.74 (m, 1H;), 2.64 (m, 1H), 2.58 (m, 1H), 2.44 (m, 3H; overlapping P-C$\underline{H}_2$ and P-C$\underline{H}_2$-C$\underline{H}_2$-P linker signals), 1.71 (s, 15H; Cp*$\underline{H}$), 1.64-1.39 (m, 7H; overlapping P-C$\underline{H}_2$ and P-C$\underline{H}_2$-C$\underline{H}_2$-C$\underline{H}_2$-Fe linker signals), 1.10 (m, 1H; P-C$\underline{H}_2$-CH$_2$-CH$_2$-Fe linker), 0.76 (m, 1H; P-CH$_2$-C$\underline{H}_2$-CH$_2$-Fe linker), -0.05 (m, 1H; P-CH$_2$-CH$_2$-C$\underline{H}_2$-Fe linker). **^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 298 K):** δ_C = 135.1 (m; $\underline{C}$H(allyl)), 134.2 (m; $\underline{C}$H(allyl)), 133.9 (m; $\underline{C}$H(allyl)), 115.9 (m; two overlapping $\underline{C}$H$_2$(allyl) signals), 115.5 (m; $\underline{C}$H$_2$(allyl)), 84.8 (s; Cp*(aromatic)), 36.9-36.0 (m; overlapping P-$\underline{C}$H$_2$ and P-$\underline{C}$H$_2$-$\underline{C}$H$_2$-P linker signals), 35.0 (m; overlapping P-$\underline{C}$H$_2$ and P-$\underline{C}$H$_2$-$\underline{C}$H$_2$-P linker signals), 29.6 (m; P-$\underline{C}$H$_2$-CH$_2$-CH$_2$-Fe), 28.9 (m; overlapping P-$\underline{C}$H$_2$ and P-$\underline{C}$H$_2$-$\underline{C}$H$_2$-P linker signals), 22.5 (m; P-CH$_2$-$\underline{C}$H$_2$-CH$_2$-Fe), 17.25 (m; P-CH$_2$-CH$_2$-$\underline{C}$H$_2$-Fe), 11.6 (s; Cp*-$\underline{C}$H$_3$). **^{31}P{^{1}H} NMR (202.5 MHz, C$_6$D$_6$, 298 K):** δ_P = + 113.3 (d, $^2J_{P\text{-}P}$ = 22.4 Hz), + 94.6 (d, $^2J_{P\text{-}P}$ = 22.4 Hz).

[Cp*Fe^{II}(κ^2:η^2-C=CPP$^{allyl}_3$)]BPh$_4$ (**7**; C$_{48}$H$_{59}$BFeP$_2$, M$_W$ = 765 g/mol): In the glovebox, **3** (15 mg, 0.03 mmol) was dissolved in approximately 10 mL of Et$_2$O in a 20 mL scintillation vial equipped with a stir bar. NaBPh$_4$ (10 mg, 0.03 mmol, 1 equiv.) was added and the reaction allowed to stir for 1 hour. The solvent was removed *in vacuo* and the orange solid washed with 3 x 4 mL of pentane to remove unreacted **3**. The yellow solid was dried and then extracted into THF, filtered through Celite®, and the THF removed *in vacuo*. The orange oil was washed with 4 x 4 mL of pentane and dried to give the titled compound as a flocculent orange powder. Crystals were grown overnight from a saturated THF solution layered with pentane at -35 °C (18 mg, 77%). **^{1}H NMR (500 MHz, d$_8$-THF, 298 K):** δ_H = 7.24 (m, 8H; *o*-C$_6$H$_5$ [BPh$_4$]), 6.82 (m, 8H; *m*-C$_6$H$_5$ [BPh$_4$]), 6.68 (m, 4H; *p*-C$_6$H$_5$ [BPh$_4$]), 6.05 (m, 1H; C$\underline{H}$(allyl)), 5.79 (m, 1H; C$\underline{H}$(allyl)), 5.58 (m, 1H; C$\underline{H}$(allyl)), 5.27-5.08 (m, 6H; overlapping C$\underline{H}_2$(allyl)), 3.30 (m, 2H), 3.18-3.07 (m, 3H; overlapping P-CH$_2$ signals), 2.92 (m, 1H), 2.75 (m, 1H), 2.16 (m, 1H), 1.99-1.86 (m, 2H), 1.58 (s, 15H; Cp*-C$\underline{H}_3$), 1.40-1.19 (m, 3H; overlapping P-CH$_2$ signals), 0.87 (m, 1H; P-CH$_2$-CH=(Fe)C$\underline{H}_2$), 0.74 (m, 1H; P-CH$_2$-CH=(Fe)C$\underline{H}_2$).**^{13}C{^{1}H} NMR (125.8 MHz, d$_8$-THF, 298 K):** δ_C = 165.0 (q; quaternary $\underline{C}$ [BPh$_4$]), 137.0 (s, *o*-C$_6$H$_5$ [BPh$_4$]), 132.4 (d, $\underline{C}$H(allyl), $^2J_{C\text{-}P}$ = 8.8 Hz), 131.1 (d, $\underline{C}$H(allyl), $^2J_{C\text{-}P}$ = 10.4 Hz), 129.3 (d, $\underline{C}$H(allyl), $^2J_{C\text{-}P}$ = 12.3 Hz), 125.5 (m, *m*-C$_6$H$_5$ [BPh$_4$]), 121.6 (s, *p*-C$_6$H$_5$ [BPh$_4$]), 120.2 (d, $\underline{C}$H$_2$(allyl), $^3J_{C\text{-}P}$ = 9.0 Hz), 119.6 (d, $\underline{C}$H$_2$(allyl), $^3J_{C\text{-}P}$ = 8.0 Hz), 119.5 (d, $\underline{C}$H$_2$(allyl), $^3J_{C\text{-}P}$ = 9.0 Hz), 92.0 (s, Cp*(aromatic)), 45.0 (m), 33.8 (m), 29.8-29.2 (m; overlapping P-$\underline{C}$H$_2$ signals), 22.1-21.8 (m; overlapping P-CH$_2$-$\underline{C}$H=(Fe)$\underline{C}$H$_2$ signals), 20.1-19.7 (m; overlapping P-CH$_2$-$\underline{C}$H=(Fe)$\underline{C}$H$_2$ signals), 10.3 (s, Cp*-$\underline{C}$H$_3$). **^{31}P{^{1}H} NMR (202.5 MHz, d$_8$-THF, 298 K):** δ_P = + 83.0 ($^2J_{P\text{-}P}$ = 59.6 Hz), - 8.3 ($^2J_{P\text{-}P}$ = 59.6 Hz). **^{11}B{^{1}H} NMR (160.5 MHz, C$_6$D$_6$, 298 K):** δ_B = - 8.3 (s; [BPh$_4$]).

[Cp*Fe^{II}(d*n*ppe)H] (**8**; C$_{24}$H$_{48}$FeP$_2$, M$_W$ = 454 g/mol): In the glovebox, **4** (20 mg, 0.04 mmol) was dissolved in approximately 4 mL of THF in a 20 mL scintillation vial equipped with a stir bar. K[HBEt$_3$] (1 equiv., 1.0 M in THF) was added and the reaction allowed to stir for 1 hour. The solvent was removed *in vacuo* and the yellow solid was extracted into pentane, filtered through Celite®, and the solvent removed *in-vacuo* giving **8** (13 mg, 71%). **^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K):** δ_H = 1.96 (s, 15H; Cp*-C$\underline{H}_3$ signals), 1.86 (m, 2H; C$\underline{H}_2$), 1.65-1.47 (12H; multiple overlapping C$\underline{H}_2$ resonances), 1.22 (6H; multiple overlapping C$\underline{H}_2$ resonances), 1.13 (m, 2H; C$\underline{H}_2$), 1.03 (t, 6H; $\underline{C}$H$_3$ on P-ligand), 1.00 (t, 6H; $\underline{C}$H$_3$ on P-ligand), -17.9 (t, 1H; [Fe]-$\underline{H}$ ($^2J_{H\text{-}P}$ = 70.2 Hz)). **^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$, 298 K):** δ_C = 83.8 (s; Cp*(aromatic)), 35.8 (m), 35.7 (m), 27.3 (m), 19.1 (br. s), 18.7 (br. s), 16.7 (app. t; $\underline{C}$H$_3$ on P-ligand), 16.5 (app. t; $\underline{C}$H$_3$ on P-ligand), 12.9 (s; Cp*-$\underline{C}$H$_3$). **^{31}P{^{1}H} NMR (202.5 MHz, C$_6$D$_6$, 298 K):** δ_P = + 98.1. **FT-IR (ATR):** 1865 cm^{-1} (ν[Fe—H]).

[Cp*Fe^{II}(P$_2$B$^{Cy}_4$)(H)]; (**9**, C$_{72}$H$_{132}$B$_4$FeP$_2$, M$_W$ = 1159 g/mol): In the glovebox, **5** (18 mg, 0.015 mmol) was dissolved in approximately 4 mL of THF in a 20 mL scintillation vial equipped with a stir bar. K[HBEt$_3$] (1 equiv., 1.0 M in THF) was added and the reaction allowed to stir for 1 hour. The solvent was removed *in vacuo* and the orange oil was extracted into pentane and filtered through Celite®. The pentane was removed *in vacuo* giving the titled compound as a yellow oil (11 mg, 63%). **^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K):** δ_H = 2.08 (s, 15H; Cp*-C$\underline{H}_3$ signals), 1.84-1.26 (multiple overlapping C(sp^3)–H resonances). -17.7 (t, 1H; [Fe]-$\underline{H}$ ($^2J_{H\text{-}P}$ =

70.2 Hz)). **^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K):** δ_C = 83.9 (s; Cp*(aromatic)), 37.6 (m), 36.3 (m), 34.5 (m), 33.3 (m), 31.6 (m), 28.1-27.6 (multiple overlapping C(sp^3)-H resonances), 22.7 (m), 20.5 (m), 20.2 (m), 14.3 (m), 13.1 (s; Cp*-$\underline{C}H_3$). **^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 298 K):** δ_P = + 97.3. **^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6, 298 K):** δ_B = + 84 ($\Delta_{1/2}$ = 920 Hz). **FT-IR (ATR):** 1834 cm^{-1} (ν[Fe]-H).

[Cp*Fe^{II}((κ^3-CPP^{BCy_2})]; (**10**, $C_{60}H_{109}B_3FeP_2$, M_W = 981 g/mol): In the glovebox, **6** (10 mg, 0.022 mmol) was weighed into a 20 mL scintillation vial equipped with a stir bar. C_6D_6 was added, along with $HBCy_2$ (12 mg, 0.066 mmol, 3 equivs.). The reaction was stirred for 30 min and ^{1}H NMR spectroscopic data was acquired, which showed complete disappearance of the allylic proton signals. This complex was produced in >99% conversion by ^{31}P{^{1}H} NMR spectroscopy and used immediately for the synthesis of [**10**]$^{3-}$. **^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 298 K):** δ_P = 117.3 ($^2J_{P-P}$ = 28.3 Hz), 98.6 ($^2J_{P-P}$ = 28.3 Hz). **^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6, 298 K):** δ_B = 83.4 ($\Delta_{1/2}$ = 1031 Hz).

[Cp*Fe^{II}(CPP^{BCy_2nBu_3})]$^{3-}$; ([**10**]$^{3-}$, [$C_{72}H_{136}B_3FeP_2$]$^{3-}$): Following the synthesis of **10** (*vide supra*), the reaction solvent was removed *in-vacuo*. To the oily product was added 500 µL THF followed by *n*-BuLi (3 equivs., 1.6 M in hexane). By ^{31}P{^{1}H} NMR spectroscopy, [**10**]$^{3-}$ was produced in >99% conversion. **^{31}P{^{1}H} NMR (202.5 MHz, THF, 298 K):** δ_P = 118.2 ($^2J_{P-P}$ = 31.8 Hz), 93.7 ($^2J_{P-P}$ = 31.8 Hz). **^{11}B{^{1}H} NMR (160.5 MHz, THF, 298 K):** δ_B = - 16.4 (multiple overlapping [$Cy_2B(Pr)(^nBu)$]$^-$ signals).

[Cp*Fe^{II}(d*n*ppe)CH$_3$]; (**11**, $C_{25}H_{50}FeP_2$, M_W = 469 g/mol): In the glovebox, **4** (20 mg, 0.04 mmol) was dissolved in 2 mL of THF. With stirring, CH_3Li (1 equiv., 1.6 M in Et_2O) was added. The reaction mixture was stirred for 1 hour during which time the solution became gradually orange. The solvent was removed *in vacuo* and the orange solid extracted with 3 x 2 mL of pentane and filtered through Celite®. The titled compound was recrystallized from a saturated pentane solution at -35 °C overnight (16 mg, 85%). **^{1}H NMR (500 MHz, C_6D_6, 298 K):** δ_H = 1.89 (m; 2H; $C\underline{H}_2$), 1.74 (s, 15H; Cp*-$C\underline{H}_3$), 1.52 (m; 6H; multiple overlapping $C\underline{H}_2$ signals), 1.36 (m; 6H; multiple overlapping $C\underline{H}_2$ signals), 1.22 (m; 6H; multiple overlapping $C\underline{H}_2$ signals), 0.97 (m; 12H; multiple overlapping $C\underline{H}_3$ signals), -0.94 (t; 3H; Fe-$C\underline{H}_3$ ($^3J_{H-P}$ = 6.7 Hz)). **^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K):** δ_C = 84.2 (s; Cp*(aromatic)), 33.5 (m; $\underline{C}H_2$), 29.8 (m; $\underline{C}H_2$), 25.1 (m; $\underline{C}H_2$), 19.0 (m; $\underline{C}H_2$), 18.7 (m; $\underline{C}H_2$), 16.7 (m; overlapping $\underline{C}H_3$ signals), 11.5 (s; $\underline{C}H_3$-Cp*), - 11.3 (t, [Fe]-$\underline{C}H_3$, $^2J_{C-P}$ = 24.1 Hz). **^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 298 K):** δ_P = + 93.4.

Reactions of 5 with *n*-BuLi or CH_3Li: To **5** (10 mg, 0.008 mmol) was added 500 µL THF followed by *n*-BuLi or CH_3Li (1-10 equivs.). By ^{31}P{^{1}H} NMR spectroscopy, the respective *n*-Bu or CH_3- analogue of [**10**]$^{3-}$ was produced in >99% conversion. <u>For *n*-BuLi:</u> **^{31}P{^{1}H} NMR (202.5 MHz, THF, 298 K):** δ_P = 118.2 ($^2J_{P-P}$ = 31.8 Hz), 93.7 ($^2J_{P-P}$ = 31.8 Hz). **^{11}B{^{1}H} NMR (160.5 MHz, THF, 298 K):** δ_B = - 16.4 (multiple overlapping [$Cy_2B(Pr)(^nBu)$]$^-$ signals). <u>For CH_3Li:</u> **^{31}P{^{1}H} NMR (202.5 MHz, THF, 298 K):** δ_P = 118.4 ($^2J_{P-P}$ = 32.1 Hz), 94.6 ($^2J_{P-P}$ = 32.1 Hz). **^{11}B{^{1}H} NMR (160.5 MHz, THF, 298 K):** δ_B = - 16.4 (multiple overlapping [$Cy_2B(Pr)(CH_3)$]$^-$ signals).

Reaction of 11 with $BCy_2{}^nOct$. In the glovebox, **11** (10 mg, 0.21 mmol) and $BCy_2{}^nOct$ (6 mg, 0.21 mmol) were weighed into a 20 mL scintillation vial; 500 µL Et_2O was added, and the reaction mixture was transferred to a J. Young NMR tube and monitored by ^{31}P{^{1}H} NMR spectroscopy – no reaction was observed over a period of 24 h at 298 K nor after 24 h at 333 K.

ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{11}B NMR spectra for all complexes. CCDC **2239598-2239602** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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