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## CO Reduction to $\text{CH}_3\text{OSiMe}_3$ : Electrophile-Promoted Hydride Migration at a Single Fe Site

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### Abstract

One of the major challenges associated with developing molecular Fischer-Tropsch catalysts is the design of systems that promote the formation of C-H bonds from  $\text{H}_2$  and CO while also facilitating the release of the resulting CO-derived organic products. To this end, we describe the synthesis of reduced iron-hydride/carbonyl complexes that enable an electrophile-promoted hydride migration process, resulting in the reduction of coordinated CO to a siloxymethyl ( $\text{L}_n\text{Fe}-\text{CH}_2\text{OSiMe}_3$ ) group. Intramolecular hydride-to-CO migrations are extremely rare, and to our knowledge the system described herein is the first example where such a process can be accessed from a thermally stable  $\text{M}(\text{CO})(\text{H})$  complex. Further addition of  $\text{H}_2$  to  $\text{L}_n\text{Fe}-\text{CH}_2\text{OSiMe}_3$  releases  $\text{CH}_3\text{OSiMe}_3$ , demonstrating net four-electron reduction of CO to  $\text{CH}_3\text{OSiMe}_3$  at a single Fe site.

### Graphical abstract



In the industrial Fischer-Tropsch (FT) process, pressurized mixtures of CO and  $\text{H}_2$  are heated over a heterogeneous transition metal catalyst, most commonly Fe or Co, to yield a mixture of liquid organic products.<sup>1</sup> Interestingly, it was recently demonstrated that nitrogenase enzymes also facilitate some degree of FT reactivity, with H-atom equivalents provided as protons and electrons.<sup>2</sup> Well-defined model complexes can be used to explore viable pathways for mechanistically relevant CO reductions under controlled reaction conditions. In particular, Fe-mediated model systems are of interest owing to the role of iron in both industrial and (presumably) biological FT systems.

One of the major challenges associated with molecular CO reduction reactivity is early stage C-H bond formation from  $\text{H}_2$ .<sup>3</sup> Migratory insertion of CO into M-H bonds is generally presumed to be thermodynamically unfavorable.<sup>4,5</sup> For early transition metal systems, C-H bond formation is concomitant with strong M-O bond formation.<sup>6</sup> Mid-to-late transition

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metal systems are thought to lack this driving force, and C-H bond forming steps have instead been established using strong hydride donors that are not generated from H<sub>2</sub>.<sup>7,8</sup> Recently, it has been demonstrated that weaker, H<sub>2</sub>-derived hydride sources can be used to facilitate C-H bond formation from H<sub>2</sub> in Lewis acid-activated Re-CO complexes.<sup>9,10</sup> C-H bond formation in this latter case is driven by the formation of strong B-O bonds.

Our group has previously studied reduced Fe-CO complexes that react with silyl electrophiles at oxygen to generate carbyne products (e.g., Fe-CO<sup>-</sup> + SiMe<sub>3</sub><sup>+</sup> → Fe≡C-OSiMe<sub>3</sub>).<sup>11</sup> We wondered whether related O-functionalization at reduced Fe(CO)(H)<sub>n</sub> species might promote concomitant hydride migration to carbon. Herein, we describe the synthesis of a series of reduced Fe(CO)(H)<sub>n</sub> complexes. One of these complexes serves as a key intermediate from which functionalization of the coordinated CO promotes the migration of two hydride equivalents to carbon.

In this study we employ the P<sub>3</sub><sup>B</sup> Fe-system<sup>12</sup> (P<sub>3</sub><sup>B</sup> = B(*o*-Pr<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>)<sup>13</sup>, for which its monocarbonyl complex, P<sub>3</sub><sup>B</sup> Fe-CO, was previously shown to activate H<sub>2</sub> to generate P<sub>3</sub><sup>B</sup> (μ-H)Fe(H)(CO), **1**.<sup>14</sup> Two-electron reduction of **1** can be readily accomplished with excess potassium metal in THF, leading to a distinct color change from yellow to dark red-brown. NMR spectroscopy reveals that a new diamagnetic species, **2**, is cleanly generated, with hydridic resonances observed in the <sup>1</sup>H NMR spectrum at -19.12 ppm (B-*H*-Fe, br, 1H) and -20.76 ppm (Fe-*H*, t, <sup>2</sup>J<sub>HP</sub> = 65 Hz, 1H). The <sup>31</sup>P NMR spectrum has two resonances at 102.3 and -1.5 ppm (2:1 integration), indicating that one of the phosphine arms has dechelated from the Fe center, while the thin film IR spectrum of **2** indicates a highly activated CO ligand with a stretch at 1575 cm<sup>-1</sup>. Structural characterization of dianionic **2** confirms that the product has two coordinated phosphine ligands and the CO ligand in an approximate trigonal geometry (average Σ(trigonal plane) = 359.4),<sup>15</sup> with the axial sites presumably occupied by the hydride and borohydride ligands that are not crystallographically observed (Figure 1). Among Fe-CO complexes, **2** has an unusually short Fe-C distance (1.70 Å; average) with corresponding elongation of the C-O bond (1.24 Å; average), consistent with significant contribution of carbyne character in this species. Note that **2** is ion-paired with the K<sup>+</sup> cations (see SI for details), contributing to elongation of the C-O bond. For relevant comparison, P<sub>3</sub><sup>B</sup> Fe-CO (ν(CO) = 1857 cm<sup>-1</sup>) has an Fe-C distance of 1.752(3) Å and a C-O distance of 1.167(3) Å,<sup>12</sup> while the carbyne complex P<sub>3</sub><sup>Si</sup>Fe≡C-OSiMe<sub>3</sub> has an Fe-C distance of 1.671(2) Å and a C-O distance of 1.278(3) Å.<sup>11a</sup>

A number of structurally unusual reduced hydride species are readily available from **2**. For example, complex **2** can be protonated selectively by water *via* addition of wet N<sub>2</sub> (produced by bubbling N<sub>2</sub> through water) yielding the anionic trihydride complex [P<sub>3</sub><sup>B</sup> (μ-H)Fe(H)<sub>2</sub>(CO)][K(THF)<sub>n</sub>], **3**. NMR spectroscopy reveals inequivalent <sup>31</sup>P NMR resonances at 106.7 and -9.6 ppm (2:1 integration) and three hydridic resonances in the <sup>1</sup>H NMR spectrum at -8.40 ppm (Fe-*H*, td, <sup>2</sup>J<sub>HP</sub> = 66 Hz, <sup>2</sup>J<sub>HH</sub> = 16 Hz, 1H), -14.69 ppm (B-*H*-Fe, br, 1H), and -20.53 ppm (Fe-*H*, t, <sup>2</sup>J<sub>HP</sub> = 48 Hz, 1H). An IR stretch is observed for Fe-ligated CO at 1787 cm<sup>-1</sup>. The coordinated phosphine ligands are located *trans* to one another in the solid state, with one of the terminal hydride ligands *trans* to the terminal CO (Figure 1).<sup>16</sup>

The trihydride complex **3** is unstable to the loss of H<sub>2</sub> in solution, with clean, irreversible conversion to the anionic and diamagnetic monohydride complex [P<sub>3</sub><sup>B</sup>Fe(H)(CO)] [K(THF)<sub>n</sub>], **4**, observed over 2 d ( $\nu(\text{CO}) = 1754 \text{ cm}^{-1}$ ; see SI for NMR details). In the solid state, **4** adopts an approximately octahedral geometry, with the hydride ligand located in the difference map as a terminal Fe-H (Figure 1). Oxidation of **4** using [Cp<sub>2</sub>Co][PF<sub>6</sub>] generates the doublet product (P<sub>3</sub><sup>B</sup>-H)Fe(CO), **5**, featuring a broad, axial EPR signal at 77 K. The IR spectrum of **5** shows an intense CO stretch at 1862 cm<sup>-1</sup> and a broad hydride stretch at 2588 cm<sup>-1</sup>, consistent with a boron-coordinated hydride, as revealed in its solid-state structure (Figure 1).

With these complexes in hand, we next canvassed their reactivity with electrophiles. Accordingly, clean *in situ* generation of a THF solution of dianion **2** followed by treatment with at least two equivalents of Me<sub>3</sub>SiOTf at low temperature generates a new paramagnetic species, P<sub>3</sub><sup>B</sup>Fe-CH<sub>2</sub>OSiMe<sub>3</sub>, **6**, as the major product (Scheme 2).<sup>17</sup> <sup>57</sup>Fe Mössbauer spectroscopy indicates that **6** is generated in ~80% chemical yield and its parameters ( $\delta = 0.49 \text{ mm/s}$ ;  $\Delta E_Q = 2.05 \text{ mm/s}$ ) are consistent with an  $S = 3/2$  P<sub>3</sub><sup>B</sup>Fe species.<sup>18</sup> For representative comparison, the previously reported complex P<sub>3</sub><sup>B</sup>Fe-Me has the following parameters:  $\delta = 0.50 \text{ mm/s}$ ,  $\Delta E_Q = 1.84 \text{ mm/s}$ .<sup>19</sup> Structure determination of **6** by XRD analysis confirms its assignment and clearly establishes that the carbonyl ligand has been O-functionalized by the silyl electrophile, with both hydride equivalents having migrated to the carbonyl carbon; one equivalent of electrophile (Me<sub>3</sub>Si<sup>+</sup>) presumably serves as a one-electron oxidant. Despite repeated attempts, we have been unable to isolate complex **6** in analytically pure form owing to its high hydrocarbon solubility. Persistent  $S = 1/2$  Fe-containing impurities that are similarly soluble, including **5** as an oxidation side-product, are consistently present in preparative scale, worked-up reactions.<sup>20</sup>

We next surveyed conditions for the release of the CO-derived organic fragment.<sup>21</sup> For related P<sub>3</sub><sup>B</sup>Fe-Me, treatment with acid results in methane release.<sup>19</sup> For complex **6**, treatment with acid ([H(OEt)<sub>2</sub>][BAr<sup>F</sup>], [LutH][Cl] and H<sub>2</sub>O, for example) invariably results in unproductive decomposition to regenerate P<sub>3</sub><sup>B</sup>( $\mu$ -H)Fe(H)(CO), **1**, as the major product, presumably *via* acidic cleavage of the Si-O bond.<sup>22</sup> We therefore canvassed the reactivity of **6** towards hydrogen and silanes (Scheme 3).

Treatment of **6** with an atmosphere of H<sub>2</sub> at RT results in the release of CH<sub>3</sub>OSiMe<sub>3</sub> over 24 h in moderate yields (50%, average of three runs; assumes **6** present at 80% purity initially based on Mössbauer analysis; *vide supra*). Product release can also be affected by the addition of excess PhSiH<sub>3</sub> (5 equiv), with C-Si bond formation in this case and similar yields of the CO-derived product, PhSiH<sub>2</sub>CH<sub>2</sub>OSiMe<sub>3</sub> (46%, average of three runs; again assumes **6** present at 80% purity initially). The Fe-containing products of these reactions have not yet been identified; spectroscopic analysis indicates complex mixtures of P<sub>3</sub><sup>B</sup>Fe-containing products.<sup>23</sup>

To track the origin of the H equivalents delivered to the terminal organic product, CH<sub>3</sub>OSiMe<sub>3</sub>, upon H<sub>2</sub> addition we undertook a series of labeling studies. These experiments are particularly valuable given our inability to isolate **6** in analytically pure form.

Use of the dianionic complex **2** as a precursor to the alkyl complex **6** resulted in full H incorporation into the free organic product, CH<sub>3</sub>OSiMe<sub>3</sub> as determined by <sup>1</sup>H NMR spectroscopy (Scheme 4A). Likewise, using the <sup>2</sup>H-labeled analog **2-D<sub>2</sub>** to generate **6-D<sub>2</sub>**, followed by treatment with D<sub>2</sub>, resulted in (nearly) complete incorporation of deuterium in the released product CD<sub>3</sub>OSiMe<sub>3</sub> (Scheme 4B; ~5% CD<sub>2</sub>HOSiMe<sub>3</sub> was also detected). These results suggest that the three H equivalents delivered to the CO C-atom are derived from the hydride ligands and/or the added H<sub>2</sub> gas; scrambling into the alkyl phosphine substituents or incorporation of H-equivalents from solvent, is therefore not kinetically relevant. Interestingly, when **6-D<sub>2</sub>** was treated with an atmosphere of H<sub>2</sub>, the partially-deuterated organic products CDH<sub>2</sub>OSiMe<sub>3</sub> and CD<sub>2</sub>HOSiMe<sub>3</sub> were obtained in a 5:1 ratio (Scheme 4C). Similarly, when **6** was treated with D<sub>2</sub> a mixture of products was observed, with CD<sub>2</sub>HOSiMe<sub>3</sub> and CDH<sub>2</sub>OSiMe<sub>3</sub> obtained in a 3:1 ratio, and ~5% CH<sub>3</sub>OSiMe<sub>3</sub> also detected (Scheme 4D). These results are suggestive of a facile exchange process between the alkyl C-H bonds and the added H<sub>2</sub> or D<sub>2</sub> prior to product release. One scenario by which such an exchange could occur involves reversible alpha elimination from **6-D<sub>2</sub>** to generate a carbene-deuteride intermediate (i.e., P<sub>3</sub><sup>B</sup>Fe-CD<sub>2</sub>OSiMe<sub>3</sub> ⇌ P<sub>3</sub><sup>B</sup>(μ-D)Fe=C(D)(OSiMe<sub>3</sub>)) that then reacts with H<sub>2</sub>.<sup>24</sup>

To probe the possibility of intermolecular C-H bond forming steps we undertook a crossover experiment wherein the dianionic complex **2** was synthesized as a 50:50 mixture of its [P<sub>3</sub><sup>B</sup>(μ-D)Fe(D)(<sup>13</sup>CO)]<sup>2-</sup> and [P<sub>3</sub><sup>B</sup>(μ-H)Fe(H)(<sup>12</sup>CO)]<sup>2-</sup> variants. Standard functionalization of this labeled mixture to generate the corresponding alkyl complexes **6**, and product release *via* the addition of H<sub>2</sub>, showed deuterium incorporation exclusively in the <sup>13</sup>C-labeled complex (Scheme 4E). This result is fully consistent with an intramolecular pathway for the initial C-H bond-forming steps to generate the alkyl complex **6**, and also the subsequent C-H bond formation from H<sub>2</sub> to promote the release of the organic product.

To conclude, using a mononuclear iron system we have explored a silyl electrophile promoted hydride-to-CO migration process that allows for the net 4-electron reduction of CO, releasing CH<sub>3</sub>OSiMe<sub>3</sub> upon hydrogenolysis. Use of the bifunctional tris(phosphine)borane ligand, P<sub>3</sub><sup>B</sup>, is key to the hydride migration step as it helps to stabilize the unusual bis(phosphine)-dihydride-carbonyl precursor, **2**, *via* a bridging interaction of one of the hydride ligands with the borane. Isotopic labeling studies establish that the C-H bond forming steps are unimolecular. Intramolecular hydride-to-CO migrations are extremely rare; to our knowledge the iron system described herein is the first thermally stable M(CO)(H) complex to exhibit such reactivity. Future studies will be aimed at expanding the scope of this reactivity, for example by replacing the silyl electrophile Me<sub>3</sub>Si<sup>+</sup> with H<sup>+</sup> as a route to CH<sub>3</sub>OH generation.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

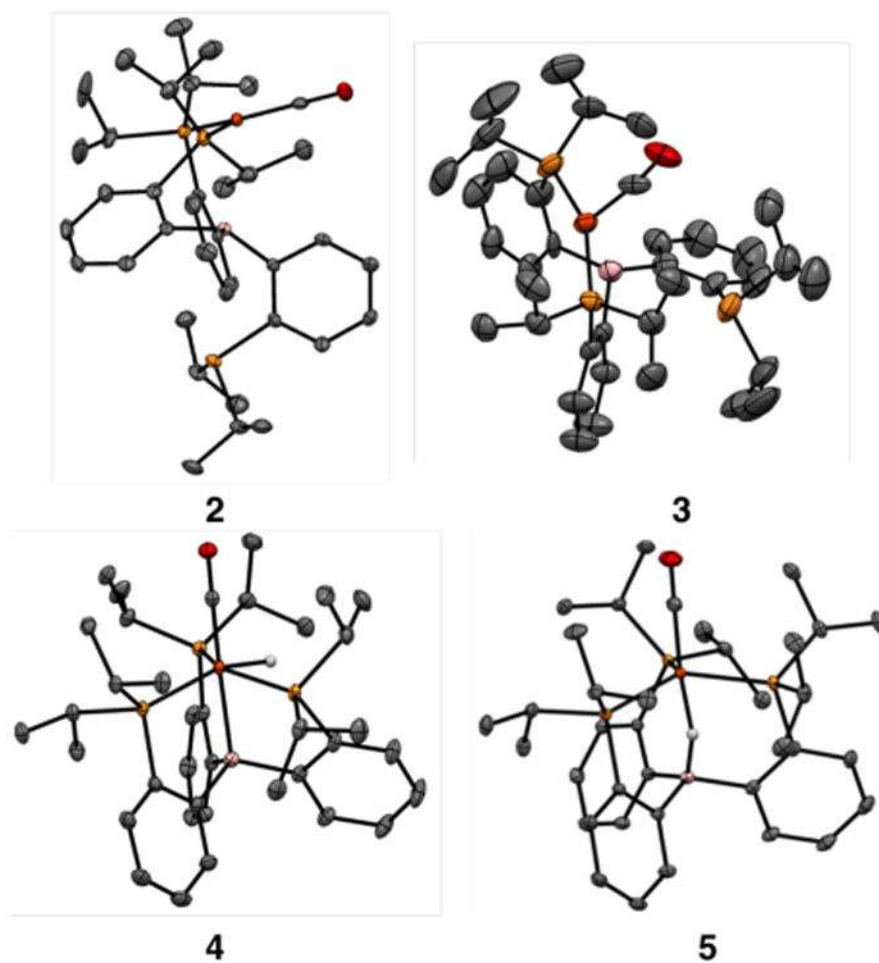
## Acknowledgments

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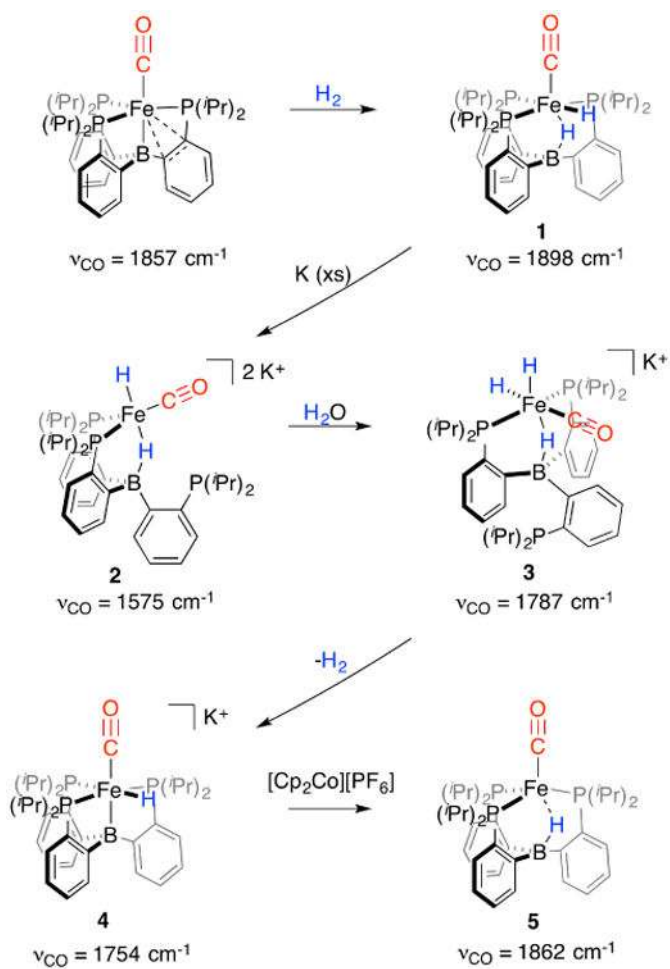
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15. The dianionic dihydride complex **2** crystallizes as a cluster with four crystallographically distinct iron centers and eight associated potassium counteranions (See SI).
16. Analysis of the detailed bond metrics of this complex is complicated by the presence of a constitutional disorder, with the trihydride complex **3** cocrystallizing with a ~10% impurity of the monoanionic hydride complex **4**.
17. When one equivalent of silyl electrophile is used a new diamagnetic product is observed as the major species. This new complex does not appear to be an intermediate in the formation of **6** (see SI).
18. For a discussion of the trend observed relating spin-state and isomer shift in  $\text{P}_3\text{B}$ -supported Fe complexes see: Del Castillo TJ, Thompson NB, Peters JC. *J Am Chem Soc.* 2016; 138:5341. [PubMed: 27026402]
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20. The product mixture generated in the conversion of **2** to **6** is highly soluble in nonpolar solvents (e.g. alkanes, hexamethyldisiloxane, tetramethylsilane), even at low temperature. While the mixtures show some insolubility in polar solvents (e.g. MeCN), reaction impurities and **6** exhibit similar solubility properties, precluding further purification of **6**.

21. Note: Owing to our inability to obtain analytically pure **6**, reactions were by necessity carried-out in the presence of remaining iron impurities.
22. Treatment of **6** with MeOTf or H-atom sources (e.g. TEMPO-H, Bu<sub>3</sub>Sn-H) similarly leads to unproductive decomposition of **6**. Me<sub>3</sub>SiOTf did not react with **6** under conditions we have explored.
23. The addition of PMe<sub>3</sub> to these reactions leads simpler product mixtures, but the major species has not yet been identified (see SI).
24. A normal KIE is observed for the reaction of **6** with H<sub>2</sub>/D<sub>2</sub>.

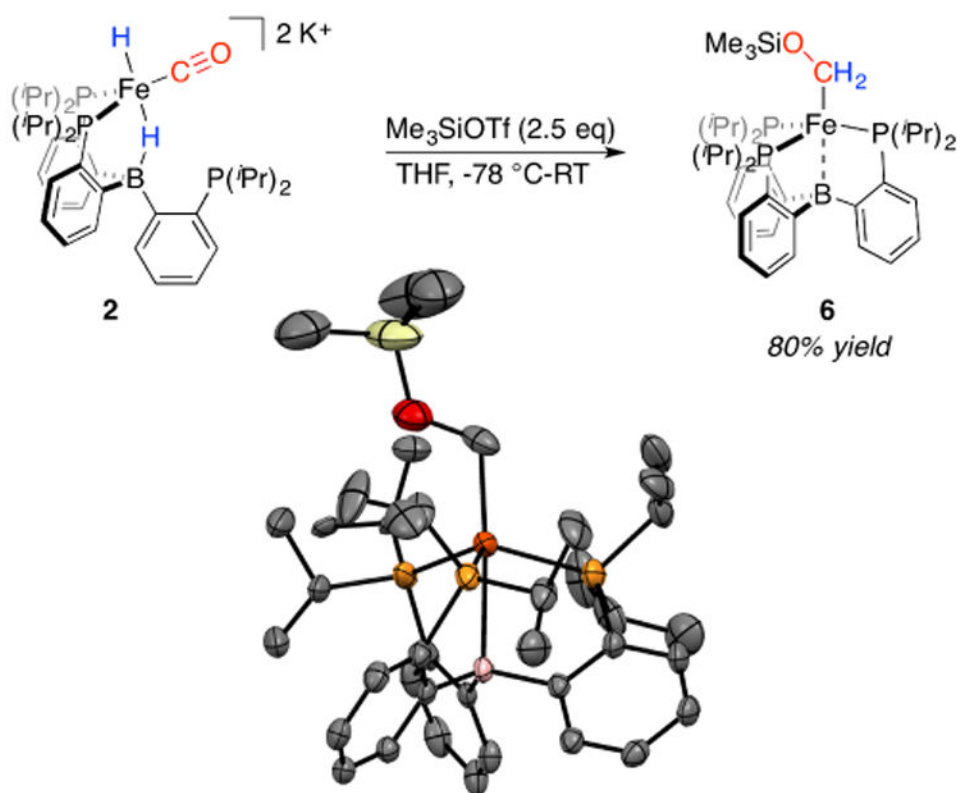


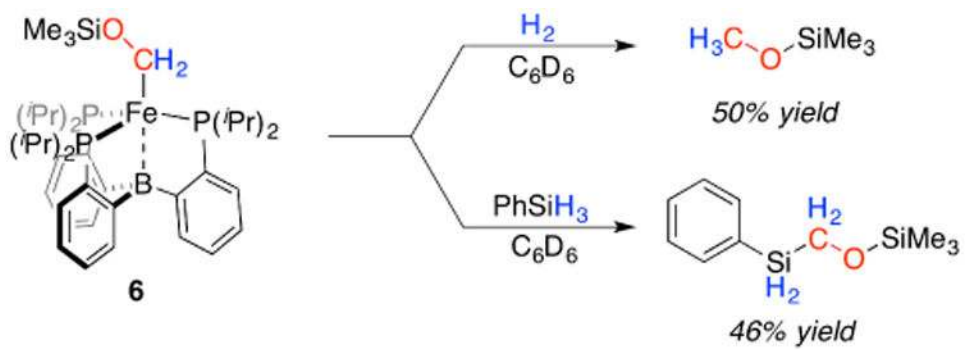
**Figure 1.** Crystal structures of  $\text{Fe}(\text{CO})(\text{H})_n$  complexes **2-5**. Displacement ellipsoids shown at 50% probability; hydrogen atoms (except for hydride ligands found in the difference map), solvent molecules, counter cations, and disorder of **3** (see SI) omitted for clarity.



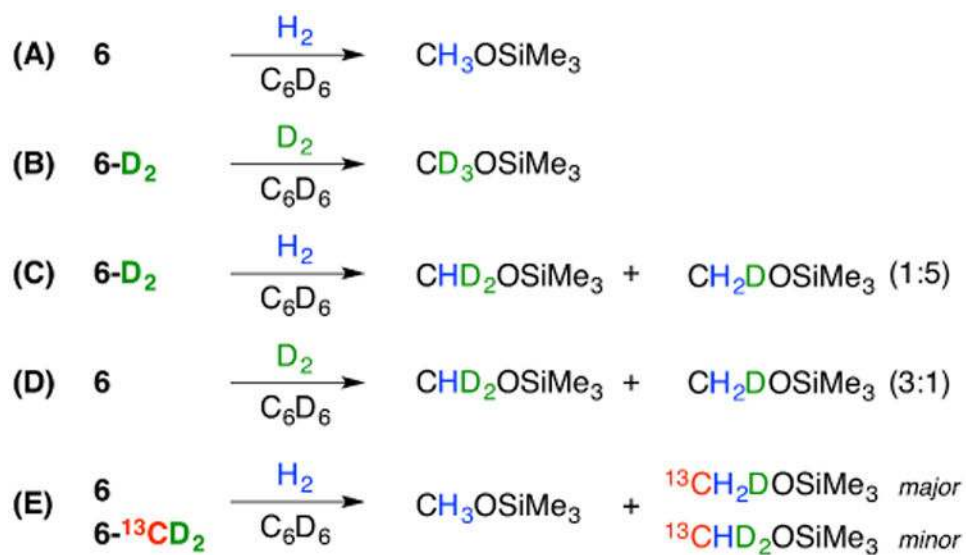
Scheme 1. Synthesis Of  $\text{P}_3\text{BFe}(\text{Co})(\text{H})_N$  Complexes



Scheme 2. Reaction of **2** with  $\text{Me}_3\text{SiOTf}$



Scheme 3. E-H promoted product release



Scheme 4. Summary of Labeling Experiments