

CO Reduction to CH₃OSiMe₃: Electrophile-Promoted Hydride Migration at a Single Fe Site

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S Supporting Information

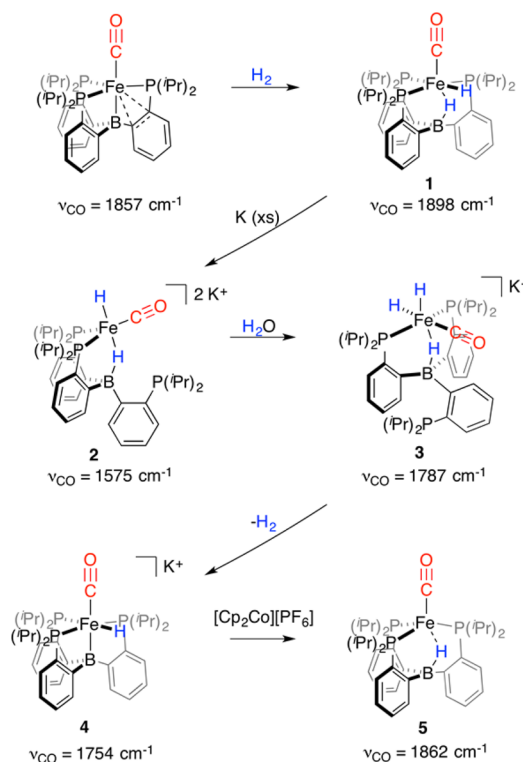
ABSTRACT: One of the major challenges associated with developing molecular Fischer–Tropsch catalysts is the design of systems that promote the formation of C–H bonds from H₂ and CO while also facilitating the release of the resulting CO-derived organic products. To this end, we describe the synthesis of reduced iron-hydride/carbonyl complexes that enable an electrophile-promoted hydride migration process, resulting in the reduction of coordinated CO to a siloxymethyl (L_nFe–CH₂OSiMe₃) 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 M(CO)(H) complex. Further addition of H₂ to L_nFe–CH₂OSiMe₃ releases CH₃OSiMe₃, demonstrating net four-electron reduction of CO to CH₃OSiMe₃ at a single Fe site.

In the industrial Fischer–Tropsch (FT) process, pressurized mixtures of CO and H₂ 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 H₂.³ 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 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-functionaliza-

Scheme 1. Synthesis of P₃^BFe(CO)(H)_n Complexes



tion 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^BFe system¹² (P₃^B = B(*o*-iPr₂PC₆H₄)₃),¹³ for which its monocarbonyl complex, P₃^BFe–CO, was previously shown to activate H₂ to generate P₃^B(μ-H)Fe(H)(CO), **1** (see Scheme 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).

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The ^{31}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^{-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 $\sum(\text{trigonal plane}) = 359.4$),¹⁵ with the axial sites presumably occupied by the hydride and borohydride ligands that are not crystallographically observed (Figure 1). Among

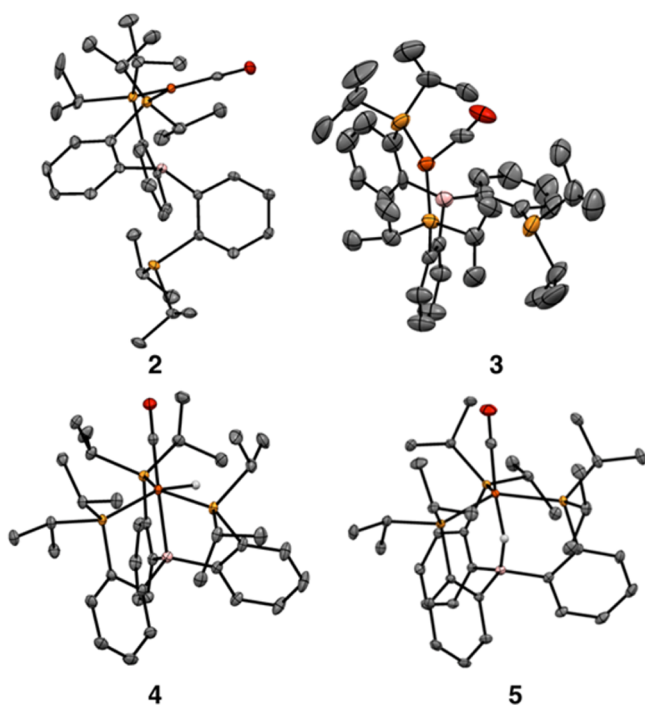


Figure 1. Crystal structures of $\text{Fe}(\text{CO})(\text{H})_n$ complexes **2–5**. Displacement ellipsoids shown at 50% probability; hydrogen atoms (except for hydride ligands found in the difference map), solvent molecules, counter cations, and disorder of **3** (see SI) omitted for clarity.

Fe–CO complexes, **2** has an unusually short Fe–C distance (1.70 \AA average) with corresponding elongation of the C–O bond (1.24 \AA average), consistent with significant contribution of carbyne character in this species. Note that **2** is ion-paired with the K^+ cations (see the Supporting Information (SI) for details), contributing to elongation of the C–O bond. For relevant comparison, $\text{P}_3^{\text{B}}\text{Fe–CO}$ ($\nu(\text{CO}) = 1857\text{ cm}^{-1}$) has an Fe–C distance of $1.752(3)\text{ \AA}$ and a C–O distance of $1.167(3)\text{ \AA}$,¹² while the carbyne complex $\text{P}_3^{\text{Si}}\text{Fe}\equiv\text{C–OSiMe}_3$ has an Fe–C distance of $1.671(2)\text{ \AA}$ and a C–O distance of $1.278(3)\text{ \AA}$.^{11a}

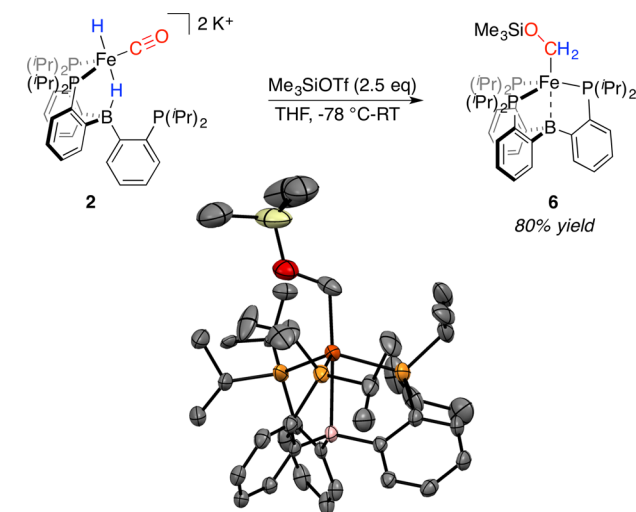
A number of structurally unusual reduced hydride species are readily available from **2**. For example, complex **2** can be protonated selectively by water via addition of wet N_2 (produced by bubbling N_2 through water), yielding the anionic trihydride complex $[\text{P}_3^{\text{B}}(\mu\text{-H})\text{Fe}(\text{H})_2(\text{CO})][\text{K}(\text{THF})_n]$, **3**. NMR spectroscopy reveals inequivalent ^{31}P 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, $^2J_{\text{HP}} = 66\text{ Hz}$, $^2J_{\text{HH}} = 16\text{ Hz}$, 1H), -14.69 ppm (B–H–Fe , br, 1H), and -20.53 ppm (Fe–H , t, $^2J_{\text{HP}} = 48\text{ Hz}$, 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 H_2 in solution, with clean, irreversible conversion to the anionic and diamagnetic monohydride complex $[\text{P}_3^{\text{B}}\text{Fe}(\text{H})(\text{CO})][\text{K}(\text{THF})_n]$, **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 $[\text{Cp}_2\text{Co}][\text{PF}_6]$ generates the doublet product $(\text{P}_3^{\text{B}}\text{-H})\text{Fe}(\text{CO})$, **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 2 equiv of Me_3SiOTf at low temperature generates a new paramagnetic species, $\text{P}_3^{\text{B}}\text{Fe–CH}_2\text{OSiMe}_3$, **6**, as the major product (Scheme 2).¹⁷ ^{57}Fe Mössbauer spectroscopy

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

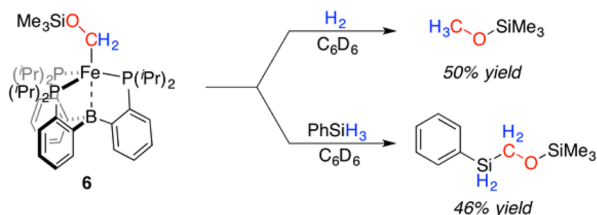


indicates that **6** is generated in $\sim 80\%$ chemical yield, and its parameters ($\delta = 0.49\text{ mm/s}$; $\Delta E_{\text{Q}} = 2.05\text{ mm/s}$) are consistent with an $S = 3/2$ $\text{P}_3^{\text{B}}\text{Fe}$ species.¹⁸ For representative comparison, the previously reported complex $\text{P}_3^{\text{B}}\text{Fe–Me}$ has the following parameters: $\delta = 0.50\text{ mm/s}$, $\Delta E_{\text{Q}} = 1.84\text{ mm/s}$.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 (Me_3Si^+) 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 $\text{P}_3^{\text{B}}\text{Fe–Me}$, treatment with acid results in methane release.²⁰ For complex **6**, treatment with acid ($[\text{H}(\text{OEt}_2)_2][\text{BAR}^F]$, $[\text{LutH}][\text{Cl}]$ and H_2O , for example) invariably results in unproductive decomposition to

regenerate $P_3^B(\mu-H)Fe(H)(CO)$, **1**, as the major product, presumably via acidic cleavage of the Si–O bond.²² We therefore canvassed the reactivity of **6** toward hydrogen and silanes (Scheme 3).

Scheme 3. E-H-Promoted Product Release

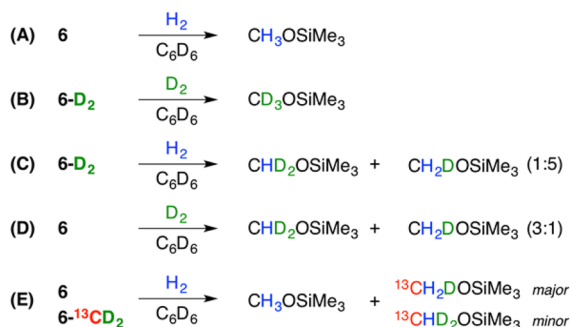


Treatment of **6** with an atmosphere of H_2 at RT results in the release of CH_3OSiMe_3 over 24 h in moderate yields (50%, average of three runs; assumes **6** present at 80% purity initially based on Mössbauer analysis; vide supra). Product release can also be affected by the addition of excess $PhSiH_3$ (5 equiv), with C–Si bond formation in this case and similar yields of the CO-derived product, $PhSiH_2CH_2OSiMe_3$ (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_3^BFe -containing products.²³

To track the origin of the H equivalents delivered to the terminal organic product, CH_3OSiMe_3 , upon H_2 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_3OSiMe_3 , as determined by 1H NMR spectroscopy (Scheme 4A). Likewise, using the 2H -labeled analogue **2-D₂** to

Scheme 4. Summary of Labeling Experiments



generate **6-D₂**, followed by treatment with D_2 , resulted in (nearly) complete incorporation of deuterium in the released product CD_3OSiMe_3 (Scheme 4B; ~5% $CD_2HOSiMe_3$ 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_2 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 H_2 , the partially deuterated organic products CHD_2OSiMe_3 and $CH_2DOSiMe_3$ were obtained in a 5:1 ratio (Scheme 4C). Similarly, when **6** was treated with D_2 a mixture of products was observed, with CHD_2OSiMe_3 and $CH_2DOSiMe_3$ obtained in a 3:1 ratio, and

~5% CH_3OSiMe_3 also detected (Scheme 4D). These results are suggestive of a facile exchange process between the alkyl C–H bonds and the added H_2 or D_2 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., $P_3^BFe-CD_2OSiMe_3 \rightleftharpoons P_3^B(\mu-D)Fe=C(D)(OSiMe_3)$) that then reacts with H_2 .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 $[P_3^B(\mu-D)Fe(D)(^{13}CO)]^{2-}$ and $[P_3^B(\mu-H)Fe(H)(^{12}CO)]^{2-}$ variants. Standard functionalization of this labeled mixture to generate the corresponding alkyl complexes **6**, and product release via the addition of H_2 , showed deuterium incorporation exclusively in the ^{13}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_2 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_3OSiMe_3 upon hydrogenolysis. Use of the bifunctional tris(phosphine)borane ligand, P_3^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 Me_3Si^+ with H^+ as a route to CH_3OH generation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12444.

Synthetic and spectroscopic details (PDF)

Crystallographic information for **2–6** (CIF)

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Notes

The authors declare no competing financial interest.

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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 ~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 P₃^B-supported Fe complexes, see: Del Castillo, T. J.; Thompson, N. B.; Peters, J. C. *J. Am. Chem. Soc.* **2016**, *138*, 5341.

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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 to 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.