

Multisite Ligand Noninnocence of $(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3^+$ with Exogenous Hydride Donors: Kinetics and Mechanism

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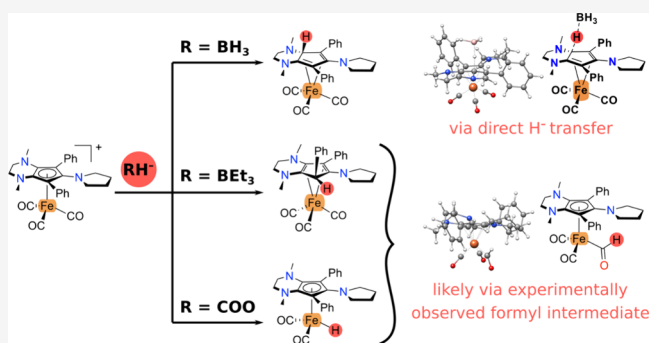
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ABSTRACT: We show that amine-rich Cp^{N^3} ligands coordinated to iron display chemically noninnocent behavior in the presence of exogenous hydride donors ($\text{Cp}^{\text{N}^3} = 1,4\text{-dimethyl-5,7-diphenyl-6-(pyrrolidin-1-yl)-2,3,4,6-tetrahydro-1H-cyclopenta}[b]\text{pyrazin-6-yl}$). The reaction of piano-stool iron complex $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3]^+$ with three different hydride reagents furnishes three different iron complexes, two of which result in net H^- transfer to the Cp^{N^3} ligand. Exposure of $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3]^+$ to NaHBET_3 results in endo hydride addition to the Cp^{N^3} ligand, reaction with NaBH_4 yields an *exo*- $\text{Cp}^{\text{N}^3}\text{H}$ product, and an iron hydride complex forms in the presence of $[\text{Bu}_4\text{N}][\text{HCOO}]$. While state-of-the-art DFT computations indicate that NaBH_4 addition to $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3]^+$ happens via direct H^- transfer to the Cp^{N^3} ligand, reactions with HBET_3^- or HCOO^- initially generate a key iron formyl intermediate which has been experimentally observed. Herein, we present a blend of experimental and computational data to unravel some elementary steps that lead to the formation of these chemically distinct hydride addition products.



INTRODUCTION

Cyclopentadienyl (Cp) ligands are privileged in organometallic chemistry and most often operate as ancillary ligands, retaining their maximum hapticity ($\eta^5\text{-Cp}$) when coordinated to transition metals.^{1–5} However, coordinatively saturated metal complexes bearing $\eta^5\text{-Cp}$ have been shown to react with nucleophiles, electrophiles, or radicals, undergoing an η^5 to η^4 hapticity change.⁶ Nucleophilic addition reactions to metallocenes $[\text{Cp}_2\text{M}]^+$ ($\text{M} = \text{Co}, \text{Rh}$) were pioneered by Wilkinson by using lithium aluminum hydride to give $(\eta^4\text{-CpH})\text{MCp}$ complexes (**A**; $\text{R} = \text{H}$, Scheme 1).⁷ Additionally, $(\eta^4\text{-C}_5\text{H}_4\text{RH})\text{CoCp}$ complexes (**A**; $\text{R} = \text{Alkyl}, \text{Ph}, \text{PhO}^-$) were accessed by addition of nucleophiles to cobaltocenium salts.^{8–10} These *exo* addition products have been rationalized within the context of the Davies–Green–Mingos rules for nucleophilic addition to hydrocarbon ligands (i.e., preferential nucleophilic attack on the *exo* face of coordinated polyene rings).¹¹ Reactivity was also expanded to include the piano-stool complex $\text{CpFe}(\text{CO})_2(\text{PPh}_3)$ (**B**) via reaction with NaBH_4 .¹² The synthesis of **B** was later revisited by Astruc, who found that the iron formyl intermediate $\text{CpFe}(\text{CO})\text{-(CHO)}(\text{PPh}_3)$ is generated prior to Cp ring activation, suggesting that *endo* ring activation might be operative; however, no further mechanistic work was carried out to delineate between *endo* and *exo* ring addition.¹³

The movement of hydride (H^-), the simplest nucleophile, is of major importance in chemical energy conversion processes,¹⁴ and it has recently been shown that $(\eta^4\text{-CpH})\text{M}$ complexes bearing an $\text{C}(\text{sp}^3)\text{--H}$ bond in the diene ring can act as hydride transfer agents to small molecules. The *endo*- Cp^*H complex $(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{RhCl}(\text{bpy})$ (**C**) has an aqueous hydricity (ΔG_{H^-}) of 23 kcal/mol and performs hydride transfer to the enzyme cofactor NAD^+ ($\Delta G_{\text{H}^-}(\text{NADH}) = 28$ kcal/mol).¹⁵ The complex $(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{Fe}(\text{dppe})(\text{CO})$ (**D**) can be synthesized as the *endo*- or *exo*- Cp^*H adduct with *exo* formation occurring via addition of LiHBET_3 to $[(\text{Cp}^*\text{Fe}(\text{dppe})(\text{CO}))]^+$.^{16,17} *endo*-**D** and the *exo* complex $(\eta^4\text{-C}_5\text{Me}_5\text{H})\text{CoCp}^*$ (**E**) are capable of transferring H^- to CO_2 to generate formate (HCOO^-) in acetonitrile.^{17,18} Notably, the *endo* hydrogens in complexes **C** and *endo*-**D** are generated through intramolecular metal-to-ligand migration via $\text{Rh}\text{--H}$ and $\text{Fe}\text{--H}$ intermediates and not via nucleophilic attack using exogenous hydride donors.

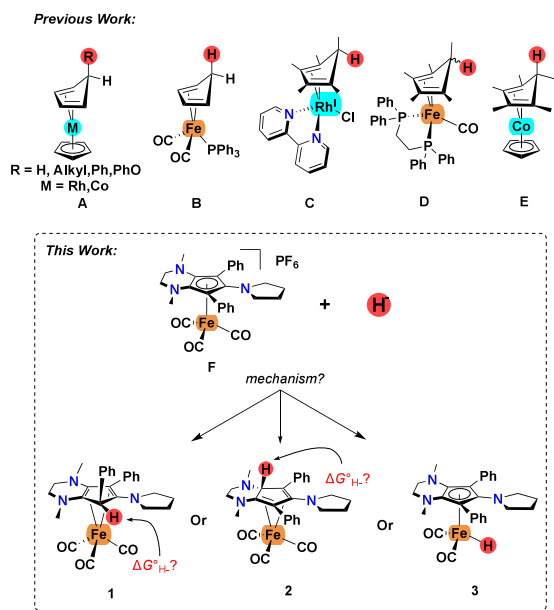
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Scheme 1. Previous Work on Nucleophilic Cp Ring Activation, and the Focus of This Work



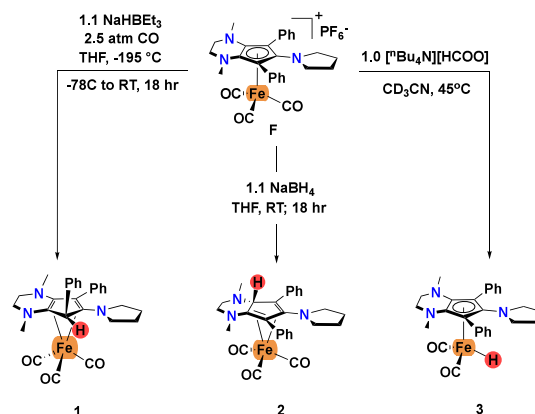
We recently determined that amine-rich Cp^{N^3} ligands with the general formula $[\text{Cp}^{\text{N}^3}\text{Fe}(\text{CO})_2(\text{NCMe})]^+$ are active H_2 production electrocatalysts in the presence of exogenous acid.^{19,20} Mechanistic studies revealed that exogenous acid selectively protonates the Cp^{N^3} ring in the *endo* position, and this transient intermediate rapidly generates an $\text{Fe}-\text{H}$ complex under reducing conditions via ligand-to-metal proton migration. To experimentally support the formation of an *endo*- $\text{Cp}^{\text{N}^3}\text{H}$ intermediate during catalysis, the model complex (*endo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (**1**) was independently synthesized via reduction of $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3]^+$ (**F**) using the strong hydride donor NaHBET_3 (Scheme 1).²⁰ Although low temperatures and elevated pressures of CO were needed to form the product in reasonable yield, the mechanism of H^- addition to generate **1** remained unclear. The kinetic and thermodynamic C–H hydricities of **1** also remained unknown, motivating us to consider that the $\eta^4\text{-Cp}^{\text{N}^3}\text{H}$ motif might be useful as a conduit for transferring H^- to substrates such as CO_2 , especially if the thermodynamic hydricity ($\Delta G^\circ_{\text{H}^-}$) was found to be less than 44 kcal/mol in acetonitrile.^{14,21,22}

Herein, we study the divergent mechanistic pathways toward the formation of three different Fe complexes: an *endo* hydride addition product (**1**),²⁰ an *exo* hydride addition product (**2**), and an $\text{Fe}-\text{H}$ complex (**3**),²⁰ all of which can be accessed from starting material **F** by simply changing the hydride reagent used (Scheme 1). We also show that the experimental hydricities for **1** and **2** are not accessible via equilibrium hydricity measurements for kinetic reasons, even though DFT calculations predict that their thermodynamic hydricities ($\Delta G^\circ_{\text{H}^-}$) are amenable to thermochemical equilibrium measurements (51.0 and 49.4 kcal/mol, respectively). In studying the mechanism of formation for complexes **1** and **3**, kinetic studies reveal that the rate-limiting formation of iron formyl intermediates is in excellent agreement with theory. However, subsequent $\alpha\text{-H}$ elimination pathways are found to be prohibitively high, suggesting that the H transfer mechanism(s) involved are more convoluted than initially expected.

RESULTS AND DISCUSSION

The salt $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3][\text{PF}_6]$ (**F**) was prepared as previously published.¹⁹ In the Experimental Section, we provide a modified protocol for synthesizing the ligand synthon 4-hydroxy-2,5-diphenylcyclopentane-1,3-dione. The Supporting Information includes a solid-state structure of free ligand $[\text{Cp}^{\text{N}^3}][\text{B}(\text{C}_6\text{F}_5)_4]$. We previously reported that synthesis of (*endo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (**1**) is performed under 2.5 atm of CO and requires addition of the CO prior to addition of NaHBET_3 to the reaction mixture (Scheme 2).²⁰

Scheme 2. Reactivity of F with Hydride Donors



This is performed via cryogenic condensation of CO followed by addition of NaHBET_3 under a stream of nitrogen. Under these conditions, the reaction mixture remains pumpkin orange, and upon workup and crystallization it gives a 35% yield of **1**. Without the addition of CO, uncontrolled decomposition is observed, producing a green-brown reaction mixture with trace amounts of $\text{Cp}^{\text{N}^3}\text{FeH}(\text{CO})_2$ (**3**). To alleviate the need for low-temperature conditions and excess CO, we sought an alternative method to access **1** by surveying its reactivity with milder hydride donors. Thus, we used NaBH_4 under nitrogen at room temperature, and the color remained lemon yellow over the course of the reaction. The unique ^1H NMR signal at 4.76 ppm in C_6D_6 corresponding to the CpH proton of **1** was not observed, and a new singlet at 3.92 ppm appeared. To our surprise, single crystals suitable for X-ray diffraction revealed that *exo* attack at a different Cp^{N^3} position had occurred, producing (*exo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (**2**) in 56% isolated yield (Figure 1).

X-ray crystallographic characterization of **2** reveals structural similarities to **1**. Bond lengths along the unsaturated portion of

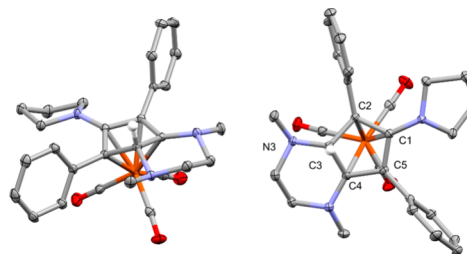


Figure 1. X-ray crystallographic structure of **2** with 50% probability ellipsoids (most hydrogens omitted for clarity). A top-down image is shown on the right with atom labels; see discussion for relevant bond lengths.

the η^4 -Cp group (C1–C2 = 1.452(2) Å, C1–C5 = 1.440(3) Å, C4–C5 = 1.441(2) Å) are within a typical range for conjugated C(sp²)–C(sp²) systems, while the C–C bonds to tetrahedral C3 are elongated (C2–C3 = 1.537(2) Å; C4–C3 = 1.521(3) Å) into the expected range for C(sp²)–C(sp³) bonds.^{20,23,24} This indicates a high degree of delocalization along the diene component of the ring system, likely owing to π -back bonding from the formally Fe(0) center. The C–N bond connected to tetrahedral C3 (C3–N3 = 1.459(2) Å) is significantly elongated relative to the other C–N bonds (C4–N2 = 1.388(2) Å; C1–N1 1.378(2) Å), indicating a break in delocalization and putting the C3–N3 into the range for a C(sp³)–N(sp³) bond.^{23,24}

To probe the oxidative stabilities of **1** and **2**, cyclic voltammetry (CV) experiments in the anodic direction reveal that the oxidation of **1** complex shows a redox wave at scan rates ≥ 30 V/s ($E_{1/2} = 0.27$ V; Table 1). The oxidation of

Table 1. Computed Hydricities and Experimentally Determined Potentials via Cyclic Voltammetry

complex	ΔG_{H^-} (kcal mol ^{−1}) ^a	E (V vs Fc ^{+/0}) ^b
1	51.0	−0.27 ($E_{1/2}$) ^c
2	49.4	0.20 (E_{pa}) ^c
3	53.9	0.00 (E_{pa}) ²⁰

^aComputed relative to the hydricity of BIMH in acetonitrile at the ω B97X-V²⁸/def2-QZVPP²⁹+COSMO-RS(MeCN)^{30,31}//r²SCAN-3c³²+COSMO(MeCN)³³ level of theory. ^bConditions: N₂, MeCN, 0.1 M [Bu₄N][PF₆], 1.0 mM analyte. See the SI for voltammograms. ^cMeasured at 30 V/s.

complex **2** remains irreversible, even at high scan rates ($E_{pa} = 0.20$ V), which is analogous to hydride complex **1**. In all three cases, GC analysis reveals that ca. 1 equiv of CO is released, suggestive of product decomposition.

Next, we surveyed the reactivity of **1** and **2** with hydride acceptors both computationally and experimentally (see the SI for the computational isodesmic schemes employed). Quantifying hydricities (hydride donor abilities; ΔG_{H^-}) via thermochemical equilibrium measurements provides valuable information about the capability of molecules to transfer H[−] moieties in stoichiometric and catalytic transformations.^{14,25} Computational modeling indicates that $\Delta G_{H^-}(\mathbf{1}) = 51.0$ kcal mol^{−1} and $\Delta G_{H^-}(\mathbf{2}) = 49.4$ kcal mol^{−1} (Table 1), which are computed relative to the known hydricity of 1,3-dimethyl-2-phenylbenzimidazole (BIMH) in acetonitrile ($\Delta G_{H^-} = 50.1$ kcal/mol).²⁶ Based on the computed hydricity of **2**, we chose 1,2,3,5,6-pentamethylbenzimidazole (Me₅BzImH; $\Delta G_{H^-} = 43.0$ kcal mol^{−1})²⁷ as the hydride donor, which should favorably transfer H[−] to F on thermochemical grounds ($\Delta G_{rxn} = -6.4$ kcal/mol; Figure 2).

Surprisingly, no reaction between F and Me₅BzImH was observed, and for the sake of completion, mixing the 1,2,3,5,6-pentamethylbenzimidazolium salt [Me₅BzIm][B(C₆F₅)₄] with **2** elicited no reaction (the B(C₆F₅)₄[−] variant was prepared to facilitate solubility in acetonitrile; see the Experimental Section for details). Similar experiments were performed using F, **1**, BIMH, and [BIM][B(C₆F₅)₄], and again, no equilibration was observed from either direction. Since these ground state thermochemical measurements were unsuccessful, we hypothesized that the significant steric bulk surrounding the *endo*- and *exo*-Cp^{N3}H positions might inhibit hydride transfer, and DFT modeling with **1** validates that the hydride transfer transition

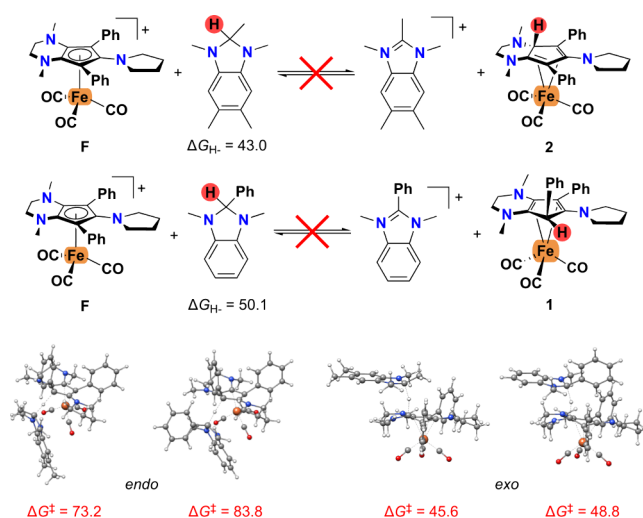


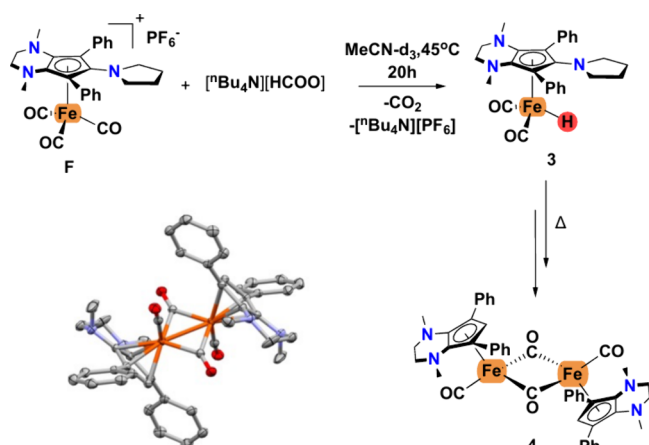
Figure 2. (Top) Attempted equilibration experiments with hydride donors and acceptors along with hydricities for BIMH and Me₅BzImH. (Bottom) Transition state structures and free energies for the reaction of BIMH and Me₅BzImH with [(Cp^{N3})Fe(CO)₃]⁺ (F) to generate **1** or **2**. All energies are given in kcal/mol.

states to the *endo* and *exo* positions are massive ($\Delta G^\ddagger = 73.2$ and 83.8 kcal mol^{−1} for *endo*, $\Delta G^\ddagger = 45.6$ and 48.8 kcal mol^{−1} for *exo*), barring us from obtaining experimental hydricities (Figure 2, bottom).

After establishing that sluggish kinetic hydricities were preventing us from using benzimidazolium salts for equilibrium measurements, we shifted to using formate (HCOO[−]), a sterically unencumbered hydride donor that might smoothly transfer H[−] to the Cp^{N3} ring ($\Delta G_{H^-} = 44$ kcal mol^{−1}, MeCN).¹⁵ In a J. Young NMR tube, [nBu₄N][HCOO] was combined with F in CD₃CN, and no reaction was observed at room temperature. Heating the sample to 45 °C for 20 h cleanly produced a product with a characteristic singlet at −10.72 ppm via ¹H NMR spectroscopy, corresponding to Cp^{N3}FeH(CO)₂ (**3**) in solution (Scheme 2). Based on the computed hydricity of 53.9 kcal/mol for **3** (Table 1), this result is consistent with the liberation of CO₂ over the course of the reaction. However, prolonged heating also leads to gradual decomposition, and black insoluble crystals suitable for X-ray diffraction consistently form at the bottom of unstirred reaction vessels. These black crystals correspond to the dimeric decomposition product (Cp^{N2}Fe(CO)₂)₂ (**4**, Scheme 3). The fate of the pyrrolidine moiety remains unclear. Due the poor solubility of **4** in common organic solvents, characterization was limited to IR spectroscopy with CO stretches at 1921 and 1730 cm^{−1} for the terminal and bridging carbonyls, respectively. Importantly, the formation of ring-activated products **1** or **2** was not spectroscopically observed via ¹H NMR during the reaction.

Flummoxed by the divergent outcomes upon reacting F with different hydride donors, we sought to obtain more information about initial hydride attack in the presence of HBET₃[−], HCOO[−], and BH₄[−] as shown in Figure 3. Based on the calculated hydricities at standard state conditions in MeCN, all three hydride donors are hydridic enough to form complexes **1**–**3** (see Table S1). To mirror the experimental conditions used, reactions with HBET₃[−] and BH₄[−] are modeled at 25 °C in THF while reactions with HCOO[−] are modeled at 45 °C in MeCN. The elevated temperature increases the

Scheme 3. Reaction of **F with $[\text{NBu}^n_4][\text{HCOO}]$, and Molecular Structure of **4**^a**



^aStructure shown with 50% probability ellipsoids, and hydrogens omitted for clarity.

reaction free energy barriers with HCOO^- , since the entropy penalty of the transition states (two particles form one in the TS) is increased. Also, THF is less polar than MeCN, which stabilizes the ionic reactants less but results in more exothermic reaction free energies and smaller barriers to generate products with net neutral charges. DFT calculations reveal that direct hydride transfer to the endo position is insurmountable with all reagents, as the free energy barriers range from 54.2 to 60.4 kcal/mol (Figure 3a). Therefore, hydride donor sterics are not a factor, as hypothesized in our reactions with Me_3BzImH and BIMH . Direct hydride transfer to form *exo* product **2** is kinetically accessible with HBET_3^- and BH_4^- (Figure 3b), while the barrier for HCOO^- addition is highest, even at 45°C ($\Delta G^\ddagger = 27.3$ kcal/mol). In line with experiment, the barrier for BH_4^- attack in the *exo* position is most favorable ($\Delta G^\ddagger = 14.8$ kcal/mol).

The most favorable reaction pathways are HBET_3^- or HCOO^- attack on CO to generate iron formyl intermediate **5** (Figure 3c; $\Delta G^\ddagger = 7.4$ and 25.6 kcal/mol, respectively). Unfortunately, a true transition state could not be located for BH_4^- addition to generate **5** since the saddle point on the minimal energy pathway is flat and its transition state optimizations ran either into the reactants or into the product. The reaction free energy for BH_4^- addition to generate **5** is endothermic ($\Delta G = 19.3$ kcal/mol) and remains so even after considering BH_3 dimerization ($\Delta G = 4.5$ kcal/mol) and is therefore unfeasible. Finally, direct attack of HCOO^- or BH_4^- on the metal center to form hydride complex **6** is also energetically unfeasible (Figure 3d). Therefore, these computational data signify that direct hydride attack to make **1** or **6** is not operative, and generation of complexes **1** and **3** proceeds via initial formation of iron formyl intermediate **5** in the presence of HCOO^- and HBET_3^- .

The effects of the spin state and multireference character have also been computationally probed. We performed single-point calculations for the ground states and transition states shown in Figure 3 on the high-spin triplet state with three different hybrid DFT methods that employ varying amount of Hartree–Fock-like exchange. All spin splittings are larger than 5 kcal/mol (and often much larger; see Table S2). Therefore, our assumption that all species are in a low-spin ground state appears to be justified. To investigate whether multireference

character is of importance, we employed fractional occupation number weighted density (FOD) analysis³⁴ for $\text{TS}_{\text{F},5}$ with $\text{R} = \text{CO}_2$ (Figure S11). Since the FOD is mostly centered on the iron atom and the integrated N_{FOD} value is relatively small ($N_{\text{FOD}} = 0.45$), multireference character seems to be unproblematic.

The relatively straightforward reaction conditions to synthesize **3** using HCOO^- are amenable to reaction monitoring via NMR spectroscopy with the hopes of spectroscopically identifying iron formyl intermediate **5** via hydride transfer from HCOO^- . The synthesis and reactivity of iron formyl intermediates has been reported in detail by Astruc upon reacting $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{R}]^+$ ($\text{R} = \text{CO}$, PMe_3 , PBu_3 , PPh_3) with 1 equiv of NaBH_4 at temperatures $\leq -30^\circ\text{C}$; however, these complexes are all unstable at room temperature.¹³ In a J. Young NMR tube, **F** was combined with 1 equiv of $[\text{NBu}^n_4][\text{HCOO}]$ in CD_3CN , and the vessel was pressurized with 6.5 atm (95 psi) of CO to inhibit the formation of hydride complex **3**. The weakly coordinating NBu_4^+ was specifically chosen in order to minimize the influence of counteranion participation during the course of the reaction.¹³ In addition to a ^1H NMR signal at 8.02 ppm for $[\text{NBu}^n_4][\text{HCOO}]$, we observe the appearance of a broad ^1H NMR signal at 9.41 ppm, assigned to be the formyl proton for intermediate **5** (Figure 4, top).

We also sought to understand the influence of BET_3 on the formation of formyl intermediate **5**. First, we performed a reaction under 6.5 atm of CO with 1 equiv of $[\text{NBu}^n_4][\text{HCOO}]$, and ^1H NMR spectroscopic analysis indicated the presence of **5**. Then, the J. Young NMR tube was vented under an N_2 atmosphere, 1 equiv of BET_3 was quickly added, and the tube was again pressurized to 6.5 atm of CO. ^1H NMR spectroscopic analysis reveals **5**· BET_3 , with a sharp deshielded multiplet at 9.69 ppm due to ^1H – ^{11}B coupling (Figure 4, bottom). Although it was difficult to obtain well-resolved ^{13}C NMR spectral data of the carbonyl/formyl resonances for **5** and **5**· BET_3 , ^1H – ^{13}C HSQC on **5**· BET_3 reveals a cross-peak at 207.7 ppm for the formyl carbon, solidifying our peak assignment (Figure S3). This chemical shift contrasts dramatically with the ^{13}C NMR assignment of the deshielded formyl carbon atom in $\text{Cp}^*\text{Fe}(\text{CO})(\text{CHO})(\text{PBu}_3)$ (306.5 ppm),¹³ underscoring the strong electron donor properties of $\text{Cp}^{\text{N}3}$ ligands.¹⁹

We then studied the kinetics of the formation of **3** in the presence of $[\text{NBu}^n_4][\text{HCOO}]$. By utilizing the method of initial rates, we observe a linear dependence when varying the initial concentrations of $[(\text{Cp}^{\text{N}3})\text{Fe}(\text{CO})_3]^+$ (**F**) or $[\text{NBu}^n_4][\text{HCOO}]$ and monitoring the reaction rates by ^1H NMR spectroscopy (Figure 5 and Figure S6). In both cases, log–log plots indicate a first-order dependence on the concentration of **F** and $[\text{NBu}^n_4][\text{HCOO}]$, thereby giving the following rate law, where **Fe** is the tricyclopentadienyliron tricarbonyl complex **F**: $\text{rate} = k[\text{Fe}][\text{HCOO}^-]$. To observe the effects of isotopic substitution on the reaction rate, we ran reactions under pseudo-first-order conditions by using an excess of $[\text{NBu}^n_4][\text{HCOO}]$ or $[\text{NBu}^n_4][\text{DCOO}]$ at 45°C and monitored by ^1H NMR spectroscopy (Figure 6). The rate of formation of **3** was found to be $3.0 \pm 0.1 \times 10^{-5} \text{ s}^{-1}$, and the rate of formation of the deuterated analogue **3-D** was found to be $1.9 \pm 0.1 \times 10^{-5} \text{ s}^{-1}$, with $k_{\text{H}}/k_{\text{D}} = 1.8$. This kinetic isotope effect (KIE) is comparable to primary kinetic isotope effects involving formate-centered hydride transfers in Mo-containing formate dehydrogenase ($k_{\text{H}}/k_{\text{D}} = 2.44$).³⁵ Table 2 compares the kinetic data between experiment and

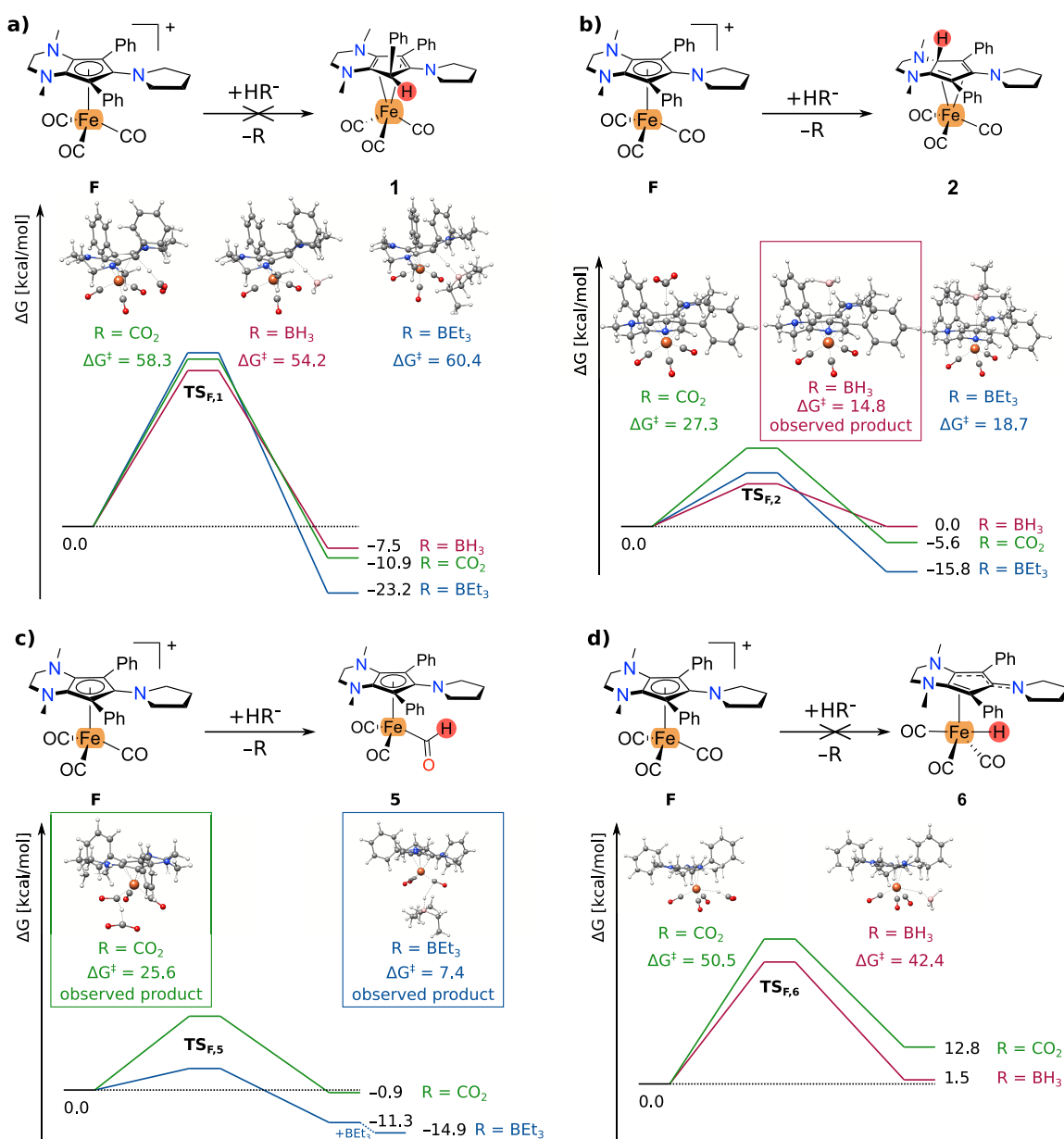


Figure 3. DFT-computed free energy profiles on the ω B97X-V/def2-QZVPP+COSMO-RS level of theory of hydride addition to generate an *endo*- $\text{Cp}^{\text{N}^3}\text{H}$ intermediate (a), *exo*- $\text{Cp}^{\text{N}^3}\text{H}$ intermediate (b), formyl intermediate (c), or hydride adduct (d) via reaction with HCOO^- , HBet_3^- , or BH_4^- . Energies are given in kcal/mol. Implicit solvation for THF is used with HBet_3^- and BH_4^- , and implicit MeCN solvation is used with HCOO^- . Reactions involving HCOO^- were modeled at 45°C , while all others were modeled at 25°C .

theory, and all values are in excellent agreement, indicating that $\text{TS}_{\text{F},5}$ is rate limiting during the formation of **3**.

So far, our combined experimental and computational data to generate **3** via HCOO^- are consistent with the formation of formyl intermediate **5**. The following question remains: how does Fe-H complex **3** form when using HCOO^- and how does *endo*- $\text{Cp}^{\text{N}^3}\text{H}$ adduct **1** form in the presence of HBet_3^- ? Thus far, our data suggests that the formation of **1** and **3** occurs via formation of 5-BEt_3 and **5**, respectively, and we modeled several different intramolecular rearrangements starting from these molecules. Surprisingly, all computed pathways were prohibitively high, and the key transition states are shown in Figure 7 (complete reaction pathways are shown in Figures S9 and S10). Starting from **5**, α -H elimination from the formyl ligand with concomitant CO dissociation ($\text{TS}_{5,3}$) has a barrier of 40.4 kcal/mol in MeCN while α -H elimination

without CO dissociation has a barrier of 30.0 kcal/mol ($\text{TS}_{5,6}$). Stepwise CO dissociation followed by α -H elimination is also prohibitively high ($\text{TS}_{7,3} = 39.3$ kcal/mol). Starting from formyl intermediate 5-BEt_3 , direct H migration to the *endo*- Cp^{N^3} ring to form **1** has a TS free energy of 67.5 kcal/mol in THF ($\text{TS}_{\text{SBet}_3,1}$). Dissociation of BEt_3 followed by direct H migration to the *endo*- Cp^{N^3} ring is also unfavorable (59.3 kcal/mol; $\text{TS}_{5,1}$). Potential lower lying high-spin states were investigated by calculations of vertical singlet-triplet spin splittings (see Table S3), which suggest that no lower lying high-spin transition states are present. These computational data suggest that implicit solvation, bimetallic reaction pathways, or a combination of both may play important roles in the formation of **1** and **3**.

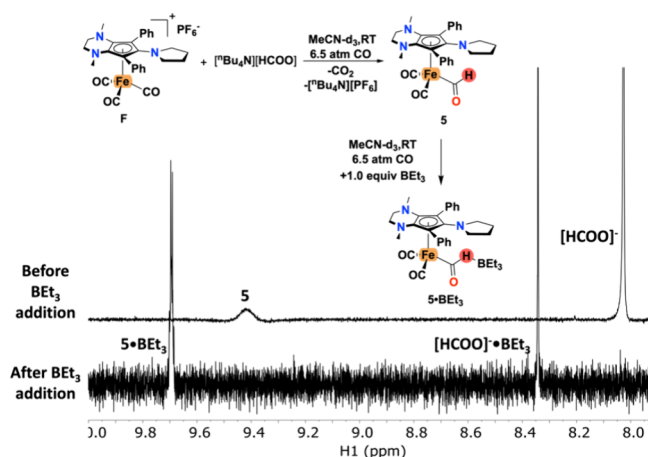


Figure 4. (Top) Reactivity of **F** with $[\text{NBu}_4][\text{HCOO}]$ and BEt_3 under a CO atmosphere to generate **5** and **5-BEt₃**. (Bottom) ^1H NMR spectral data showing the formyl resonances of **5** and **5-BEt₃**.

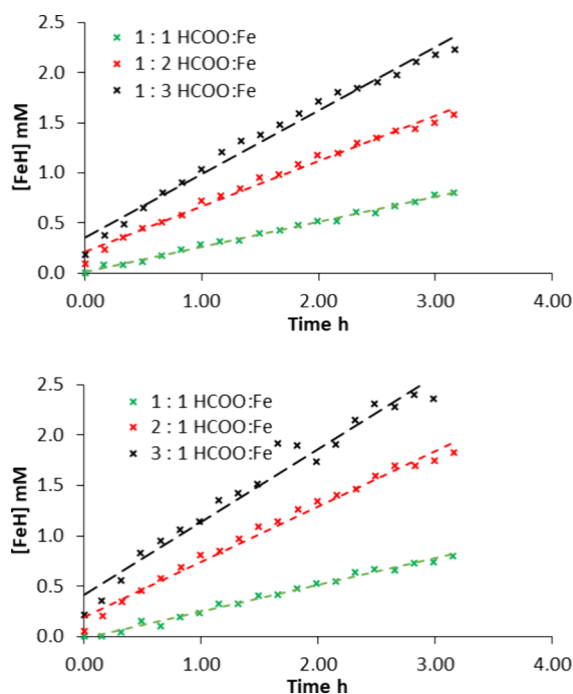


Figure 5. Kinetic traces for the conversion of **1** to **3** in CD_3CN at 45°C . (Top) Varying the initial concentration of **1** (12.6, 26.8, and 38.4 mM) with a constant initial concentration of $[\text{NBu}_4][\text{HCOO}]$ (18.5 mM). (Bottom) Varying the initial concentration of $[\text{NBu}_4][\text{HCOO}]$ (14.8, 29.6, and 41.0 mM) with a constant initial concentration of **1** (15.9 mM).

CONCLUSIONS

In this report, we sought to further explore the ring activation chemistry of the tricarbonyl iron complex $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3]^+$ (**F**). Our previous work demonstrated the synthesis of an *endo*- $\text{Cp}^{\text{N}^3}\text{H}$ addition product (**1**) via hydride addition to the chemically noninnocent Cp^{N^3} ligand using NaHBet_3 .²⁰ In search of more user-friendly reaction conditions, we serendipitously discovered that the weaker hydride donor NaBH_4 forms an *exo*- $\text{Cp}^{\text{N}^3}\text{H}$ addition product (**2**). Moreover, using HCOO^- as the hydride donor furnishes a known FeH complex (**3**) which decomposes with prolonged heating.

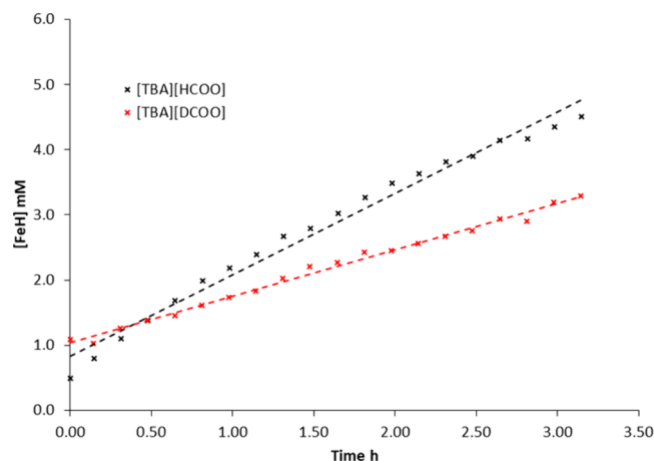


Figure 6. Kinetic traces (first-order fit) for the conversion of **F** to **1** (black) and **1-D** (red) in CD_3CN at 45°C using $[\text{TBA}][\text{HCOO}]$ and $[\text{TBA}][\text{DCCO}]$, respectively.

Table 2. Kinetics Data for the Reaction of **F** To Generate **3** via $[\text{NBu}_4][\text{HCOO}]$ or $[\text{NBu}_4][\text{HCOO}]$ at 45°C

	experiment	DFT ($\text{TS}_{\text{F},5}$) ^a
k (s^{-1})	$3.0 \pm 0.1 \times 10^{-5}$	1.70×10^{-5}
$\Delta G^\ddagger_{318}$ (kcal/mol)	25.2	25.6
$k_{\text{H}}/k_{\text{D}}$	1.8	1.8

^aSee Table 1 for level of theory.

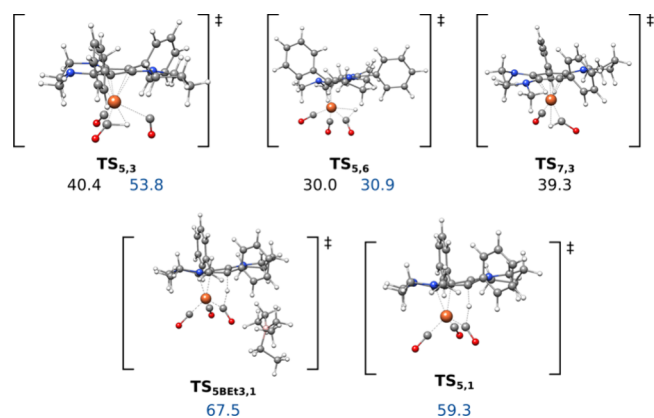


Figure 7. DFT-computed TS barriers for high-energy pathways that were considered after formation of **5-BEt₃** and **5**. Free energies are given in kcal/mol relative to **5** for numbers in black and **5-BEt₃** for numbers in blue. Free energies in blue are modeled in THF at 25°C , and free energies in black are modeled in acetonitrile at 45°C .

The impact of the hydride donor on the regioselectivity of these hydride transfers led us to undertake mechanistic studies. In an attempt to differentiate the site selectivity of the hydride transfer on thermodynamic grounds, we sought to experimentally measure the hydricities of (*endo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (**1**) and (*exo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (**2**). The prohibitively sluggish kinetic hydricities of **1** and **2** led to no reaction in the presence of hydride acceptors, as supported by experiment and DFT calculations. We then undertook a guided experimental and computational study to help explain their reactivity with different hydride donors. Formation of **2** likely occurs via direct hydride transfer to the *exo* position with NaBH_4 , and direct hydride attack with exogenous hydride donors to give **1** and **3** can be excluded due to massive DFT-computed

transition state free energies. Based on kinetic data, there is an overall second-order rate law for rate-determining hydride transfer with HCOO^- , which is in excellent agreement with DFT calculations. We were able to observe an iron formyl intermediate (**5**) via ^1H NMR spectroscopy, and addition of the Lewis acid BeT_3 improved spectral resolution to form the adduct $5\cdot\text{BeT}_3$, which is a likely intermediate en route to *endo*- $\text{Cp}^{\text{N}^3}\text{H}$ adduct **1**. While it was challenging to rationalize the mechanisms of formation for the experimentally isolated **1** and FeH complex **3**, state-of-the-art DFT calculations were valuable to rule out several potential rearrangement pathways. Collectively, this synergistic computational and experimental mechanistic study highlights the unexpected subtleties of exogenous hydride selectivity with FeCp^{N^3} complexes, and we continue to explore the unique reactivity patterns of Cp^{N^3} ligands coordinated to transition metals.

EXPERIMENTAL SECTION

General Comments. All reactions were carried out under an atmosphere of nitrogen or argon using standard glovebox or high-vacuum line (Schlenk) techniques unless stated otherwise. All reagents and solvents were stored in a nitrogen-filled glovebox prior to use unless stated otherwise. Acetonitrile and pentane were dried and degassed over activated alumina using an IT/Inert solvent purification system. Additionally, THF, acetonitrile, and toluene were dried over 20% w/v activated 3 Å molecular sieves. CD_3CN and C_6D_6 were subjected to three freeze–pump–thaw cycles and dried over 10% w/v activated 3 Å molecular sieves in a glovebox.³⁶ Glassware was dried overnight at 140 °C and cooled under dynamic vacuum in a glovebox antechamber. Infrared spectra were recorded on a Thermo Nicolet FT-IR instrument by preparing a KBr pellet or ATR cell. Elemental analyses were run by the CENTC Elemental Analysis Facility, Department of Chemistry, University of Rochester. Microanalysis samples were weighed with a PerkinElmer model AD6000 Autobalance, and their composition was determined with a PerkinElmer 2400 Series II Analyzer. Infrared spectra were recorded on a Thermo Nicolet FT-IR instrument. 1,4-Dimethyl-5,7-diphenyl-octahydro-6H-cyclopenta[b]pyrazin-6-one, $[\text{Cp}^{\text{N}^3}][\text{BF}_4]$,¹⁹ $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3][\text{PF}_6]$ (**F**),^{19,20} (*endo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (**1**),²⁰ $\text{Cp}^{\text{N}^3}\text{FeH}(\text{CO})_2$ (**3**),²⁰ $[\text{Bu}_4\text{N}][\text{HCOO}]$,³⁷ $[\text{Me}_3\text{BzIm}][\text{I}]$,²⁷ and $[\text{BIM}][\text{I}]$ ³⁸ were synthesized according to previously published procedures and matched published spectroscopic data. The salts $[\text{Me}_3\text{BzIm}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{BIM}][\text{B}(\text{C}_6\text{F}_5)_4]$ were prepared by ion exchange of $[\text{Me}_3\text{BzIm}][\text{I}]$ and $[\text{BIM}][\text{I}]$ with $[\text{K}][\text{B}(\text{C}_6\text{F}_5)_4]$ in diethyl ether followed by filtration using a 0.4 μm PTFE syringe filter and drying under high vacuum. The compounds were used without further purification.

NMR. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance III 500 MHz NMR with autosampler capability using either a 5 mm BBO broadband probe or 5 mm BBFO broadband probe. NMR spectra were referenced internally to residual ^1H and ^{13}C signals in the deuterated solvent. Deuterated solvents were degassed via three freeze–pump–thaw cycles and dried over 10% w/v activated 3 Å molecular sieves in a nitrogen-filled glovebox.

To determine the reaction order for the formation of **3** in the presence of $[\text{NBu}_4][\text{HCOO}]$, stock solutions of complex **F** and $[\text{Bu}_4\text{N}][\text{HCOO}]$ (or $[\text{Bu}_4\text{N}][\text{DCCO}]$) were prepared in CD_3CN . The samples were diluted to a total volume of 0.5 mL in a J. Young tube and added to an NMR probe heated to 45 °C. Spectra were automatically collected every 10 min. The concentration of reagents was determined by integrating the peak at 3.13 ppm (^1H) and assuming the initial concentration of ^1H was equal to the initial concentration of $[\text{Bu}_4\text{N}][\text{HCOO}]$. The initial ratio of $\text{F}:\text{HCOO}^-$ was determined using the integrations of the peaks at 3.13 and 2.21 ppm (**F**) in the first spectrum collected. The concentration of the final product was determined using the integration of the peak at −11.19 ppm (FeH) at all time points.

X-ray Diffraction. Single crystals were mounted on a nylon loop and cooled to 100 K under a dry nitrogen stream before data collection unless otherwise stated. SCXRD was performed on a Rigaku XtaLAB Synergy-I diffractometer using $\text{Cu K}\alpha$ with a HyPIX HPC detector. Structures were refined by full-matrix least-squares based on F^2 with all reflections (SHELXTL V5.10; G. Sheldrick, Siemens XRD, Madison, WI). Non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contribution. SADABS (Sheldrick, 12 G.M. SADABS (2.01), Bruker/Siemens Area Detector Absorption Correction Program; Bruker AXS: Madison, WI, 1998) absorption correction was applied. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center and is available free of charge through the CCDC online database.

4-Hydroxy-2,5-diphenylcyclopentane-1,3-dione. This known compound was synthesized using a modified procedure which avoids the use of sodium metal.^{39,40} A stoppered Schlenk flask was charged with 25 mL of absolute ethanol, which had been dried overnight over 20% w/v activated molecular sieves under a blanket of nitrogen. The liquids were transferred via syringe to an air-free Schlenk flask. Under a dynamic stream of nitrogen, sodium ethoxide powder (47.5 mmol, 3.24 g, 2.0 equiv) was added, and the solution was vigorously stirred until the NaOEt dissolved. Then, 1,3-diphenyl-2-propanone (23.8 mmol, 5.00 g, 1.0 equiv) and diethyl oxalate (23.8 mmol, 3.49 g, 1.0 equiv) were weighed on the benchtop and added to the solution. Upon addition of these reagents, the reaction mixture turned orange. The reaction was stirred for 2 h at room temperature under inert gas, during which the reaction mixture changed color from orange to purple. At this point, the reaction was moved to an ice bath and cooled to 0 °C, and the remaining workup was conducted under air. Glacial acetic acid was added dropwise until equimolar amounts of $[\text{K}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{Cp}^{\text{N}^3}][\text{BF}_4]$ were dissolved in a minimum amount of diethyl ether, giving a white precipitate suspended in a blue solution. This suspension was filtered with a PTFE syringe filter giving a blue solution, which was layered with pentane and stored at −30 °C in a glovebox freezer. Overnight, a viscous blue oil formed on the bottom of the vial, and after several weeks at −30 °C, this oil crystallized, giving X-ray-quality crystals (Figure S12). This product was not characterized any further; pH $\approx$ 7 was measured with pH test strips. At this point, a yellow precipitate began to form, and the complete reaction was transferred to a beaker containing ca. 50 g of ice. The reaction was further acidified by dropwise addition of concentrated sulfuric acid until the pH measured $\approx$ 1. During this time, more yellow precipitate formed. The yellow precipitate was collected on a medium-pore glass filter frit, transferred to a round-bottom flask, and dried overnight under high vacuum. Redissolving the product in a minimal amount of acetone followed by addition of hexanes precipitates a light-yellow microcrystalline product in 90% yield (5.69 g) and matches previously published spectroscopic data.⁴⁰

(*exo*- $\text{Cp}^{\text{N}^3}\text{H}$) $\text{Fe}(\text{CO})_3$ (2**).** In a glovebox, $[(\text{Cp}^{\text{N}^3})\text{Fe}(\text{CO})_3][\text{PF}_6]$ (**F**) (122 mg, 186 μmol , 1.0 equiv) was dissolved in THF (3 mL). To this solution was added LiAlH_4 (45 mg, 1.19 mmol), and the yellow solution was stirred for 18 h at room temperature. The solvent was removed under high vacuum; the residue was dissolved in a minimum amount diethyl ether (ca. 4 mL) and filtered using a 0.45 μm Teflon syringe filter. The red-orange solution was layered with pentane (ca. 12 mL) and cooled to −35 °C in a glovebox freezer until crystals formed. The mother liquor was decanted, and the crystals were washed with pentane (3×1 mL) and dried under high vacuum to give **2** as a yellow crystalline solid (53 mg, 56%). These crystals were suitable for X-ray analysis. ^1H NMR (500 MHz, CD_3CN) δ 7.71 (s, 3H, broad, Arom), 7.54 (s, 2H), 7.48–7.36 (m, 2H, Arom.), 7.36–7.05 (m, 3H, Arom), 3.88 (s, 1H, CpH), 2.70–2.48 (m, 4H, overlapping, en), 2.22–2.10 (m, 4H, overlapping, Pyrr), 1.57 (s, 3H, Me), 1.54 (s, 3H, Me), 1.36–1.28 (m, 4H, overlapping, Pyrr). ^{13}C NMR (126 MHz, CD_3CN) δ 219.15 (3 CO), 144.21 (1 Arom), 136.33 (1 Arom), 134.35 (1 Arom), 129.72 (2 Arom), 129.11 (2 Arom), 128.72 (1 Arom), 128.63 (1 Arom), 127.92 (1 Arom), 116.45 (Cp), 104.57 (Cp), 97.51 (Cp), 73.75 (Cp), 67.00 (2 CH_2 Pyrr), 52.65 (1 CH_2 en), 51.96 (1 CH_2 en), 48.52 (2 CH_2 Pyrr), 42.71 (1 C

CH₃), 42.13 (1C CH₃), 24.70 (2 C Pyrr). IR (KBr) 1968, 1910, 1900 cm⁻¹ (ν_{CO}). Anal. Calcd (%) for C₂₈H₂₉FeN₃O₃: C, 65.76; H, 5.72; N, 8.22. Found: C, 65.35; H, 5.76; N, 8.04.

[ⁿBu₄N][DCCO]. This compound was synthesized using a modified procedure based on a known synthesis of the protonated compound.⁴ Outside of the glovebox with no consideration taken for exposure to moisture or air, 500 mg of [Na][DCCO] was dissolved in 2 mL of D₂O, and concentrated DCl was added until the pH measured ~1 using pH test strips (ca. 0.05 mL). [ⁿBu₄N][OH] (7.24 mL; 1.0 M solution in MeOH) was added. Solvent was removed under high vacuum with heating to 100 °C. The flask containing the light brown residue was brought into a nitrogen-filled glovebox and dissolved in acetonitrile. This light brown solution was run through a plug of silica gel to give a clear colorless solution. Solvent was removed under high vacuum to give a white solid. ¹H NMR (500 MHz, CD₃CN) δ 3.17–3.10 (m, 1H), 1.63 (p, *J* = 7.9 Hz, 1H), 1.38 (h, *J* = 7.4 Hz, 1H), 1.03–0.96 (m, 12H). ¹³C NMR (126 MHz, CD₃CN) δ 58.90, 23.92, 19.90, 13.37. IR (KBr) 1473, (ν_{CO}). Anal. Calcd (%) for C₁₇H₃₆DN₂O₂·0.5H₂O: C, 68.63; H, 13.21; N, 4.71. Found: C, 68.43; H, 12.97; N, 4.92. Although all precautions were taken to dry the product completely, repeated analyses on independently prepared batches consistently show that it retains 0.5 H₂O before combustion analysis.

(1-(Cp^{N2})Fe)₂ (4). In a glovebox, F (15 mg, 22.9 μ mol) was dissolved in acetonitrile, along with [ⁿBu₄N][HCOO] (6.6 mg, 22.9 μ mol) in a 25 mL Schlenk flask with a Teflon screw valve containing a Teflon-coated stir bar. The flask was heated to 45 °C for 5 days, during which time a black crystalline solid was collected. This material was isolated by filtration, and were suitable crystals for single crystal X-ray diffraction were obtained (5.3 mg, 6.4 μ mol, 55%). IR (KBr) 1921, 1730 cm⁻¹ (ν_{CO}). Poor solubility prevented solution-phase characterization.

[Cp^{N3}][B(C₆F₅)₄]. Equimolar amounts of [K][B(C₆F₅)₄] and [Cp^{N3}][BF₄] were dissolved in a minimum amount of diethyl ether, giving a white precipitate suspended in a blue solution. This suspension was filtered with a PTFE syringe filter giving a blue solution, which was layered with pentane and stored at –30 °C in a glovebox freezer. Overnight a viscous blue oil formed on the bottom of the vial, and after several weeks at –30 °C, this oil crystallized, giving X-ray-quality crystals (Figure S12). This product was not characterized any further.

Equilibrium Hydricity Measurement Attempts with BIM and BIMH. In a nitrogen-filled glovebox, to a J. Young NMR tube were added 2 (10 mg, 19.6 μ mol) and [Me₃BzIm][B(C₆F₅)₄] (17 mg, 19.6 μ mol) in 0.5 mL of acetonitrile-*d*₃ and heated to 45 °C. The reaction was monitored by ¹H NMR for several weeks, and no change occurred. Similar experiments were performed using 1 and [BIM]-[B(C₆F₅)₄], and the same outcome was observed.

Computational Details. Geometries were optimized in the Turbomole⁴¹ v.7.5.1 program package on the efficient r²SCAN-3c³² level of theory with the implicit COSMO³¹ solvation model for acetonitrile and tetrahydrofuran (with ϵ = 35.688 for MeCN and ϵ = 7.58 for THF). The m4 integration grid was employed with the radsize increased to 15. With this level of theory, initial guesses for the transition states were obtained with the DE-GSM^{42,43} method and then optimized in Turbomole. Single-point energy calculations (ΔE) were conducted in Orca⁴⁴ v. 5.0.4 with the ω B97X-V²⁸ functional employing the large def2-QZVPP basis set.²⁹ This method was selected because of its robust performance that has been extensively benchmarked.⁴⁵ Thermostatistical corrections (ΔG_{mRRHO}) were obtained with the modified RRHO¹⁶ scheme with *T* = 318.15 K for the reactions with [HCOO][–] in MeCN and with *T* = 298.15 K for all other reactions. Solvation free energies were obtained ($\delta\Delta G_{\text{solv}}$)¹¹ with the implicit solvation model COSMO-RS (DFT; COSMOtherm Version C3.0, release 16.01, 2016 parametrization, parameter file: BP_TZVP_C30_1601.ctd; default Gsol option) with parametrizations for THF and MeCN.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.4c00137>.

NMR spectra, kinetics plots, electrochemistry, additional computational data (PDF)

Computed Cartesian coordinates (ZIP)

Accession Codes

CCDC 2346231–2346233 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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