





Hydride Reactivity

Carbon Dioxide Insertion into Bridging Iron Hydrides: Kinetic and Mechanistic Studies

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Abstract: The reduction of CO_2 to formic acid by transition metal hydrides is a potential pathway to access reactive C1 compounds. To date, no kinetic study has been reported for insertion of a bridging hydride in a weak-field ligated complex into CO_2 ; such centers have relevance to metalloenzymes that catalyze this reaction. Herein, we report the kinetic study of the reaction of a tri(μ -hydride)triiron(II/II/II) cluster supported by a tris(β -diketimine) cyclophane (1) with CO_2 monitored by ¹H-NMR and temperature-controlled UV/Vis spectroscopy. We found that 1 reacts with CO_2 to traverse the reported monofor-

mate (**1-CO**₂) and a diformate complex (**1-2CO**₂) at 298 K in toluene, and ultimately yields the triformate species (**1-3CO**₂) at elevated temperature. The second order rate constant, H/D kinetic isotope effect, ΔH^{\dagger} , and ΔS^{\dagger} for formation of **1-CO**₂ were determined as 8.4(3) × 10⁻⁴ m⁻¹ s⁻¹, 1.08(9), 11(1) kcal mol⁻¹, and -3(1) × 10 cal mol⁻¹ K⁻¹, respectively at 298 K. These parameters suggest that CO₂ coordination to the iron centers does not coordinate prior to the rate controlling step whereas Fe–H bond cleavage does.

Introduction

Reduction of carbon dioxide to formic acid is one pathway for the utilization of CO_2 as a carbon source and leverages a more favored two proton-coupled two-electron reduction as compared to the one electron process via the CO_2 radical anion.^[1–5] Independent of formic acid being a more reactive C1 reagent as compared to CO_2 , this molecule is itself a liquid hydrogen storage material and has been employed in fuel cell technologies.^[6,7] Proton-coupled electron transfers to formic acid can afford hydrocarbons derived from CO_2 closing a cycle for carbon-neutral liquid fuel synthesis. Approaches to hydrogenate CO_2 catalytically to more reduced C1 fragments have focused on metal hydrides as reactive species and the reactivity of nucleophilic hydrides in this context has consequently drawn significant interest.^[3–5]

There are few reports detailing the kinetic parameters for hydride transfer from a transition metal center to CO_2 .^[8–13] Independent of this dearth of detailed kinetic studies, two mechanistic pathways are proposed: normal insertion wherein an H⁻ attacks the π^* orbital of CO_2 , and abnormal insertion in which a metallocarboxylate is generated.^[14,15] The latter pathway is typically invoked for CO_2 reduction to CO and H₂O, whereas the former leads to formate. With respect to terminal metal hydrides, the two generally accepted normal insertion mechanisms and their respective rate controlling steps are depicted in

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejic.201801404. Scheme 1.^[16,17] Coordinatively unsaturated complexes typically proceed through an inner sphere mechanism: CO₂ binds to the metal centers at a vacant coordination site, followed by a concerted M–H bond breaking and C–H bond forming event to generate the (formato)metal complex.^[13] Contrastingly, the outer sphere mechanism results from hydride insertion fol-



Scheme 1. Proposed hydride transfer mechanisms of CO_2 by (a) metal hydrides or by (b) FeMo-cofactor.

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lowed by reorientation and coordination of the resultant formate, and is expected for coordinatively saturated complexes.^[8–12] Here, the highly polarized transition state can be stabilized by exogenous Lewis acids or secondary coordination sphere interactions.^[13,18–20]

Although bridging hydrides are common motifs in cluster chemistry, the kinetics of insertion of a bridging hydride into CO_2 are even less explored than for monometallic species. Bridging hydrides are proposed or characterized transients in a number of metalloenzymes as well as on surfaces of metal catalysts.^[21-24] The molecular insight provided from homogeneous compounds into the reactivity of these motifs, therefore, informs mechanistic considerations for biological and heterogeneous systems. For example, the proposed μ -hydrides in the two-electron two-proton reduced (or E2) state of the FeMocofactor of molybdenum-dependent nitrogenase are calculated to react with CO_2 through an outer sphere rather than inner sphere pathway (Scheme 1b).^[25] Similarly, H-atoms adsorbed on the surface of the Mittasch catalyst are key players in the Haber–Bosch process.^[26]

We have previously reported the synthesis and reactivity towards CO₂ of hexagonal $[M_3(\mu-H)_3]^{3+}$ (M=Fe²⁺ or Co²⁺) clusters supported by a tris(β-diketiminate) cyclophane.^[27] These complexes exhibit exceptional substrate specificity; for example, hydride insertion into CO₂ readily occurs whereas reaction with weak acids is markedly slower or unobserved. Reaction of $Fe_3H_3L^{Et/Me}(1)$ with CO_2 results in the isolation of the (µ-1,1formato)di(µ-hydride)triiron(II/II/II) complex (1-CO2) at ambient temperature in THF and the tri(µ-1,1-formato)triiron compound (1-3CO₂) at elevated temperatures in toluene (Scheme 2). Executing the reaction in toluene at room temperature leads to greater product speciation as compared to THF as evidenced by the number of C=O stretches in IR spectra of the reaction mixture. Previously, hydridicity of metal hydrides has been correlated to solvent acceptor number, consistent with the observed solvent effect for reaction of 1 with CO₂.^[9,10,12,13] Taken together with the reactivity of Fe₃H₃L^{Et/Me} with CO which re-



Scheme 2. Reaction scheme for 1 with CO2. ^a Previously reported conditions.

sults in H₂ reductive elimination,^[28] we proposed that the hydrides in these clusters are coordinatively fluxional and capable of adopting semi-bridging or terminal modes. Herein, we report a detailed kinetic study of the reaction of **1** with CO₂ to generate **1-CO₂** using in situ ¹H-NMR and UV/Visible spectroscopy. Our results support rate controlling hydride insertion and the observed thermodynamic parameters are consistent with those estimated for related iron hydride complexes.

Results and Discussion

As an initial probe into the kinetics for hydride insertion, we monitored the reaction of 1 with CO₂ by in situ ¹H-NMR spectroscopy using hexamethylbenzene as an internal standard. We will first consider the predominant species generated in solution, and subsequently address the minor reaction components. Upon introduction of CO₂, the five resonances associated with the D_{3h} symmetric **1** decrease exponentially with the increase in intensity of twelve new signals corresponding to the monoformate complex, 1-CO₂ (Figure 1, S2). The concentration of 1-CO₂ maximizes at approximately 15 h, and then decreases over the subsequent 7 d with the concomitant appearance of thirteen new peaks arising from a new $C_{2\nu}$ transient. This assignment as a single intermediate generated from 1-CO₂ is inferred from the relative integrals of these resonances and comparable time dependence. Preliminarily, ¹H-NMR data imply an $\mathbf{A} \rightarrow \mathbf{B}$ \rightarrow **C** model for the reaction of **1** with CO₂.

Assuming a pseudo-first order condition for the concentration of CO₂, the intensity of a number of resonances for each of the three observed species as a function of time can be fit to the proposed $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$ model (Figure 1, Figure S2, Table S1). From ¹H-NMR spectra recorded at 20 °C, the integrals for resonances corresponding to 1 decrease exponentially and are well fit with the proposed model to afford $k_{1.obs}$ = $3.5(1) \times 10^{-5}$ s⁻¹ (Figure 1a). Similar analysis of the time course for resonances corresponding to $1-CO_2$ yield values for $k_{1,obs}$ and $k_{2,obs}$ of $3.5(3) \times 10^{-5} \text{ s}^{-1}$ and $1.1(1) \times 10^{-5} \text{ s}^{-1}$ for (Figure 1b). Gratifyingly, the determined values of $k_{1,obs}$ from the decay kinetics of 1 are consistent with those of formation for **1-CO₂**. We note that errors associated with $k_{2,obs}$ are large and likely arise from the incomplete conversion of 1-CO₂ to 1-2CO₂ over the time course; that is, the lack of a spectroscopic end point preclude accurate simulation of the slow decay process. Our primary focus here, however, is interrogating the conversion of 1 to 1-CO₂ as a model of understanding hydride transfer from weak-field ligated multimetallic centers. With that said, a comparable value for $k_{2,obs}$ of $1.3(1) \times 10^{-5} \text{ s}^{-1}$ is obtained from fits of the integrals of resonances corresponding to 1-2CO₂ vs. time (Figure 1c). Here again, however, we were unable to obtain comparable agreement for $k_{1,obs}$ given the poor signal-to-noise ratio for integrals of resonances for 1-2CO₂ at early reaction times.

In situ UV/Visible spectroscopic measurements provide further support for the three-component kinetic model in this time domain. Two observations support fitting the absorption data to this kinetic model. First, we do not observe an isosbestic point in spectra recorded for the reaction of **1** with \approx 1 atm.







Figure 1. Plots of absolute integral vs. time (min) for the reaction between 1 (11 mm) and CO_2 (100 mm) in $[D_8]$ toluene at 20 °C. (a) Integrals for resonances corresponding to concentration changes to 1 (a), 1- CO_2 (b), and 1- $2CO_2$ (c). Datasets correspond to the changes to the integral at the chemical shifts listed in the figure legends.

 CO_2 in toluene (Figure S4), indicating one or more transient species in this reaction. Moreover, maxima are observed at \approx 5 h in plots of absorption at wavelengths under 424 nm vs. time (Figure 2a, Figure S4), whereas absorption decreases over the entire time course for wavelengths above 424 nm.

Second, absorption at 495 nm decreases over the first \approx 10 h and is unchanged for the remainder of the experiment (Figure 2b). This late isosbestic point strongly suggests the conversion of an intermediate to the reaction product. Given the NMR data analysis and these observations, we globally fit plots of absorption at various wavelengths between 415 and 495 nm vs. time to a simple three-component kinetic model (i.e., $\mathbf{A} \rightarrow \mathbf{B} \rightarrow \mathbf{C}$). The pseudo-first order rate constants for hydride insertion by **1** into CO₂ ($k_{1,obs}$ and $k_{2,obs}$) from this global analysis are consistent with those determined by NMR spectroscopy if one considers the differences in temperature (Table 1, S1, S2).



Figure 2. In situ UV/Visible spectra recorded for reaction of **1** (0.41 mm) with CO_2 (98 mm), in toluene at 25 °C. a) Stack plot of spectra recorded from 400 to 700 nm. Inset: plot of absorbance at selected wavelengths vs. time. Black solid lines correspond to global fits to the data using a two-step irreversible reaction model with the shared parameters, $k_{1,obs}$ and $k_{2,obs}$. b) Absorption at selected wavelengths vs. time with the speciation plot generated from the calculated rate constants overlaid.

IR spectra of the reaction mixture after 7 d – corresponding to accumulation of predominantly the unknown $C_{2\nu}$ species observed in ¹H-NMR spectra after 15 h – reveal two intense absorptions at 1657 and 1609 cm⁻¹ (Figure S1). The higher energy absorption likely corresponds to the asymmetric COO vibration and is intermediate relative to those observed in **1-CO₂** (1676 cm⁻¹) and **1-3CO₂** (1642 cm⁻¹).^[27] Notably, this unknown species further reacts with CO₂ if the reaction temperature is increased to afford **1-3CO₂**. Taken together then, we assign this unknown $C_{2\nu}$ species as the di(µ-formato)hydridotriiron(II) com-



Table 1. Rate constants determined for conversion of 1 to 1-CO2.

Method	[1] [mM]	[CO ₂] ^[a] [mM]	T [K]	Fitting target	k _{1,obs} [× 10 ⁻⁵ s ⁻¹]	k ₁ [× 10 ⁻⁴ м ⁻¹ s ⁻¹]
NMR	11	100	293	1	3.5(1)	3.5(1)
NMR	11	100	293	1-CO ₂	3.5(3)	3.5(3)
NMR	11	100	293	1-2CO ₂	20(6)	20(6)
UV/Vis	0.43	98	298	415–495 nm	8.2(3)	8.4(3)
UV/Vis	0.43	95	300	415–495 nm	9.4(4)	9.9(4)
UV/Vis	0.42	91	303	415–495 nm	10.7(3)	11.8(3)
UV/Vis	0.28 ^[b]	98	298	415–495 nm	7.6(6)	7.8(6)

[a] Calculated values as described in the experimental section. [b] $1-D_3$ used instead of 1. Errors are reported as: [x] statistical average of the fit error and the instrumental error, [y] instrumental error, or [z] fit error. Additional details regarding error analysis provided in Table S3.

plex, **1-2CO₂**. Therefore, the proposed reaction model corresponds to $1 \rightarrow 1$ -CO₂ $\rightarrow 1$ -2CO₂ with formation of 1-2CO₂ observed primarily after 10 h of reaction time.

As we stated above, the monoformate and diformate complexes are the major species formed during reaction of 1 with CO₂. However, two minor impurities are also observed in the reaction of which one is assigned as the trihydroxide complex, $Fe_3(\mu-OH)_3L^{Et/Me}$, and the second is as-yet-identified (Figure S3). The five resonances from the D_{3h} -symmetric trihydroxide complex appear rapidly upon adding CO₂, and the integrals remain constant for the remainder of the time course. The rapid formation of trihydroxide complex is unexpected as these trimetallic trihydrides (e.g., Zn₃H₃L^{Et/Me}) react significantly faster with CO₂ as compared to H₂O at even higher concentrations than the trace water levels expected in the CO₂ gas stream and reaction solvent.^[29] A small population of a water-reactive species in a pre-equilibrium with 1 could account for this rapid formation of the trihydroxide. However, such a scheme would necessitate a slow approach to equilibrium between 1 and this water-reactive transient, which is not supported by our data here or in previous work. With respect to the as-yet-identified species, the ten resonances associated with this product increased with a rate constant of $8.5(5) \times 10^{-6}$ s⁻¹, assuming the species follows a two-component reaction model. Although the rate constant for formation for the unidentified species is comparable to that of 1-2CO₂, formation of this unknown is readily apparent and discernable across multiple data sets. This product contributes to the electronic absorption data and thus introduces error in determining $k_{2,obs}$ (Table S2). Insofar as the derived rates of consumption and formation of 1 and 1-CO₂ agree across the ¹H-NMR and UV/Visible datasets, we surmise that this unidentified species is a downstream product from 1-CO₂, such as a hydroxidoformatotriiron complex.

To gain further insight into the hydride insertion mechanism, we then examined the CO_2 concentration and the temperature dependencies of $k_{1,obs}$ by UV/Visible spectroscopy. To control the concentration of CO_2 , the solution of **1** was saturated under 1 atm CO_2 , or mixed with CO_2 -saturated toluene solution. The equilibrated CO_2 concentration was calculated using the Henry's law constant,^[30] which we assumed to be obeyed under our experimental conditions. Due to the slow kinetics at low CO_2 concentrations, only the early stages of the reaction can be fitted to a single exponential model. The values of $k_{1',obs}$



determined from the global fit of the absorption at 415–495 nm vs. time data are positively linearly correlated with CO₂ concentration; the first hydride insertion step is first-order in CO₂ and yields a second-order rate constant of 8.4(3) × 10⁻⁴ M⁻¹ s⁻¹ (Figure 3, Figure S5–S8). Eyring analysis for k_1 values determined from UV/Visible spectra recorded over the temperature range 298–303 K affords values of ΔH^{\ddagger} and ΔS^{\ddagger} of 11(1) kcal mol⁻¹ and $-3(1) \times 10$ cal mol⁻¹ K⁻¹, respectively (Figure 4, Figure S9–S11).



Figure 3. Plot of $k_{1,obs}$ determined from UV/Visible spectra vs. [CO₂] reveals a first order dependence on CO₂ for conversion of **1** to **1-CO₂**. $R^2 = 0.9911$. Error bars represent one standard deviation and lie within the data point symbol where not visible.



Figure 4. Eyring plot for k_1 and T for which k_1 was determined by UV/Visible spectroscopy. ΔH^{\ddagger} and ΔS^{\ddagger} were determined as 11(1) kcal mol⁻¹ and $-3(1) \times 10$ cal mol⁻¹ K⁻¹ ($R^2 = 0.9788$). Error bars represent one standard deviation.

We also measured the kinetic isotope effect for the reaction of **1-D**₃ with CO₂ (Figure S12). We similarly fitted UV/Visible spectra vs. time data for **1-D**₃ with CO₂ to an **A** \rightarrow **B** \rightarrow **C** model and calculated pseudo-first order rate constants of 7.6(6) × 10⁻⁵ s⁻¹ for $k_{1,obs}$. The value corresponds to a minimal normal KIE of 1.08(9) for the first hydride insertion event. This result contrasts the inverse KIE reported for insertion of the







Scheme 3. Possible mechanisms for hydride transfer.

terminal hydride into CO₂ by a rhenium hydride complex (0.52– 0.58) or a nickel hydride species (0.61–0.79).^[8,13] Assuming that this differences arises from the greater bond strength of one or both Fe–(µ-H) bonds for the hydride being transferred from **1** to CO₂ as compared to the reported monometallic complexes, we surmise that one or more Fe–H bonds is substantially weakened during hydride transfer to CO₂ (Scheme 3). We note that a direct hydride transfer from the bridging hydride (Scheme 3a) in **1** to CO₂ disagrees with the limited reactivity observed for the bis[β -diketoiminatoiron(II)] di(µ-hydride) and the absence of reactivity for its cobalt congener.^[31–33] We conclude that an opening of the hydride bridge to an asymmetric or terminal mode likely precedes hydride transfer from **1** to CO₂.

The solvent dependence of the hydride transfer reaction in prior systems correlates with the solvent acceptor number (AN), and rate constants for a few of these systems have been reported in a number of solvents.^[34,9,10,12,13] Given that reported reactivity studies have not been conducted in toluene, we first must estimate the value of k in benzene for these reported compounds by determining the linear function correlating AN to rate constant (Entries 1–4 in Table 2, Figure S12). In addition, we assume that benzene and toluene have identical AN values because an AN is not reported for toluene. Our second order rate constant for $1 \rightarrow 1$ -CO₂ is within an order of magnitude of those for the coordinatively saturated second row transition metal complexes estimated in benzene (viz. 2–10 × 10⁻⁴ m⁻¹ s⁻¹). In contrast, our second order rate constant is significantly

smaller than those for the four coordinate nickel hydride pincer complexes (15–3700 M^{-1} s⁻¹; Entries 5–6 in Table 2).^[13]

Of note is the substantial difference in CO₂ reactivity across the Ir series of which all are predicted to traverse an outersphere pathway (Entries 7-9 in Table 2). Ir(H)₃(ENE) reacts \approx 10⁷-fold faster than the related 5-coordinate Ir(H)₂(POCOP) and Ir(H)₂(PCP) compounds.^[11,13] This rate enhancement for Ir(H)₃(ENE) vs. the other Ir examples is attributed to secondary coordination sphere hydrogen bonding interactions between the N-H on the ligand backbone and substrate, thereby orienting CO₂ for hydride transfer and stabilizing the formate product.^[19,20] In addition, exogenous Lewis acids can increase the rate constant for hydride transfer from Ir(H)₃(ENE) to CO₂ whereas added Lewis acids had minimal effect on insertion by Ni(H)(^{tBu}PCP), which operates by an inner sphere mechanism.^[13] Future experiments then in which the effect of exogenous Lewis acids on the rate constant for hydride transfer from 1 to CO₂ can provide additional evidence in support of an outer sphere pathway.

Although tempting to draw conclusions on mechanism as either inner or outer sphere from this literature comparison, this analysis is arguably complicated by the relative bond dissociation free energies for the differing M–H species. We sought then to compare our values to those for reported iron hydride species.^[31,35–40] To our knowledge, no such kinetic study has been reported for an iron hydride complex. We, therefore, estimated the lower limits of the rate constants for selected examples

Table 2	Reported	and	estimated	rate	constants	for	hydride	insertion	into	CO_{α}	
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Entry	Compound	7 [K]	ΔH^{\ddagger} (kcal mol $^{-1}$)	ΔS^{\ddagger} (cal mol ⁻¹ K ⁻¹)	k (m ⁻¹ s ⁻¹)	Ref.
1	Re(H)(bpy)(CO) ₃	298	12.8 ^[d]	-33 ^[d]	$2(1) \times 10^{-4[b,c]}$	[8]
2	[Ru(H)(bpy)(tpy)] ⁺	r.t.	N.A.	N.A.	$1(1) \times 10^{-3[b,c]}$	[9,10]
3	$[Ru(H)(bpy)_2(PPh_3)]^+$	298	N.A.	N.A.	$4(1) \times 10^{-4[b,c]}$	[12]
4	[Ru(H)(bpy) ₂ (PTA)] ^{+ [a]}	298	N.A.	N.A.	$6(3) \times 10^{-4[b,c]}$	[12]
5	Ni(H)(^{tBu} PCP)	298	6.3 ^[d]	-33 ^[d]	15(2) ^[b]	[13]
6	Ni(H)(^{Cy} PCP)	298	3.0 ^[b]	-31 ^[b]	$3.7(4) \times 10^{3[b]}$	[13]
7	Ir(H) ₃ (ENE)	298	11.1 ^[b]	-6 ^[b]	$2.0(2) \times 10^{3[b]}$	[13]
8	Ir(H) ₂ (POCOP)	208	N.A.	N.A.	$4.4(2) \times 10^{-4[d]}$	[11]
9	Ir(H) ₂ (PCP)	208	N.A.	N.A.	$1.00(8) \times 10^{-2[d]}$	[11]
10	$Fe_3(\mu-H)_3L$	298	11 ^[e]	-30 ^[e]	$8.4(3) \times 10^{-4[e]}$	this work

[a] PTA = 1,3,5-Triaza-7-phosphaadamantane. [b] In benzene. [c] Determined by extrapolation from reported AN dependence. [d] In THF. [e] In toluene.





based on reported yields and reaction times, cognizant of the limitations. To account for the solvent effect and possible differences in CO₂ concentration in the reaction, we also only considered those cases in which the reaction solvent has an AN smaller than benzene and the reaction mixture was saturated with and executed under 1 atm CO₂ at room temperature. The diiron complexes with bridging hydrides reported by Holland and Limberg react with two equivalent of CO₂ to form two µ-1,3-formate donors over a 20 h reaction time,[31,35] corresponding to estimated pseudo first order rate constants of which are approximately an order of magnitude faster than our case for the combined first and second hydride transfer steps. The CO₂ insertion rates of these reported hydridoiron β -diketiminate complexes are themselves two orders of magnitude smaller than those for pincer complexes; for example, one (PNP)FeCO dihydride complex reacts to completion within 25 min and has been calculated to proceed by an outer-sphere pathway.^[36,37] The tripodal phosphane-ligated iron hydride reacts to completion with CO₂ in 12 h; the lower limit for the estimated rate constant is comparable to 1.^[38] The related $C_{3\nu} P_3 E$ iron hydride complexes (E = B, N, Si) exhibit 10- to 100-fold faster reaction rates compared to our case. Finally, Field reported octahedral cis-Fe(dmpe)₂H₂ (dmpe= Me₂PCH₂CH₂PMe₂) for which the reaction with CO₂ is complete within 1 min.^[39,40] Notably, the complexes with ligands with stronger trans effect afford larger rate constants. Unfortunately, we do not observe a discernable trend in reaction rate as a function of coordination number, oxidation state, or spin state of the iron centers, within the bounds of our analysis.

Drawing parallels to the diiron dihydride complexes reported by Holland, we recall the proposed pathways for H/D scrambling in which Fe–H–Fe motifs partially open to afford a terminal Fe–H.^[41] This transient open conformer has been implicated as the reactive species, facilitating hydride transfer to a variety of substrates. Relatedly, reaction of **1** with CO results in an intramolecular H₂ reductive elimination to generate a [Fe₃(µ₃-H)-(CO)₂]³⁺ cluster. With these precedent in mind together with the observed normal KIE, we propose that a similar cleavage of one Fe–H bond in an Fe–H–Fe unit occurs prior to hydride transfer to CO₂. Fluxional coordination of and access to terminal iron hydrides in **1** are potentially an integral part of the substrate specificity and reactivity of **1** with substrates.

Conclusions

We have reported a kinetic analysis of insertion of a bridging hydride in the triiron complex (**1**) into CO₂ by in situ ¹H NMR and temperature-controlled UV/Visible spectroscopy. From these combined datasets, we calculate a second-order rate constant of $8.4(3) \times 10^{-4} \text{ m}^{-1} \text{ s}^{-1}$ for this reaction, as well as a KIE for H/D insertion of 1.08(9) and activation parameters of ΔH^{\ddagger} of 11(1) kcal mol⁻¹ and ΔS^{\ddagger} of $-3(1) \times 10$ cal mol⁻¹ K⁻¹. The primary KIE value is consistent with the proposed opening of μ -hydrides prior to hydride transfer to CO₂ in related diiron dihydride complexes. Such fluxional coordination of bridging hydrides in the weak-field regime agrees with our earlier proposed pathway for H₂ reductive elimination upon reaction of **1**

with CO. Our findings also align with the proposed outer sphere pathway for hydride insertion from the E_2 state of FeMoco into CO₂ elucidated from DFT.^[25] Mechanistic studies for the reaction of hydrides in **1** with other substrates will be important to elucidate the mechanisms of reaction of weak-field ligated iron hydride complexes.

Experimental Section

General Considerations: All manipulations except ligand synthesis were performed in a N₂-filled Innovative Technologies glovebox or at a CO₂-filled and purged vacuum gas manifold by Schlenk techniques. Tetrahydrofuran (THF), benzene, toluene, and n-hexane were purchased from Sigma-Aldrich, then purified through drying columns from Innovative Technologies, and stored over activated 3A molecular sieves. [D₆]Benzene and [D₈]toluene were purchased from Cambridge Isotope Laboratories, dried with CaH₂ under reflux, then distilled and degassed and stored over 3A molecular sieves. Fe_3H_3L (1) and $Fe_3H_2(HCO_2)L^{Et/Me}$ (1-CO₂) were prepared by published procedures.^[27] ¹H Nuclear Magnetic Resonance (¹H NMR) spectra were recorded on a 500 MHz Varian Inova spectrometer or a 300 MHz Mercury spectrometer equipped with a three-channel 5 mm indirect detection probe with z-axis gradients. Chemical shifts were reported in δ (ppm) and were referenced to solvent resonances $\delta H = 7.16$ ppm for [D₆]benzene, 2.08 ppm for [D₈]toluene. Fourier Transform Infrared (FT-IR) spectra were recorded as solids on a Thermo Fisher iS5 instrument using also equipped with an ATR diamond crystal stage using OMNIC software package.

NMR Spectroscopic Monitoring of Reaction Kinetics: 1 in $[D_8]$ toluene (11 mM, 0.408 mL) and a capillary charged with hexamethylbenzene standard solution were transferred to a resealable J-young NMR tube, and the tube was degassed by 5 cycles of freeze-pump-thaw. In the meantime, a 50-mL Schlenk flask connected to the NMR tube through 3-way valve was evacuated. After evacuation, the Schlenk flask was charged with CO₂ and brought together with the NMR tube connected. CO₂ gas was charged to the headspace of NMR tube and shaken several times just before starting measurements. Equilibrated CO₂ concentration was determined by following equation:

$$[CO_2]_{eqm} = n_{CO_2, \ total} \gamma_{soln} / V_{soln}$$

$$\gamma_{soln} = 1/(1 + \mathcal{H}(V_{head} + V_{flask})/n_{solv}RT)$$

Where *R*, γ_{soln} , V_{soln} , V_{head} , V_{flask} , n_{solv} are the ideal gas constant, the ratio of CO₂ remained in solution, volume of the solution, head-space volume of the J-young NMR tube, volume of the Schlenk flask, and mol of solvent, respectively. The Henry constant, H, of toluene is 9.11 × 10⁶ Pa at 293 K.^[30]

NMR spectra was measured upto 7 days at logarithmic time interval. Every spectrum was measured with the same power, gain, and shimming parameters. After phase correction and setting reference peak, baseline was corrected by Whittaker smoother method (Filter: 50, 28.57 Hz; Smooth factor: 10^{6}) provided by MestReNova 8.1. Identical integration ranges were used for all spectra, and absolute integral values were collected in a spreadsheet. Since the baseline correction gave negative integration values for the peaks in -18-11 ppm, second baseline correction was done with the same method but with different parameters (Filter: 50, 28.57 Hz; Smooth factor: 3×10^{4}). Absolute integration values (y) over time (t) were





plotted for each integration range and fitted using one of the following equations:

For
$$A \to B \to C \mod l^{[42]}$$

 $A = C_A \exp(-k_1 t)$
 $B = C_B \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)]$
 $C = C_c \{1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)]\}$

Where A, B, and C are types of integration values over time following the starting, intermediate, and product kinetic models for 2 step irreversible reactions, $C_{A\nu}$ $C_{B\nu}$ and C_C are arbitrary constant, and k_1 and k_2 are the pseudo-first-order rate constants or each reaction step.

UV/Visible Kinetic Experiments: A Cary 50 spectrophotometer, equipped with a temperature-controlled Unisoku single-cell accessory (± 0.1 °C) was used for all kinetics experiments. All measurements were performed in Schlenk-adapted cuvettes with a 1 cm optical path length, and baseline of which were corrected by the spectra of pure toluene solvent at the same temperature. The two standard procedures for sample preparation are described below.

(1) Variable concentration: A saturated CO_2 solution in toluene (98 mM, 2 mL) was added to a stock solution of **1** in toluene (0.41–1.2 mM, 1–2 mL) with a magnetic stir bar in a Schlenk cuvette, which was sealed with a glass stopper in the glovebox and placed in the UV/Vis apparatus. Equilibrated CO_2 concentration was determined by following equation:

$$[CO_2]_{eqm} = n_{CO_2, total} \gamma_{soln} / V_{soln}$$

 $\gamma_{soln} = 1/(1 + \mathcal{H}V_{head}/n_{solv}RT)$

Where *R*, γ_{soln} , *V*_{soln}, *V*_{head}, *n*_{solv} are the ideal gas constant, the ratio of CO₂ remained in solution, volume of the solution, headspace volume of the Schlenk cuvette, and mol of solvent, respectively. The Henry constant, H, of toluene is 9.705×10^6 Pa at 298.15 K.^[30]

(2) Variable temperature: A stock solution of **1** in toluene (0.41 mM, 2 mL) and a magnetic stir bar were transferred to a solid addition tube, which was sealed with a Schlenk cuvette in the glovebox. After 5 cycles of freeze-pump-thaw, the solution in the tube was transferred to the Schlenk cuvette, and the cuvette was placed in the UV/Vis apparatus. Multiple UV/Vis spectra were measured until they converged by temperature stabilization. CO_2 gas was introduced to the evacuated headspace just before starting a measurement and the flow was maintained for an hour to saturate the solution with CO_2 under atmospheric pressure. Concentration of saturated CO_2 was calculated by following equation:

 $\ln x_{CO_2} = -13.921 + 1547.7/(T/K) + 0.72764 \ln(T/K)$

Where T range is 203.2–316.2 K and standard deviation of x_{CO_2} is 0.00128.^[30]

UV/Vis spectra were recorded between 1000 and 400 nm with a 600 nm/min scan rate at 10–15 min intervals by an hour, at 30 min intervals by a day, and at 240 min intervals up to 3 days. The interval time and measurement time were varied depending on the reaction temperature. The first points up to 1 hours were discarded as the temperature or the concentration of carbon dioxide had not been equilibrated. Kinetic traces for each reaction were generated by plotting absorbance (y) vs. reaction time (t) at the peak wavelengths selected within 415–495 nm, which were analyzed using Origin

v.8.5. These data were globally fit to the general first-order integrated kinetic equations for one- or two-step irreversible reactions with the shared rate constants:

For
$$A \rightarrow B$$
 models,
 $Abs_{total}(t) = Abs_A(t) + Abs_B(t)$
 $= [A]_0\epsilon_A \exp(-k_1t) + [A]_0\epsilon_B[1 - \exp(-k_1t)]$

and for $A \rightarrow B \rightarrow C$ models,^[42] $Abs_{total}(t) = Abs_A(t) + Abs_B(t) + Abs_C(t)$ $= [A]_0\epsilon_A \exp(-k_1t) + [A]_0\epsilon_B \frac{k_1}{k_2 - k_1} [\exp(-k_1t) - \exp(-k_2t)]$ $+[A]_0\epsilon_C \{1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1t) - k_1 \exp(-k_2t)]\}$

Where $[A]_0$, ε_A , ε_B and ε_C are initial concentration of the starting material and absorption constants of each A, B and C species at specified wavelength, and k_1 and k_2 are same as above.

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