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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 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 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 H_2 are heated over a heterogeneous transition metal catalyst, most commonly Fe or Co, to yield a mixture of liquid organic products.¹ Interestingly, it was recently demonstrated that nitrogenase enzymes also facilitate some degree of FT reactivity, with H-atom equivalents provided as protons and electrons.² 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 H_2 .³ Migratory insertion of CO into M-H bonds is generally presumed to be thermodynamically unfavorable.^{4,5} For early transition metal systems, C-H bond formation is concomitant with strong M-O bond formation.⁶ 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 H₂.^{7,8} Recently, it has been demonstrated that weaker, H₂-derived hydride sources can be used to facilitate C-H bond formation from H₂ in Lewis acid-activated Re-CO complexes.^{9,10} 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⁻ + SiMe₃⁺ → Fe≡C-OSiMe₃).¹¹ We wondered whether related O-functionalization at reduced Fe(CO)(H)_n species might promote concomitant hydride migration to carbon. Herein, we describe the synthesis of a series of reduced Fe(CO)(H)_n 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 P₃^B Fe-system¹² (P₃^B = B(*o*-Pr₂PC₆H₄)₃)¹³, for which its monocarbonyl complex, P₃^B Fe-CO, was previously shown to activate H₂ to generate P₃^B (μ-H)Fe(H)(CO), **1**.¹⁴ 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 ¹H NMR spectrum at -19.12 ppm (B-*H*-Fe, br, 1H) and -20.76 ppm (Fe-*H*, t, ²J_{HP} = 65 Hz, 1H). The ³¹P 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⁻¹. 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),¹⁵ 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⁺ cations (see SI for details), contributing to elongation of the C-O bond. For relevant comparison, P₃^B Fe-CO (ν(CO) = 1857 cm⁻¹) has an Fe-C distance of 1.752(3) Å and a C-O distance of 1.167(3) Å,¹² while the carbyne complex P₃^{Si}Fe≡C-OSiMe₃ has an Fe-C distance of 1.671(2) Å and a C-O distance of 1.278(3) Å.^{11a}

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 N₂ (produced by bubbling N₂ through water) yielding the anionic trihydride complex [P₃^B (μ-H)Fe(H)₂(CO)][K(THF)_n], **3**. NMR spectroscopy reveals inequivalent ³¹P NMR resonances at 106.7 and -9.6 ppm (2:1 integration) and three hydridic resonances in the ¹H NMR spectrum at -8.40 ppm (Fe-*H*, td, ²J_{HP} = 66 Hz, ²J_{HH} = 16 Hz, 1H), -14.69 ppm (B-*H*-Fe, br, 1H), and -20.53 ppm (Fe-*H*, t, ²J_{HP} = 48 Hz, 1H). An IR stretch is observed for Fe-ligated CO at 1787 cm⁻¹. 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).¹⁶

The trihydride complex **3** is unstable to the loss of H₂ in solution, with clean, irreversible conversion to the anionic and diamagnetic monohydride complex [P₃^BFe(H)(CO)] [K(THF)_n], **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 [Cp₂Co][PF₆] generates the doublet product (P₃^B-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⁻¹ and a broad hydride stretch at 2588 cm⁻¹, 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 Me₃SiOTf at low temperature generates a new paramagnetic species, P₃^BFe-CH₂OSiMe₃, **6**, as the major product (Scheme 2).¹⁷ ⁵⁷Fe Mössbauer spectroscopy indicates that **6** is generated in ~80% chemical yield and its parameters ($\delta = 0.49 \text{ mm/s}$; $E_Q = 2.05 \text{ mm/s}$) are consistent with an $S = 3/2$ P₃^BFe species.¹⁸ For representative comparison, the previously reported complex P₃^BFe-Me has the following parameters: $\delta = 0.50 \text{ mm/s}$, $E_Q = 1.84 \text{ mm/s}$.¹⁹ 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 (Me₃Si⁺) 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.²⁰

We next surveyed conditions for the release of the CO-derived organic fragment.²¹ For related P₃^BFe-Me, treatment with acid results in methane release.¹⁹ For complex **6**, treatment with acid ([H(OEt₂)₂][BAr^F], [LutH][Cl] and H₂O, for example) invariably results in unproductive decomposition to regenerate P₃^B(μ -H)Fe(H)(CO), **1**, as the major product, presumably *via* acidic cleavage of the Si-O bond.²² We therefore canvassed the reactivity of **6** towards hydrogen and silanes (Scheme 3).

Treatment of **6** with an atmosphere of H₂ at RT results in the release of CH₃OSiMe₃ 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 PhSiH₃ (5 equiv), with C-Si bond formation in this case and similar yields of the CO-derived product, PhSiH₂CH₂OSiMe₃ (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 P₃^BFe-containing products.²³

To track the origin of the H equivalents delivered to the terminal organic product, CH₃OSiMe₃, upon H₂ 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, CH₃OSiMe₃ as determined by ¹H NMR spectroscopy (Scheme 4A). Likewise, using the ²H-labeled analog **2-D₂** to generate **6-D₂**, followed by treatment with D₂, resulted in (nearly) complete incorporation of deuterium in the released product CD₃OSiMe₃ (Scheme 4B; ~5% CD₂HOSiMe₃ 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 H₂ gas; scrambling into the alkyl phosphine substituents or incorporation of H-equivalents from solvent, is therefore not kinetically relevant. Interestingly, when **6-D₂** was treated with an atmosphere of H₂, the partially-deuterated organic products CDH₂OSiMe₃ and CD₂HOSiMe₃ were obtained in a 5:1 ratio (Scheme 4C). Similarly, when **6** was treated with D₂ a mixture of products was observed, with CD₂HOSiMe₃ and CDH₂OSiMe₃ obtained in a 3:1 ratio, and ~5% CH₃OSiMe₃ also detected (Scheme 4D). These results are suggestive of a facile exchange process between the alkyl C-H bonds and the added H₂ or D₂ prior to product release. One scenario by which such an exchange could occur involves reversible alpha elimination from **6-D₂** to generate a carbene-deuteride intermediate (i.e., P₃^BFe-CD₂OSiMe₃ ⇌ P₃^B(μ-D)Fe=C(D)(OSiMe₃)) that then reacts with H₂.²⁴

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 [P₃^B(μ-D)Fe(D)(¹³CO)]²⁻ and [P₃^B(μ-H)Fe(H)(¹²CO)]²⁻ variants. Standard functionalization of this labeled mixture to generate the corresponding alkyl complexes **6**, and product release *via* the addition of H₂, showed deuterium incorporation exclusively in the ¹³C-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 H₂ 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 CH₃OSiMe₃ upon hydrogenolysis. Use of the bifunctional tris(phosphine)borane ligand, P₃^B, 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 Me₃Si⁺ with H⁺ as a route to CH₃OH generation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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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).
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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, Bu₃Sn-H) similarly leads to unproductive decomposition of **6**. Me₃SiOTf did not react with **6** under conditions we have explored.
23. The addition of PMe₃ 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 H₂/D₂.

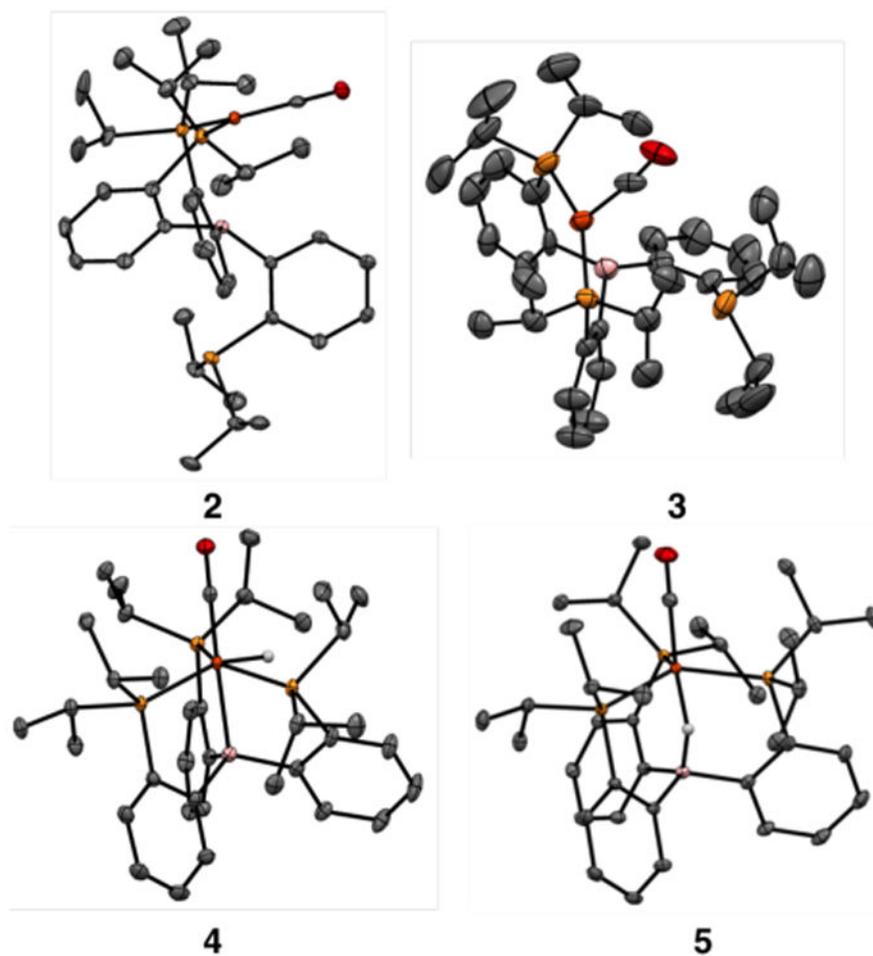
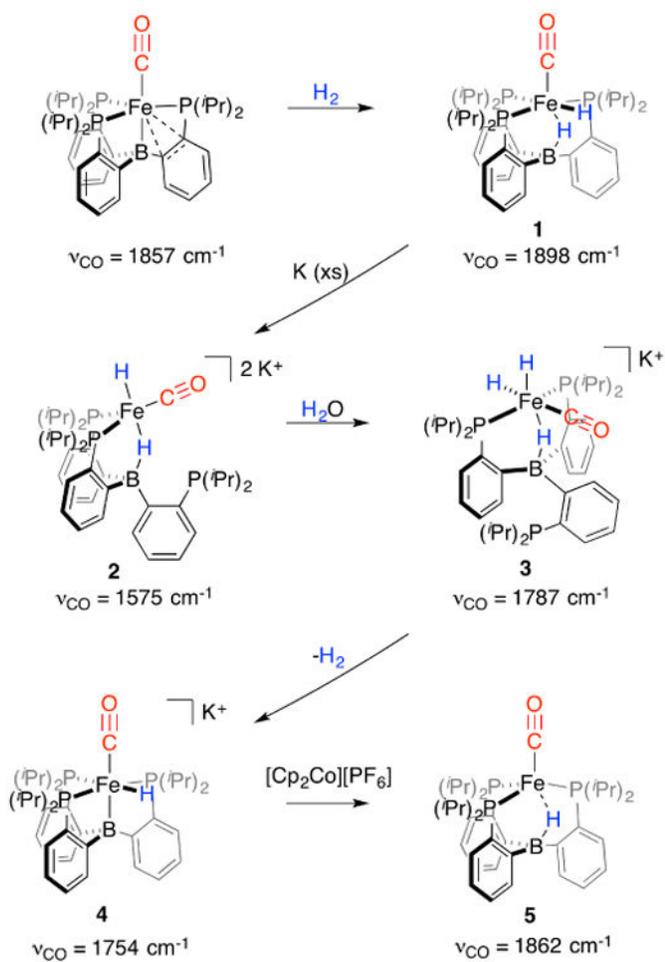
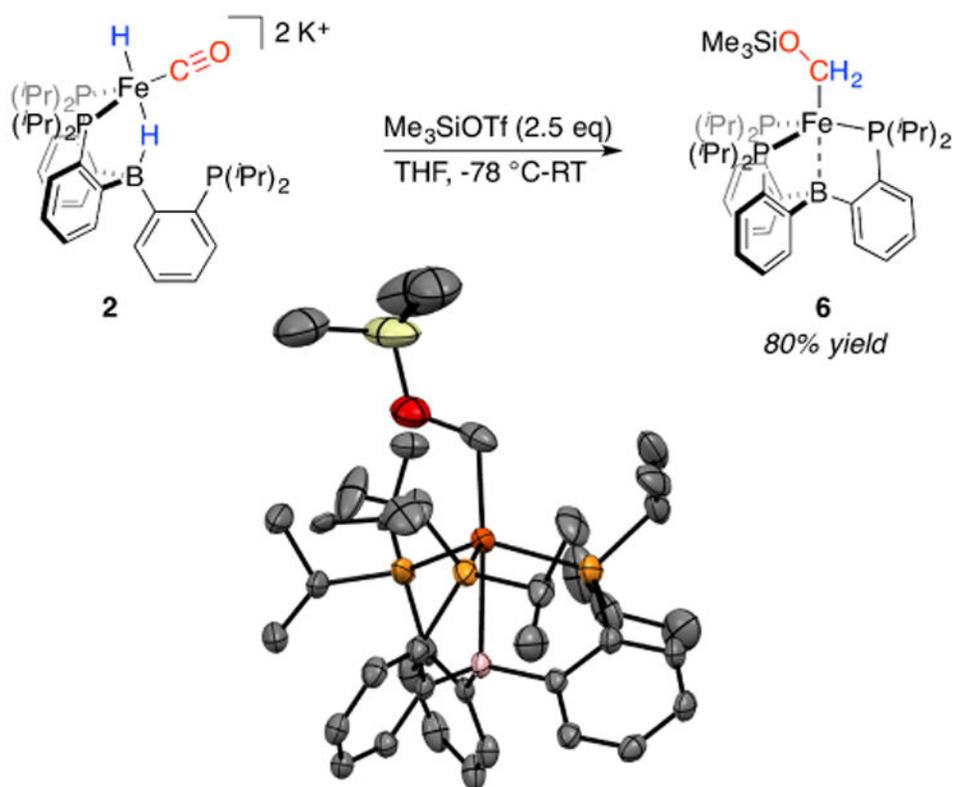
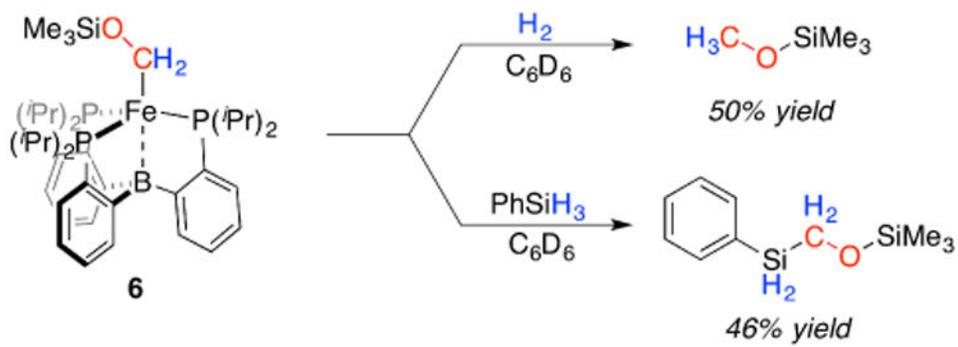


Figure 1. Crystal structures of $\text{Fe}(\text{CO})(\text{H})_n$ complexes **2-5**. Displacement ellipsoids shown at 50% probability; hydrogen atoms (except for hydride ligands found in the difference map), solvent molecules, counter cations, and disorder of **3** (see SI) omitted for clarity.

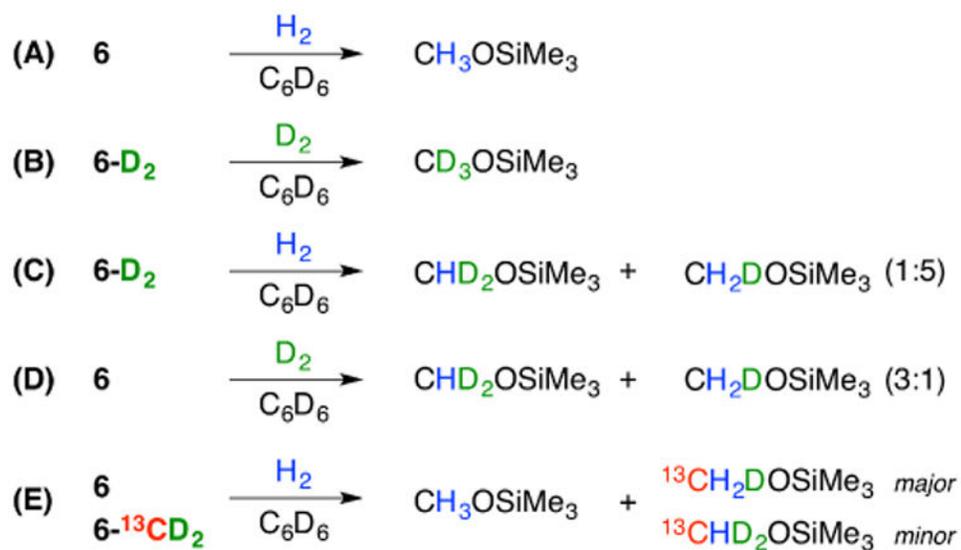


Scheme 1. Synthesis Of $P_3^BFe(Co)(H)_N$ Complexes

Scheme 2. Reaction of **2** with Me_3SiOTf



Scheme 3. E-H promoted product release



Scheme 4. Summary of Labeling Experiments