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Interplay between Terminal and Bridging Diiron Hydrides in Neutral and Oxidized States

Xin Yu,

School of Chemistry and Chemical Engineering, Shandong University, 27 South Shanda Road, Jinan, Shandong 250100, People's Republic of China

Chen-Ho Tung,

School of Chemistry and Chemical Engineering, Shandong University, 27 South Shanda Road, Jinan, Shandong 250100, People's Republic of China

Wenguang Wang,

School of Chemistry and Chemical Engineering, Shandong University, 27 South Shanda Road, Jinan, Shandong 250100, People's Republic of China

Mioy T. Huynh,

School of Chemical Sciences, University of Illinois at Urbana—Champaign, 600 South Goodwin Avenue, Urbana, Illinois 61801, United States

Danielle L. Gray,

School of Chemical Sciences, University of Illinois at Urbana—Champaign, 600 South Goodwin Avenue, Urbana, Illinois 61801, United States

Sharon Hammes-Schiffer, and

School of Chemical Sciences, University of Illinois at Urbana—Champaign, 600 South Goodwin Avenue, Urbana, Illinois 61801, United States

Thomas B. Rauchfuss

School of Chemical Sciences, University of Illinois at Urbana—Champaign, 600 South Goodwin Avenue, Urbana, Illinois 61801, United States

Graphical Abstract

Correspondence to: Wenguang Wang; Sharon Hammes-Schiffer; Thomas B. Rauchfuss.

Supporting Information: The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00297. Experimental details, NMR (^1H , ^{31}P) and IR spectra, comparison of experimentally measured and DFT calculated structures, redox potentials, and ν_{CO} values, calculated reaction free energies and spin densities, coordinates and energies of all optimized structures, and crystallographic data (PDF)

Notes The authors declare no competing financial interest.

This study describes the structural, spectroscopic, and electrochemical properties of electronically unsymmetrical diiron hydrides. The terminal hydride $\text{Cp}^*\text{Fe}(\text{pdt})\text{Fe}(\text{dppe})(\text{CO})\text{H}$ ($[\mathbf{1}(\text{t-H})]^0$, $\text{Cp}^{*-} = \text{Me}_5\text{C}_5^-$, $\text{pdt}^{2-} = \text{CH}_2(\text{CH}_2\text{S}^-)_2$, $\text{dppe} = \text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$) was prepared by hydride reduction of $[\text{Cp}^*\text{Fe}(\text{pdt})\text{Fe}(\text{dppe})(\text{CO})(\text{NCMe})]^+$. As established by X-ray crystallography, $[\mathbf{1}(\text{t-H})]^0$ features a terminal hydride ligand. Unlike previous examples of terminal diiron hydrides, $[\mathbf{1}(\text{t-H})]^0$ does not isomerize to the bridging hydride $[\mathbf{1}(\mu\text{-H})]^0$. Oxidation of $[\mathbf{1}(\text{t-H})]^0$ gives $[\mathbf{1}(\text{t-H})]^+$, which was also characterized crystallographically as its BF_4^- salt. Density functional theory (DFT) calculations indicate that $[\mathbf{1}(\text{t-H})]^+$ is best described as containing an $\text{Cp}^*\text{Fe}^{\text{III}}$ center. In solution, $[\mathbf{1}(\text{t-H})]^+$ isomerizes to $[\mathbf{1}(\mu\text{-H})]^+$, as anticipated by DFT. Reduction of $[\mathbf{1}(\mu\text{-H})]^+$ by Cp_2Co afforded the diferrous bridging hydride $[\mathbf{1}(\mu\text{-H})]^0$. Electrochemical measurements and DFT calculations indicate that the couples $[\mathbf{1}(\text{t-H})]^{+/0}$ and $[\mathbf{1}(\mu\text{-H})]^{+/0}$ differ by 210 mV. Qualitative measurements indicate that $[\mathbf{1}(\text{t-H})]^0$ and $[\mathbf{1}(\mu\text{-H})]^0$ are close in free energy. Protonation of $[\mathbf{1}(\text{t-H})]^0$ in MeCN solution affords H_2 even with weak acids via hydride transfer. In contrast, protonation of $[\mathbf{1}(\mu\text{-H})]^0$ yields 0.5 equiv of H_2 by a proposed protonation-induced electron transfer process. Isotopic labeling indicates that $\mu\text{-H/D}$ ligands are inert.

Introduction

The interaction of the most abundant metal, iron, with the most abundant element, hydrogen, is of obvious fundamental importance. Indeed, many iron hydride (Fe-H) compounds are known. Iron hydrides play important roles in biology, in industry, and even in geosciences.¹ The Fe-H bond been invoked not only in all three hydrogenases^{2,3} but also in nitrogenase.^{4,5} Molecular iron hydrides are the basis of emerging “earth-abundant” catalytic technologies.^{6,7} Iron hydrides are almost certainly involved in the Haber–Bosch process, one of the most energy intensive industrial operations.⁸

Intense studies have focused on the design and characterization of molecular iron complexes with hydride ligands.⁹ Ferrous compounds of the type H_2FeL_4 and HFeXL_4 and related cyclopentadienyl derivatives are particularly well-studied.^{9,10} With respect to redox, the system $[\text{Cp}^*\text{Fe}(\text{dppe})\text{-H}]^{n+}$ ($\text{dppe} = 1,2\text{-C}_2\text{H}_4(\text{PPh}_2)_2$) is renowned because it has been characterized in both its ferrous ($n = 0$) and ferric ($n = 1$) states.¹¹ Such work has inspired the development of CpFe -(diphosphine-amine)-based catalysts for the oxidation of H_2 .^{12–15}

In the context of biological and heterogeneous catalysis, multiple-iron hydrides are of special relevance. Of general interest are the factors that influence the regiochemistry of hydride ligands: terminal (attached to a single Fe center) vs bridging (attached to two or more Fe centers). With the exception of a few metastable models for the [FeFe]-hydrogenases,^{16–21} hydride ligands in multiple-iron complexes occupy bridging sites.^{22–24} This pattern applies to [Fe⁰]₂H systems (e.g., [HFe₂(CO)₈][–]),²⁵ [Fe^{II}H]_{*n*} systems,^{23,26,27} mixed-valence Fe^{III}Fe^{II} systems (e.g., [Fe₂(NH)(H)(PR₃)₆]²⁺),²⁸ and [Fe^{III}]₂H_{*x*} systems (e.g., [Cp*FeH₂]₂).^{26,29} A possible exception is the minor isomer of [HFe₂(S₂C₆H₄)(CO)₆][–], but this assignment is tentative.³⁰ In this paper, we report results demonstrating the isolability of a thermodynamically stable diiron complex with a terminal hydride ligand. This advance is disclosed in the context of new transformations involving all members of the series [Fe–Fe–H]^{*z*} and [Fe–H–Fe]^{*z*} (*z* = 0, 1+; Scheme 1).

Results and Discussion

Fe(II)–Fe(II)–H ([1(*t*-H)]⁰)

The key diiron hydride was prepared in three steps as described in Scheme 2. The electrophilic reagent [Cp*Fe(NCMe)₃]PF₆ condenses rapidly at room temperature with Fe(pdt)(CO)₂(dppe)³¹ to give the cation [Cp*Fe(pdt)Fe(dppe)(CO)₂]⁺ ([1(CO)]⁺). The salt [1(CO)]PF₆ was obtained in high yield (83%) as red-brown crystals. The IR spectrum of [1(CO)]PF₆ exhibits ν_{CO} bands at 1950 and 1856 cm^{–1}, assigned to terminal and bridging CO ligands, respectively.

To activate the diiron center for installation of the hydride ligand, [1(CO)]⁺ was converted to [1(MeCN)]⁺. This conversion was achieved by photosubstitution in MeCN solution. The lability of the MeCN ligand in [1(MeCN)]⁺ is indicated by its quantitative carbonylation (CH₂Cl₂ solution, 1 atm, 30 min) to regenerate [1(CO)]⁺. The ³¹P NMR spectrum of [1(MeCN)]⁺ displays a singlet at δ 65, indicating C_s symmetry. Crystallographic analysis confirms that the overall structure of the Cp*Fe(pdt)Fe(dppe)L₂ core is retained (Figure S1 in the Supporting Information). Upon replacement of the terminal CO by MeCN, the bridging CO shifts from an unsymmetrical (Fe–μ–CO) = 0.5 Å to a symmetrical (Fe–μ–CO) = 0.05 Å position. This change is reflected in an 89 cm^{–1} shift for ν_{CO} to 1769 cm^{–1}. The repositioning of the CO ligand indicates that the Fe sites in the [Fe(dppe)-(NCMe)]²⁺ and [Cp*Fe]⁺ fragments are somewhat equivalent electronically.

The salt [1(MeCN)]PF₆ reacts with Bu₄NBH₄ to give the targeted hydride [1(*t*-H)]⁰. Thus, upon addition of Bu₄NBH₄, MeCN solutions of [1(MeCN)]⁺ changed from dark brown to black, and microcrystals of the neutral product precipitated. The resulting hydride exhibited good solubility in toluene from which solutions it crystallized upon addition of cold pentane. The ν_{CO} band of [1(*t*-H)]⁰ occurs at 1752 cm^{–1}, vs 1769 cm^{–1} for [1(MeCN)]⁺. Its ¹H NMR spectrum features a triplet at δ –4.95 (*t*, *J*_{P–H} = 76 Hz), a chemical shift that is diagnostic of terminal iron hydrides.³

In contrast to other diiron complexes with terminal hydride ligands,³ [1(*t*-H)]⁰ shows no tendency to isomerize. Heating to the point of its decomposition (hours at 50 °C in THF solution) gave none of the isomeric bridging hydride [1(μ-H)]⁰, which we have prepared as

described below. The molecular structure of $[\mathbf{1}(\text{t-H})]^0$ was confirmed crystallographically (Figure 1). It has idealized C_s symmetry. As in $[\mathbf{1}(\text{NCMe})]^+$, the bridging CO is symmetrically bound ($\text{Fe}-\mu\text{-CO} = 0.02 \text{ \AA}$).

Fe(III)–Fe(II)–H ($[\mathbf{1}(\text{t-H})]^+$)

The redox properties of $[\mathbf{1}(\text{t-H})]^0$ were evaluated by cyclic voltammetry (CV, Figure 2). It is a fairly strong reducing agent, exhibiting a reversible oxidation at -0.87 V vs $\text{Fc}^{+/0}$. A second, but irreversible, oxidation was observed at 0.38 V (Figure S16 in the Supporting Information). These oxidations are assigned to the $[\mathbf{1}(\text{t-H})]^{0/+}$ and $[\mathbf{1}(\text{t-H})]^{+/2+}$ couples, respectively. The irreversibility of the $[\mathbf{1}(\text{t-H})]^{+/2+}$ couple is expected owing to the strongly enhanced acidity upon oxidation.³²

The oxidation of $[\mathbf{1}(\text{t-H})]^0$ was conducted on a preparative scale with FcBF_4 in CH_2Cl_2 solution. At -40°C , the solution turned from black to olive green immediately upon addition of the oxidant. The IR spectrum of $[\mathbf{1}(\text{t-H})]^+$ exhibits a broad ν_{CO} band at 1875 cm^{-1} , an $\sim 130 \text{ cm}^{-1}$ shift to higher energy relative to $[\mathbf{1}(\text{t-H})]^0$. This redox process is chemically reversible, as addition of Cp_2Co to the reaction mixture gave back $[\mathbf{1}(\text{t-H})]^0$. Notably, $[\mathbf{1}(\text{t-H})]^+$ is unreactive toward base.

X-ray crystallographic refinement of the structure of $[\mathbf{1}(\text{t-H})]\text{BF}_4$ was sufficient to confirm the overall connectivity. The diiron centers in $[\mathbf{1}(\text{t-H})]^+$ and $[\mathbf{1}(\text{t-H})]^0$ are similar, each with a $\mu\text{-CO}$ ligand (Figure S20 in the Supporting Information). The $1e^-$ oxidation also causes the $\text{Cp}^*\text{-Fe(1)}$ distance to increase from $1.715 \text{ \AA}$ in $[\mathbf{1}(\text{t-H})]^0$ to $1.742 \text{ \AA}$ in $[\mathbf{1}(\text{t-H})]^+$. A similar change was also observed for the oxidation of $\text{Cp}^*\text{Fe}(\text{dcpe})\text{H}$ ($\text{dcpe} = 1,2\text{-C}_2\text{H}_4(\text{P}(\text{C}_6\text{H}_{11})_2)_2$).^{33,34} The EPR spectrum of $[\mathbf{1}(\text{t-H})]^+$ is rhombic but approaches axial in symmetry (Figure 3). The spectrum was simulated as an 82:18 mixture of two rhombic subspectra with $g = 1.957, 2.074, 2.412$ and $g = 1.957, 2.062, 2.413$. These subspectra result from two “flippamers”, isomers that differ with respect to the conformation of the propanedithiolate ligand. Similar effects have been observed previously in dimetallic complexes of pdt^{2-} : e.g., in the case of $[\text{Fe}_2(\text{pdt})(\text{CO})_3(\text{PMe}_3)(\text{dppv})]\text{BF}_4$ ³⁵ and $[\text{NiFe}(\text{pdt})(\text{CO})_3(\text{dppe})]\text{BF}_4$.³⁶ The broad ν_{CO} band for $[\mathbf{1}(\text{t-H})]^+$ is also consistent with conformers. The calculated free energy difference between these two flippamers is 2.16 kcal/mol in THF, with the flippamer in which the pdt is oriented toward the $\text{Fe}(\text{dppe})\text{CO}$ center being thermodynamically more stable, which is in agreement with the crystal structure. This calculated free energy difference implicates a 97:3 ratio, which is also in qualitative agreement with the ratio from the EPR simulation. Additionally, the calculated free energy barrier for the interconversion between the two flippamers is 10.54 kcal/mol in THF, which is consistent with previous studies (Figure S39 in the Supporting Information).^{37–41}

DFT Analysis of $[\mathbf{1}(\text{t-H})]^0$ and $[\mathbf{1}(\text{t-H})]^+$

The DFT-optimized structures of $[\mathbf{1}(\text{t-H})]^0$ and $[\mathbf{1}(\text{t-H})]^+$ are in good agreement with the crystallographic results (Table 1 and Tables S2 and S3 in the Supporting Information). Since metal–hydride distances are often underestimated by X-ray crystallography,⁴² discussion of these bonds focuses on the distances calculated by DFT. Consistent with an unchanged Fe–H distance is the finding that the oxidation is localized on the Cp^*Fe center, as revealed by the

highly localized nature of the spin density (Figure 4). The greatest differences between the structures of $[\mathbf{1}(\textit{t}\text{-H})]^0$ and $[\mathbf{1}(\textit{t}\text{-H})]^+$ are associated with the Fe– μ -CO distances, which are also highly variable structural elements of the [FeFe]-hydrogenases.^{2,43} Upon oxidation, the CO ligand shifts from a nearly symmetric position between the two Fe centers to a position closer to the Fe(II) hydride center and farther from the Cp*Fe^{III} center. Such a shift is also consistent with the anticipated tendencies of neutral Fe(II) vs cationic Fe(III) centers to engage in π back-bonding. The μ -CO ligand “points” to the electron-rich Fe center.

Other DFT results are in agreement with experimental measurements. In particular, the calculated and observed ν_{CO} bands agree well for both the neutral and cationic complexes (Table 2 and Table S7 in the Supporting Information). The experimentally measured and calculated redox potentials are also in good agreement (Table S6 in the Supporting Information).

Fe(III)–H–Fe(II) ($[\mathbf{1}(\mu\text{-H})]^+$)

In contrast to the inertness of its neutral parent, the cation $[\mathbf{1}(\textit{t}\text{-H})]^+$ is labile. After a few hours at room temperature it isomerizes to $[\mathbf{1}(\mu\text{-H})]^+$ (Figure 5). This conversion, which is quantitative, was monitored by IR spectroscopy. The appearance of a ν_{CO} band at 1953 cm^{-1} indicates a terminal CO ligand, which is also consistent with the site exchange between CO and H[−] in this mixed-valence cation. The isomerization follows unimolecular kinetics with a rate constant of $3.78 \times 10^{-5} \text{ s}^{-1}$ at 24 °C (Figure 5). Interestingly, isomerization of $[\mathbf{1}(\textit{t}\text{-H})]^+$ was strongly affected by the counteranion, while remaining first order. For $[\mathbf{1}(\textit{t}\text{-H})]\text{BAr}^{\text{F}}_4$, $t_{1/2}$ increased to 98.7 h from 5.1 h (Figure S22 in the Supporting Information).

In solution, $[\mathbf{1}(\mu\text{-H})]^+$, which is NMR silent, exhibits a rhombic EPR spectrum (Figure S38 in the Supporting Information). With values of $g = 1.9827, 2.0732, \text{ and } 2.4419$, the spectrum approaches axial symmetry, consistent with a nearly C_s symmetric environment. The absence of hyperfine coupling suggests that the unpaired electron is localized on the Cp*Fe site, consistent with the spin density calculated with DFT (Figure 4). Related to $[\mathbf{1}(\mu\text{-H})]^+$ is the symmetrical mixed-valence (Fe^{II}Fe^{III}) bridging hydride $[\text{Cp}^*_2\text{Fe}_2(\text{S}_2\text{C}_6\text{H}_4)(\mu\text{-H})]^0$.⁴⁴

X-ray crystallographic analysis of $[\mathbf{1}(\mu\text{-H})]\text{BF}_4$ confirmed that this cation retains the structure of its precursor (Figure 6 and Figure S24 in the Supporting Information). Two cations are found in the asymmetric unit. Each has crystallographically imposed C_s symmetry, but they differ with respect to the conformation of the pdt^{2−} ligand. Some disorder is observed in the dppe groups. The structural details are discussed below in the context of the DFT calculations.

According to the usual oxidation state and electron-counting rules, $[\mathbf{1}(\mu\text{-H})]^+$ is a 33e[−] species, described as Fe(III)–Fe(II) or Fe(II)–Fe(III). The magnetic moment for $[\mathbf{1}(\mu\text{-H})]\text{BF}_4$ in solution was determined to be 2.53 μ_{B} by the Evans method. This value is comparable to that reported for $[\text{Cp}^*\text{Fe}(\text{dppe})\text{-X}]^+$ salts (2.16–2.79 μ_{B}).⁴⁵ Notably, isomerization of $[\mathbf{1}(\textit{t}\text{-H})]^+$ to $[\mathbf{1}(\mu\text{-H})]^+$ leads to shortening of the Cp*–Fe distances, from 1.742 Å to 1.715 and 1.727 Å, depending on the flippamer.

Fe(II)–H–Fe(II) ($[1(\mu\text{-H})]^0$)

The final member of the $[1\text{H}]^Z$ series is $[1(\mu\text{-H})]^0$, a diferrous compound with a bridging hydride. The accessibility of this species is indicated by the CV of $[1(\mu\text{-H})]^+$, which exhibits a reversible reduction at -1.06 V vs $\text{Fc}^{+/0}$ (Figure 7). Relative to $[1(\text{t-H})]^0$, the isomeric bridging hydride $[1(\mu\text{-H})]^0$ is about 200 mV more reducing. A similar trend was observed for the isomeric hydrides of $[\text{HFe}_2(\text{xdt})\text{-(CO)}_2(\text{dppv})_2]^{+/0}$ ($\text{xdt}^{2-} = \text{azadithiolate}^{2-}$ or pdt^{2-}).^{20,46,47} On a preparative scale, treatment of a CH_2Cl_2 solution of $[1(\mu\text{-H})]\text{BF}_4$ with 1 equiv of Cp_2Co ($E_{1/2} = -1.33$ V vs $\text{Fc}^{+/0}$)⁴⁸ gave a bright green product. The FT-IR spectrum features a ν_{CO} band at 1908 cm^{-1} , which is $\sim 45\text{ cm}^{-1}$ lower in energy vs $[1(\mu\text{-H})]^+$. The diamagnetism of $[1(\mu\text{-H})]^0$ is indicated by its well-behaved NMR properties. The ^{31}P NMR spectrum features a singlet at δ 80, and the ^1H NMR spectrum displays a hydride signal as a triplet at δ -12.66 with $J_{\text{P-H}} = 28$ Hz. Efforts to obtain high-quality single crystals suitable for X-ray crystallographic analysis were unsuccessful. Fortunately, this $S = 0$, diferrous, μ -hydride species is the most routine and predictable of the series of four compounds.

DFT Analysis of $[1(\mu\text{-H})]^0$ and $[1(\mu\text{-H})]^+$

In good agreement with the crystal structure, the DFT-optimized structures of the two flippamers of $[1(\mu\text{-H})]^+$ reveal C_s -symmetric species (Table 3). The two computed Fe–H bond lengths are very similar for the neutral and cationic states. As is typical, Fe–($\mu\text{-H}$) distances are longer than terminal Fe–H bonds. According to the DFT calculations, the Fe–H distances in the two flippamers change by $<0.02\text{ \AA}$. In addition to the usual challenges in determining Fe–H distances using X-ray crystallography, the present case was affected by disorder in the dppe ligands that limited the signal to noise ratio.

The most detectable structural change induced by oxidation of $[1(\mu\text{-H})]^0$ is the $\sim 0.06\text{ \AA}$ elongation of the Fe–Cp* distance, as seen by DFT. Similar differences are seen for $[\text{Cp}^*\text{Fe}(\text{dppe})\text{H}]^{+/0}$.^{49,50} The elongation of the Fe–Cp* distances upon oxidation is attributed to diminution of π back-bonding from Fe(III) to Cp*. This difference, albeit subtle, is not observed in $[1(\text{t-H})]^{0/+}$ because of the buffering effect of the strongly π acidic $\mu\text{-CO}$ ligand. These results are consistent with the EPR data and calculations indicating that the spin density is localized on the Cp*Fe center (Figure 4).

Isomerization of Neutral and Cationic Hydrides

The isolation of $[1(\mu\text{-H})]^0$ provided an opportunity to evaluate the terminal–bridging isomerization of hydride ligands. Although $[1(\text{t-H})]^0$ shows no tendency to convert to $[1(\mu\text{-H})]^0$, equilibration may be subject to high kinetic barriers. In toluene solution, $[1(\mu\text{-H})]^0$ slowly converts to $[1(\text{t-H})]^0$ but only partially. About $\sim 10\%$ conversion is observed after 36 h, competitive with decomposition. These results are consistent with DFT calculations suggesting that the reaction free energy for the isomerization of $[1(\mu\text{-H})]^0$ to $[1(\text{t-H})]^0$ is endergonic by $\sim 4\text{ kcal/mol}$. Furthermore, according to DFT, isomerization of $[1(\text{t-H})]^+$ to $[1(\mu\text{-H})]^+$ is exergonic by ca. -7 kcal/mol in THF, consistent with our observation of a full conversion in solution. As shown in Tables S8 and S9 in the Supporting Information, however, the isomerization reaction free energies vary for different functionals and should be

viewed as only qualitative estimates of relative thermodynamic stabilities. For example, all functionals studied are consistent in that the bridging hydride is more stabilized relative to the terminal hydride for the cationic species than for the neutral species. Because of this limitation of DFT for the isomerization process, the free energy barriers that would be required for a complete kinetic analysis were not calculated. However, previous computational studies on related models predict that this isomerization likely proceeds through a series of Ray–Dutt (rhombic) and Bailar (trigonal) twists.⁵¹

Protonation of Hydrides

In addition to isomerization and redox studies, the reactivity of diferrous hydrides toward protons was examined. Solutions of $[\mathbf{1}(t\text{-H})]^0$ in MeCN react with protic acids such as $\text{H}(\text{OEt}_2)_2\text{BAr}^{\text{F}}_4$, producing $[\mathbf{1}(\text{NCMe})]^+$ (eq 1).

(1)

The yield of H_2 is close to stoichiometric (quantified by GC analysis, $89 \pm 6\%$ yields in three experiments). The hydridic character of $[\mathbf{1}(t\text{-H})]^0$ is indicated by the finding that H_2 evolution is induced with even the weakly acidic pyrrolidinium tetrafluoroborate ($[\text{HPyrr}]\text{BF}_4$, $\text{p}K_{\text{a}}^{\text{MeCN}} = 19.6$ ⁵²). Solutions of $[\mathbf{1}(t\text{-H})]^+$ are unreactive toward even $\text{H}(\text{OEt}_2)_2\text{BAr}^{\text{F}}_4$, indicating its diminished hydricity.

Similar to the case for $[\mathbf{1}(t\text{-H})]^0$, the isomeric $[\mathbf{1}(\mu\text{-H})]^0$ also reacts with strong acids, but by a different pathway. The yield of H_2 was $43 \pm 5\%$ using $\text{H}(\text{OEt}_2)_2\text{BAr}^{\text{F}}_4$ as well as $[\text{HPPH}_3]\text{BF}_4$ ($\text{p}K_{\text{a}}^{\text{MeCN}} = 7.6$). The diiron product is exclusively $[\mathbf{1}(\mu\text{-H})]^+$, as indicated by IR spectral analysis. The $\sim 50\%$ yield of H_2 indicates that the $\mu\text{-H}$ ligand serves as a spectator, not as a source of H_2 . This unusual behavior, which has been reported for $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_2(\text{dppv})_2]^0$ and $[\text{Cp}^*_2\text{Fe}_2(\text{S}_2\text{C}_6\text{H}_4)(\mu\text{-H})]^0$,⁴⁴ is consistent with the reactions in Scheme 3.

This pathway is analogous to protonation-induced electron-transfer (ET) reactions implicated in the proposed H_2 evolution mechanisms for two other cases of electron-rich ($E_{\text{MHM}}^{+/0} \approx -500$ mV vs $\text{Fc}^{+/0}$) bridging hydride complexes.^{53,54} The role of the bridging hydride as a spectator in $[\mathbf{1}(\mu\text{-H})]^0$ was confirmed by conducting the same experiments starting with $[\mathbf{1}(\mu\text{-D})]^0$. Protonolysis of this deuteride with $\text{H}(\text{OEt}_2)_2\text{BAr}^{\text{F}}_4$ gave exclusively $[\mathbf{1}(\mu\text{-D})]^+$, as confirmed by IR and ^2H NMR spectroscopy (eq 2; see Figures S36 and S37 in the Supporting Information).

Conclusions

This paper describes the characterization of all four members of a square scheme for diiron hydrides (Scheme 1). The total free energy change for the cycle should be 0 kcal/mol (see eq 3):

$$\begin{aligned} \Delta G \left\{ [\mathbf{1}(t-H)]^{+/0} \right\} \\ + \Delta G \left\{ [\mathbf{1}(\mu-H)]^+ / [\mathbf{1}(t-H)]^+ \right\} - \Delta G \left\{ [\mathbf{1}(\mu-H)]^{+/0} \right\} \\ - \Delta G \left\{ [\mathbf{1}(t-H)]^0 / [\mathbf{1}(\mu-H)]^0 \right\} = 0 \end{aligned} \quad (3)$$

The uniquely well-behaved nature of this system is established by the reversibility of the redox reactions and the crystallographic analysis of several members of the cycle. The ideality of this system is attributable to a number of factors: the steric protection afforded by the dppe and Cp* ligands, the high barriers to isomerization because the CO and hydride ligands are mutually trans, and the nonequivalent environments of the two Fe centers.

While much work has been reported on monometallic hydrides, the following conclusions and hypotheses emerge from this work pertaining to bimetallic hydrides.

1. Relative to the more prevalent bridging hydrides, terminal hydrides of bimetallic complexes are more stabilized in reduced states. This effect is observed in the experimentally measured equilibrium ratios for $[\mathbf{1}(t-H)]^+ / [\mathbf{1}(\mu-H)]^+$ ($K_{298} \ll 1$) and $[\mathbf{1}(t-H)]^0 / [\mathbf{1}(\mu-H)]^0$ ($K_{298} > 0.15$) at room temperature and affirmed by DFT, which indicates that the bridging hydride is more stabilized relative to the terminal hydride for the cationic species than for the neutral species.
2. Terminal hydrides exhibit greater hydridic character. This effect is illustrated by the contrasting behavior of $[\mathbf{1}(t-H)]^0$ vs $[\mathbf{1}(\mu-H)]^0$ toward protic reagents: the terminal hydride serves as a hydride donor (eq 1), whereas its bridging isomer serves as an electron donor (Scheme 3). The contrasting hydridic character of terminal vs bridging hydrides parallels the behavior of the polyhedral boranes.⁵⁵ Although the bridging hydride ligand does not serve as a H₂ source, the bridging hydride isomer does evolve hydrogen, but with the μ -hydride ligand serving as a spectator after protonation produces a diferric dihydride. In the present case, the bridging hydride isomer is a superior electron donor. This effect is illustrated by the 220 mV difference in the $[\mathbf{1}(t-H)]^{+/0}$ vs $[\mathbf{1}(\mu-H)]^{+/0}$ couples.
3. Electronically unsymmetrical Fe₂ species stabilize terminal hydrides. Previous work has consistently shown that HFe₂L_x compounds form symmetrical structures with bridging hydrides.^{51,56} In this work, the introduction of an anionic C₅Me₅[−] ligand strongly desymmetrizes the two iron centers such that the terminal hydride is stabilized.

Future work on the new complexes will focus on the reactivity of the unusual paramagnetic hydrides.⁵⁷

Experimental Section

Materials and Methods

Unless otherwise noted, the experimental methods are the same as those described recently.¹⁶ Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II diffractometer with a CCD area detector (graphite-monochromated Mo K α radiation) at 173 K. Microanalytical data were acquired using an Exeter Analytical CE-440 elemental analyzer. EPR spectra were recorded on a Varian E-line 12" Century series X-band CW spectrometer. Infrared spectra, recorded on a PerkinElmer Spectrum Two FT-IR spectrometer, are reported for the ν_{CO} region only. Cyclic voltammetry was performed using a CHI 760e electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd.) with a glassy-carbon working electrode, Pt-wire counter electrode, and Ag-wire pseudoreference electrode. Fe(pdt)(dppe)-(CO)₂¹⁴ and [Cp*Fe(NCMe)₃]PF₆¹⁶ were prepared according to published procedures.

[Cp*Fe(pdt)Fe(dppe)(CO)₂]PF₆ ([1(CO)]PF₆)

To a solution of [Cp*Fe(NCMe)₃]PF₆ (504 mg, 1.10 mmol) in 30 mL of MeCN was added a solution of Fe(pdt)(dppe)(CO)₂ (600 mg, 1.10 mmol) in 20 mL of CH₂Cl₂ at -40 °C. The reaction solution was slowly warmed to room temperature. After it was stirred for 30 min, the solution was concentrated under vacuum. Dilution of the concentrate with 50 mL of Et₂O resulted in precipitation of a brown powder. Yield: 870 mg (83%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of [1(CO)]PF₆ at -30 °C. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.68–7.28 (m, 20 $\times$ ArH), 3.66–2.93 (m, 4H, Ph₂PCH₂), 2.76–2.32 (m, 6H, SCH₂ and CH₂CH₂CH₂) 1.38 (s, 15H, C₅Me₅). ³¹P{¹H} NMR (300 MHz, CD₂Cl₂): δ 62.7. FTIR (MeCN): ν_{CO} 1953, 1856 cm⁻¹. ESI-MS: calcd for [1(CO)]⁺, 807.1035; found, 807.1024. Anal. Calcd for C₄₁H₄₅F₆Fe₂O₂P₃S₂ (found): C, 51.70 (51.93); H, 4.76 (4.97).

[Cp*Fe(pdt)Fe(dppe)(CO)(NCMe)]PF₆ ([1(NCMe)]PF₆)

In a 50 mL Pyrex Schlenk tube, 100 mg of [1(CO)]PF₆ (0.10 mmol) was dissolved in 15 mL of MeCN. The solution was irradiated with a 365 nm LED array (15 W) until the conversion was complete (~4 h) as monitored by IR spectroscopy. The solvent was removed under vacuum, and the product was extracted into 3 mL of MeCN. The extract was filtered through Celite and diluted with 30 mL of Et₂O to precipitate a brown powder. The resulting powder was recrystallized by layering a CH₂Cl₂ solution with hexane at -30 °C. Yield: 78 mg (81%). ¹H NMR (300 MHz, CD₂Cl₂): δ 7.58–7.08 (m, 20 $\times$ ArH), 3.54–3.04 (m, 4H, SCH₂CH₂SCH₂), 2.64 (s, 1H, SCH₂CH₂SCH₂), 2.54–2.08 (m, 4H, PPh₂CH₂CH₂PPh₂), 1.90 (m, 1H, SCH₂CH₂SCH₂) 1.37 (s, 15H, C₅Me₅), 1.27 (s, 3H, CH₃CN). ³¹P{¹H} NMR (300 MHz, CD₂Cl₂): δ 65.1. FT-IR (MeCN): ν_{CO} 1769 cm⁻¹. ESI-MS: calcd for [M – (NCMe)]⁺, 779.1086; found, 779.1074. Anal. Calcd for C₄₂H₄₈NF₆Fe₂OP₃S₂ (found): C, 52.24 (52.56); H, 5.01 (5.47); N, 1.45 (1.62).

[Cp*Fe(pdt)Fe(dppe)(CO)H] ([1(*t*-H)]⁰)

To a solution of [1(NCMe)]PF₆ (100 mg, 0.1 mmol) in 15 mL of MeCN was added 27 mg of solid Bu₄NBH₄ (0.105 mmol). Over the course of 20 min at room temperature, the stirred solution deposited a black solid precipitate. Yield: 59 mg (75%). Black microcrystals were obtained by layering the toluene solution with pentane at −30 °C. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.93–7.20 (m, 20 × ArH), 2.90–2.14 (m, 5H, SCH₂CH₂SCH₂), 2.09–1.71 (m, 5H, PPh₂CH₂CH₂PPh₂, SCH₂CH₂SCH₂) 1.38 (s, 15H, C₅Me₅), −4.76 (t, 1H, J_{P-H} = 76 Hz, Fe-H). ³¹P{¹H} NMR (400 MHz, CD₂Cl₂): δ 87.7. FT-IR (CH₂Cl₂): ν_{CO} 1752 cm^{−1}. ESI-MS: calcd for [1(*t*-H)]⁰, 780.1164; found, 780.1156. Anal. Calcd for C₄₀H₄₆Fe₂OP₂S₂ (found): C, 61.55 (61.79); H, 5.94 (6.28).

[Cp*Fe(pdt)Fe(dppe)(CO)D] ([1(*t*-D)]⁰)

To a solution of [1(NCMe)]PF₆ (200 mg, 0.21 mmol) in 20 mL of THF was added 10 mg of solid NaBD₄ (0.24 mmol). Over the course of 30 min at room temperature, solvent was removed under vacuum. The residue was extracted with toluene (2 mL × 2) and filtered through Celite and then layered with n-hexane, resulting in precipitation of a black solid. Yield: 72 mg (46%). ¹H NMR (500 MHz, CD₂Cl₂): δ 7.93–7.24 (m, 20 × ArH), 2.90–2.19 (m, 5H, SCH₂CH₂SCH₂), 2.10–1.78 (m, 5H, PPh₂CH₂CH₂PPh₂, SCH₂CH₂SCH₂) 1.38 (s, 15H, C₅Me₅). ³¹P{¹H} NMR (500 MHz, CD₂Cl₂): δ 88.2. ²H NMR (500 MHz, toluene): δ −4.66 (br). FT-IR (CH₂Cl₂): ν_{CO} 1752 cm^{−1}.

[Cp*Fe(pdt)Fe(dppe)(CO)H]BF₄ ([1(*t*-H)]BF₄)

A solution of [1(*t*-H)]⁰ (100 mg, 0.026 mmol) in 2 mL of CH₂Cl₂ was treated with 1 equiv of FeBF₄ (35 mg) at −30 °C. The solution changed from brown to olive green immediately. The reaction mixture was diluted with 20 mL of cold pentane (−30 °C). The product precipitated as an olive green powder. Yield: 105 mg (94%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of [1(*t*-H)]BF₄ at −30 °C. FT-IR (CH₂Cl₂): ν_{CO} 1875 cm^{−1}. ESI-MS: calcd for [1(*t*-H)]⁺, 780.1164; found, 780.1153.

[(μ-D)Cp*Fe(pdt)Fe(dppe)(CO)]BF₄ ([1(μ-D)]BF₄)

Compound [1(μ-D)]BF₄ was prepared by oxidation of [1(*t*-D)]⁰ following the same procedure as [1(μ-H)]BF₄. Yield: 80%. FT-IR (toluene): ν_{CO} 1952 cm^{−1}.

[(μ-H)Cp*Fe(pdt)Fe(dppe)(CO)]BF₄ ([1(μ-H)]BF₄)

In a 50 mL Schlenk flask, a solution of 60 mg (0.077 mmol) of [1(*t*-H)]⁰ in 10 mL of CH₂Cl₂ was maintained at room temperature. After ~24 h, the IR spectrum indicated complete isomerization. The solution was evaporated to dryness under reduced pressure. The residue was extracted into MeCN, filtering through Celite. The filtrate was concentrated, the concentrate was diluted with 20 mL of Et₂O, and this mixture was kept at −30 °C overnight. Dark green crystals were collected by filtration. Yield: 56 mg (80%). FT-IR (CH₂Cl₂): ν_{CO} 1953 cm^{−1}. ESI-MS: calcd for [1(μ-H)]⁺, 780.1164; found, 780.1145. Anal. Calcd for C₄₀H₄₆BF₄Fe₂OP₂S₂ (found): C, 55.39 (55.73); H, 5.35 (5.68).

$[(\mu\text{-H})\text{Cp}^*\text{Fe}(\text{pdt})\text{Fe}(\text{dppe})(\text{CO})] ([1(\mu\text{-H})])^0$

To a dark green solution of $[1(\mu\text{-H})]\text{BF}_4$ (100 mg, 0.115 mmol) in 20 mL of THF was added 22 mg of Cp_2Co (0.116 mmol). The color of the solution changed immediately. After 5 min, solvent was removed under vacuum. The residue was extracted into 6 mL of toluene, and the combined extracts were filtered through Celite. The green filtrate was layered with 50 mL of hexane, and this mixture was cooled at $-30\text{ }^\circ\text{C}$ to afford green crystals. Yield: 75 mg (83%). ^1H NMR (500 MHz, toluene- d_8): δ 7.71–7.55 (m, 8H, ArH), δ 7.14–6.99 (m, 12H, ArH), 2.48–2.46 (m, 2H, $\text{SCH}_2\text{CH}_2\text{SCH}_2$), 2.23–2.20 (m, 4H, $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$), 2.13–2.03 (m, 4H, $\text{SCH}_2\text{CH}_2\text{SCH}_2$), 1.82 (s, 15H, C_5Me_5), -12.67 (t, 1H, $J_{\text{P-H}} = 28\text{ Hz}$, Fe-H-Fe). $^{31}\text{P}\{^1\text{H}\}$ NMR (500 MHz, toluene- d_8): δ 80.2. FT-IR (THF): ν_{CO} 1914 cm^{-1} . ESIMS: calcd for $[1(\mu\text{-H})]^+$, 780.1164; found, 780.1159. Anal. Calcd for $\text{C}_{40}\text{H}_{46}\text{Fe}_2\text{OP}_2\text{S}_2$ (found): C, 61.55 (61.87); H, 5.94 (6.16).

$[(\mu\text{-D})\text{Cp}^*\text{Fe}(\text{pdt})\text{Fe}(\text{dppe})(\text{CO})] ([1(\mu\text{-D})])^0$

Compound $[1(\mu\text{-D})]^0$ was prepared by reduction of $[1(\mu\text{-D})]\text{BF}_4$ following the same procedure as $[1(\mu\text{-H})]^0$. Yield: 86%. ^1H NMR (500 MHz, toluene- d_8): δ 7.69–7.53 (m, 8H, ArH), δ 7.13–6.97 (m, 12H, ArH), 2.44–2.46 (m, 2H, $\text{SCH}_2\text{CH}_2\text{SCH}_2$), 2.22–2.18 (m, 4H, $\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2$), 2.09–1.96 (m, 4H, $\text{SCH}_2\text{CH}_2\text{SCH}_2$), 1.80 (s, 15H, C_5Me_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (500 MHz, toluene- d_8): δ 79.6. ^2H NMR (500 MHz, toluene): δ -12.84 (br). FT-IR (toluene): ν_{CO} 1914 cm^{-1} .

Computational Methods

The DFT calculations were performed with the BP86 functional^{58,59} with the SDD pseudopotential and associated basis set⁶⁰ for the Fe centers, the 6-31G** basis set⁶¹ for the $\mu\text{-H}$ and $t\text{-H}$ ligands, and the 6-31G* basis set^{62,63} for all other atoms. Additional benchmarking was performed using the B3P86,^{64,65} M06-L,⁶⁶ B3LYP,^{65,67} BLYP,^{67,68} TPSSH,⁶⁹ and ωB97XD ^{70–73} functionals and is presented in Tables S6–S12 in the Supporting Information. The starting coordinates for all geometry optimizations were obtained from the available crystal structures. The conductor-like polarizable continuum model^{74,75} was used to calculate the solvation free energies using the Bondi atomic radii⁷⁶ and including nonelectrostatic contributions from dispersion,^{77,78} repulsion,^{77,78} and cavitation formation.⁷⁹ The solvent was THF unless stated otherwise. Structural and energetic information for all studied compounds is provided in Tables S13–S18 in the Supporting Information.

Herein, the geometry optimizations were performed in the gas phase; however, a comparison of the structures optimized in the gas and solution phases is provided in Tables S2–S5 in the Supporting Information. All minimum energy structures were verified to have no imaginary frequencies, and transition states (TSs) were confirmed to have only a single imaginary frequency. The TS for isomerization of the pdt^{2-} ligand was located utilizing the synchronous transit-guided quasi-Newton method,^{80,81} and the intrinsic reaction coordinate (IRC) was followed to verify that the TS leads to the correct reactant and product states (flippamers). Thermochemical data were calculated at $T = 298.15\text{ K}$. Zero-point energy, entropic contributions, and solvation effects were included in the calculated reaction free energies (G) and free energy barriers ($G^\ddagger$) in solution. For the G value of the

isomerization between the terminal and bridging hydride, an MP2^{82–84} single-point energy calculation was performed using the DFT-optimized geometry to obtain an MP2-corrected electronic energy. Thus, the electronic energy was obtained from MP2 while the zero-point energy, entropy, and solvation free energy contributions were obtained from DFT. This treatment of the electronic energy generally improves consistency among the functionals (Table S9 in the Supporting Information). This procedure was applied to the neutral species but not to the oxidized species due to spin contamination issues, which were least pervasive for the BP86 functional (Table S10 in the Supporting Information). The relative redox potentials were calculated using methodology described elsewhere.^{85–88} All calculations were performed with the *Gaussian 09* electronic structure program.⁸⁹

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Structure of $[1(\beta\text{-H})]^0$ with H atoms (except for the hydride ligand) omitted. Thermal ellipsoids are shown at the 50% probability level.

Figure 2.

Cyclic voltammogram for $[1(t-H)]^{+/0}$. *Conditions:* 1 mM sample in THF, 0.1 M Bu_4NPF_6 ; scan rate 100 mV/s; potentials vs $\text{Fc}^{+/0}$. Analysis of this CV indicates the following:
 $E_{1/2}[1(t-H)]^{+/0} = -0.87$ V, $i_{pa}/i_{pc} = 0.97$; $E_p[1(t-H)]^{2+/+} = 0.38$ V, irreversible.

Figure 3.

X-band EPR spectra ($\text{CH}_2\text{Cl}_2/\text{PhMe}$, 110 K) of $[\mathbf{1}(\Delta\text{-H})]\text{BF}_4$. The experimental spectrum (*Exp*) could be simulated as the sum of two components, denoted $A + B$, where the *A* and *B* subspectra represent the two flippamers differing in the conformation of the pdt ligand.

Figure 4.

Spin density plot for $[1(t\text{-H})]^+$ (left) and $[1(\mu\text{-H})]^+$ (right) showing predominant localization of unpaired electron on the Cp*Fe(1) center. The spin density is shown in blue wireframe. Numerical values for $[1(t\text{-H})]^+$: $\rho(\text{Fe1}) = 1.17$, $\rho(\text{Fe2}) = -0.05$. Numerical values for $[1(\mu\text{-H})]^+$: $\rho(\text{Fe1}) = 1.10$, $\rho(\text{Fe2}) = -0.03$. The hydrogen atoms, except $t\text{-H}$ and $\mu\text{-H}$, have been removed for clarity.

Figure 5.

IR spectra of $[1(t-H)]BF_4$ (1×10^{-3} M in CH_2Cl_2) (left) and the integrated absorbance of the peak at 1953 cm^{-1} vs time (right).

Figure 6.
Structure of the cation in $[1(\mu\text{-H})]\text{BF}_4$ with H atoms (except for the hydride ligand) omitted.
Thermal ellipsoids are shown at the 50% probability level.

Figure 7.

Cyclic voltammogram for $[1(\mu\text{-H})]^+$. *Conditions:* 1 mM sample in CH_2Cl_2 , 0.1 M Bu_4NPF_6 ; scan rate 100 mV/s; potentials vs $\text{Fc}^{+/0}$. Analysis of this CV indicates the following: $E_{1/2} [1(\mu\text{-H})]^{+/0} = -1.06$ V, $i_{\text{pa}}/i_{\text{pc}} = 0.99$; $E_{1/2} [1(\mu\text{-H})]^{2+/+} = 0.36$ V, $i_{\text{pa}}/i_{\text{pc}} = 1.00$.

Scheme 1. Diiron Hydrides Described in This Work

Scheme 2. Route to the Thermally Stable Terminal Hydride $[1(t-H)]^0$ ^a

^aReaction conditions: (i) $1/2$ MeCN/ CH_2Cl_2 , -30°C followed by warming to room temperature; (ii) MeCN, 365 nm; (iii) MeCN, Bu_4NBH_4 .

Protonation gives a diferric dihydride:

Electron transfer from the parent hydride to its conjugate acid gives a mixed valence dihydride:

Protonation of the dihydride results in hydrogen evolution:

Net reaction:

Scheme 3. Pathway Proposed for Hydrogen Evolution upon Protonation of $[\text{I}(\mu\text{-H})]^0$

Table 1
Crystallographic and DFT-Calculated Bond Distances (Å) for [1(*t*-H)]⁰ and [1(*t*-H)]⁺

	[1(<i>t</i> -H)] ⁰		[1(<i>t</i> -H)]BF ₄ ^a	
	exptl	calcd	exptl	calcd ^b
Fe(1)–Fe(2)	2.4615(3)	2.478	2.513(1)	2.523
Fe(2)–H(1)	1.46(2)	1.522	n.d. ^c	1.520
Fe(1)–C(11)	1.948(2)	1.923	2.359(6)	2.298
Fe(2)–C(11)	1.927(2)	1.933	1.796(7)	1.802
Fe(1)–Cp*	1.715	1.738	1.742	1.764
Fe(1)–S	2.2453(5)	2.273	2.223(2)	2.239
	2.2447(5)	2.269	2.227(2)	2.257
Fe(2)–S	2.2560(5)	2.282	2.264(2)	2.280
	2.2716(5)	2.298	2.283(2)	2.305
Fe(2)–P	2.1758(5)	2.203	2.202(2)	2.239
	2.1807(5)	2.203	2.208(2)	2.244

^aBF₄[−] was not included in the DFT calculations.

^bThe distances are reported for the flippamer in which the pdt is oriented toward the Fe(dppe)CO center. The bond distances for the flippamer with the pdt oriented toward the Cp*Fe center are given in Table S13 in the Supporting Information.

^cNot observed.

Table 2
Experimentally Measured and Calculated ν_{CO} Bands

	ν_{CO} (cm^{-1})	
	exptl	calcd
$[\text{I}(\text{t-H})]^0$	1752	1753
$[\text{I}(\text{t-H})]\text{BF}_4$	1875	1869
$[\text{I}(\mu\text{-H})]^0$	1914	1919
$[\text{I}(\mu\text{-H})]\text{BF}_4$	1953	1956

Table 3
Crystallographic and DFT-Calculated Bond Distances (Å) for $[1(\mu\text{-H})]_0^0$ and $[1(\mu\text{-H})]_1^+$

	$[1(\mu\text{-H})]\text{BF}_4$					
	exptl			calcd ^a		
	$[1(\mu\text{-H})]_0^0$ calcd	pdt ^{CO} <i>b</i>	pdt ^{Cp*} <i>c</i>	pdt ^{CO} <i>b</i>	pdt ^{Cp*} <i>c</i>	
Fe–Fe	2.600	2.586(8)(9)	2.572(1)	2.592	2.607	
Cp*Fe–H	1.650	1.64(7)	1.56(5)	1.661	1.684	
(dppe)Fe–H	1.719	1.43(6)	1.78(5)	1.710	1.697	
Fe–CO	1.742	1.754(4)	1.741(5)	1.748	1.746	
Fe–Cp*	1.680	1.727	1.715	1.748	1.742	
Cp*Fe–S	2.233	2.210(1)(9)	2.223(1)	2.243	2.255	
(dppe)Fe–S	2.315	2.265(9)	2.264(1)	2.303	2.292	
Fe–P	2.245	2.205(5), 2.221(5)	2.235(4), 2.217(5)	2.271, 2.275	2.272, 2.274	

^aBF₄[−] was not included in the DFT calculations.

^bThese bond distances correspond to the flippamer in which the central CH₂ of the pdt^{2−} is oriented toward the Fe(dppe)CO center.

^cThese bond distances correspond to the flippamer in which the central CH₂ of the pdt^{2−} is oriented toward the Cp*Fe center. The calculated free energy difference is 1.08 kcal/mol in THF between these two flippamers, with the flippamer with the pdt^{2−} oriented toward the Fe(CO)dppe center being thermodynamically favored. The calculated free energy barrier for the interconversion between the two flippamers is $G^\ddagger = 9.37$ kcal/mol in THF, consistent with previous calculations.^{37–41}