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Mechanistic Insight through Factors Controlling Effective Hydrogenation of CO_2 Catalyzed by Bioinspired Proton-Responsive Iridium(III) Complexes

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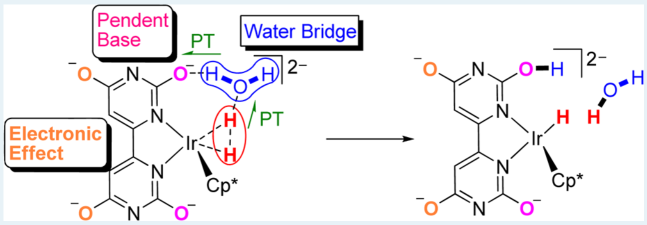
Ⓢ *Supporting Information*



ABSTRACT: Reversible H_2 storage near room temperature and pressure with pH as the "switch" for controlling the direction of the reaction has been demonstrated (*Nat. Chem.*, **2012**, *4*, 383−388). Several bioinspired "proton-responsive" mononuclear Ir(III) catalysts for CO_2 hydrogenation were prepared to gain mechanistic insight through investigation of the factors that control the effective generation of formate. These factors include (1) kinetic isotope effects by water, hydrogen, and bicarbonate; (2) position and number of hydroxyl groups on bpy-type ligands; and (3) mono- vs dinuclear iridium complexes. We have, for the first time, obtained clear evidence from kinetic isotope effects and computational studies of the involvement of a water molecule in the rate-determining heterolysis of H_2 and accelerated proton transfer by formation of a water bridge in CO_2 hydrogenation catalyzed by bioinspired complexes bearing a pendent base. Furthermore, contrary to expectations, a more significant enhancement of the catalytic activity was observed from electron donation by the ligand than on the number of the active metal centers.

KEYWORDS: *proton-responsive iridium complexes, CO_2 hydrogenation, formate, deuterium kinetic isotope effect, proton relay*

The investigation of proton transfer at the molecular level is of great interest owing to its involvement in numerous transformations involving hydrogen, especially in energy-related hydrogen storage. Enzymes such as hydrogenases use proton channels, consisting of multiple proton relays, to facilitate proton transfer between the active site and surroundings.[1−3] Mimicking the active site of [FeFe] and [FeNi] hydrogenase, DuBois et al. have made significant advances in developing synthetic complexes and understanding the proton transfer mechanism assisted by pendent amines.[4−6] It has been demonstrated that the pendent amines in the second coordination sphere act as proton relays and help the facile and precise transfer of protons between the metal center and substrate.[7−10] Moreover, such an effect can reduce the energy barrier for heterolysis or formation of H_2.[11−13] Recently, a 2-pyridonate unit has been discovered in a [Fe]-hydrogenase that is known as H_2-forming methylenetetrahydromethanopterin dehydrogenase (Hmd).[14,15] Yang and Hall have demonstrated by DFT calculations that the oxo group of 2-pyridonate adjacent to the coordination site can aid dihydrogen cleavage through hydrogen bonding.[16] The study of bioinspired synthetic catalysts with a 2-pyridonate or bipyridonate unit by Yamaguchi et al. and Papish et al. have identified experimentally the important role of the adjacent hydroxyl group in proton-transfer-related reactions.[17−19]

Our 4DHBP complex **1** (4DHBP = 4,4′-dihydroxy-2,2′-bipyridine, Chart 1) has been demonstrated to be highly efficient for CO_2 hydrogenation in aqueous solution owing to the strong electron-donating ability of the oxyanions upon the deprotonation of the hydroxyl groups. Most recently, inspired

Chart 1. Iridium Complexes for Hydrogenation of CO_2

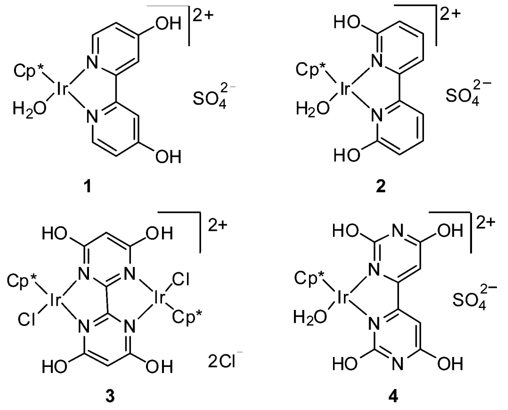


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Table 1. Hydrogenation of CO_2 to Formate with Ir Catalysts[a]

entry	cat./concn (μM)	time (h)	pressure (MPa)[b]	temp (°C)	init TOF (h^{-1})[f]	TON	final [formate] (M)
1[c]	1/50	24	0.1	25	7	92	0.005
2[c]	2/50	33	0.1	25	27	330	0.016
3[c]	2/20	9	1.0	50	1 650	5 150	0.103
4[d]	3/50	336	0.1	25	64	7 200	0.360
5[d]	3/20	8	1.0	50	4 200	24 000	0.480
6[e]	4/50	24	0.1	25	66	193	0.009
7	4/20	24	1.0	50	3 060	28 000	0.560
8	4/10	8	3.8	50	11 100	38 400	0.384
9[e]	4/20	8	3.0	80	33 300[g]	34 300	0.687

[a] The reaction was carried out in 1 M $NaHCO_3$ unless otherwise noted. [b] Total pressure of the gas mixture (H_2/CO_2 = 1:1, v/v) used. [c] Ref 20. [d] Ref 21. [e] The reaction was carried out in 2 M $KHCO_3$. [f] Average rate over initial 1 h. [g] Average rate over initial 100 min.

by the important role of the hydroxyl group adjacent to the metal center in [Fe]-hydrogenase, we modified our 4DHBP catalyst **1** by changing the position of the hydroxyl groups from para to ortho (complexes **2** and **3**, Chart 1),[20,21] resulting in a significant improvement in the CO_2 hydrogenation catalytic activity in aqueous solution. While **3** is isolated as a Cl coordinated species, the Cl ions readily dissociate in water to form the aqua complex. The catalytic activity increases 4 times and 10 times from **1** to **2** and **1** to **3**, respectively. Our theoretical studies have demonstrated that the adjacent oxyanion can function as a pendent base and accelerate the rate-limiting heterolysis of dihydrogen to produce Ir−H.[20] A question arises upon further comparison of the activity of complexes **2** and **3**: Is the difference in catalytic activity between **2** and **3** due to the presence of two active metal centers or the stronger electron-donation effect of the four oxyanions in **3**? To understand the factors controlling the catalytic activity of CO_2 hydrogenation, we have designed and synthesized a new catalyst, **4**, that incorporates the synergistic effect of electron donor and pendent base activation while retaining a mononuclear Ir complex.

In addition, it is well recognized that proton transfer through channels formed by water is the dominant pathway in biological processes.[22,23] Our quest for a more detailed mechanistic understanding has prompted us to investigate the possible cooperation of solvent (i.e., water) in the proton transfer process. Water has been recognized as an ideal solvent for CO_2 hydrogenation because it is abundant, inexpensive, and environmentally benign. The addition of a small amount of water to benzene as an organic solvent was observed to promote CO_2 hydrogenation by $Pd(diphos)_2$ (diphos = $Ph_2PCH_2CH_2PPh_2$) some time ago.[24] The promoting effect of water has been proposed to arise from the stabilizing effect of an intramolecular hydrogen bond between the aqua ligand and an oxygen of the approaching CO_2.[25,26] Musashi and Sakaki demonstrated through calculations that the acceleration stemmed from the trans effect of a coordinated H_2O ligand, but was not caused by a hydrogen bond.[27] Hydrogen bonding of the incoming CO_2 to external water has also been proposed by Lau et al.[28]

Although several mechanisms involving water have been proposed and studied,[29,30] the rate-accelerating effect of water is not yet unambiguously understood. The role of water is also unknown for the significantly accelerated H_2-production rate (TOF above 100 000 s^{-1}) using hydrogenase-model complexes, such as a synthetic Ni electrocatalyst by addition of water to the acetonitrile solution.[6] Many reports on catalytic CO_2 hydrogenation in water using water-soluble catalysts have been published;[31−39] however, the involvement of a water molecule to produce a proton-transfer channel in the rate-determining step in CO_2 hydrogenation has not been reported either experimentally or theoretically.

Herein, we report (1) clear evidence from combined experimental and computational studies of the involvement of a water molecule in the rate-determining heterolytic H_2 splitting and enhancement of proton transfer by forming a water bridge in CO_2 hydrogenation catalyzed by bioinspired complexes bearing a pendent base; and (2) similar catalytic activities of **3** and **4** toward CO_2 hydrogenation owing to a more significant enhancement from electron donation by the ligand than on the number of the active metal centers.

■ HYDROGENATION OF CO_2 WITH Ir COMPLEXES

The new complex **4** was synthesized according to our previously reported process (see the Supporting Information).[21] It was then utilized in the homogeneous hydrogenation of CO_2 in aqueous bicarbonate solutions at relatively low temperatures and pressures. The results are summarized in Table 1. Whether at ambient conditions (25 °C, 0.1 MPa) or at higher pressure and temperature, the initial TOF of complex **4** is double that of complex **2** (entries 2 and 3 vs 6 and 7). Complex **4** bearing four hydroxyl groups showed higher activity than **2**, which has only two hydroxyl substituents. The reaction rate of **4** (TOF: 66 h^{-1}) is comparable to the previously known most effective complex **3** at ambient conditions (entries 4 and 6).[21] At 50 °C and 1 MPa of H_2/CO_2, the mononuclear complex **4** also showed activity (TOF: 3060 h^{-1}) similar to that of the dinuclear complex **3** (TOF: 4200 h^{-1}, entries 5 and 7). Moreover, a high turnover of 28 000 and high concentration of formate product (0.56 M) were obtained after 24 h. The high activity of complex **4** indicates that it is among the most effective catalysts of CO_2 hydrogenation under mild conditions. Temperature and pressure have a significant impact on the reaction rate. When the pressure was increased from 1 to 3.8 MPa, the TOF was enhanced more than 3-fold (entry 8). At elevated temperature and pressure (3 MPa, 80 °C), **4** achieved the highest initial TOF of 33 300 h^{-1} and gave a high concentration of formate of 0.687 M after 8 h (entry 9) under the given conditions. In addition, from Arrhenius plots, complexes **3** and **4** showed similar activation energies of 49.5 and 49.9 kJ/mol, respectively (see the Supporting Information, Figure S1). These results clearly demonstrate that the electron-donating effect of the substituents is more important for catalytic activity than the number of catalytically active metal centers.

Table 2. Kinetic Isotope Effect in the Hydrogenation of CO_2 Catalyzed by Ir Complexes[a]

				complex **1**[b]		complex **2**[b]		complex **4**[b]	
entry	gas (1/1, 1 MPa)	reaction soln (2 M)	product	TOF, h^{-1}	KIE[c]	TOF, h^{-1}	KIE[c]	TOF, h^{-1}	KIE[c]
1	H_2/CO_2	$KHCO_3/H_2O$	HCO_2K	683		1730		2730	
2	H_2/CO_2	$KDCO_3/D_2O$	HCO_2K	697	0.98	1520	1.14	1800	1.51
3	D_2/CO_2	$KHCO_3/H_2O$	DCO_2K	572	1.19	1610	1.07	1990	1.37
4	D_2/CO_2	$KDCO_3/D_2O$	DCO_2K	570	1.20	1360	1.27	1190	2.29

[a] The reaction was carried out with catalyst (0.2 μmol) in 10 mL bicarbonate solution (2 M) under 1 MPa H_2/CO_2 or D_2/CO_2 (1/1) at 50 °C for 1 h. [b] Errors of TOFs and KIEs are typically less than 2% and 4%, respectively. [c] KIE = TOF(entry 1)/TOF(entry *n*), (*n* = 2, 3, and 4).

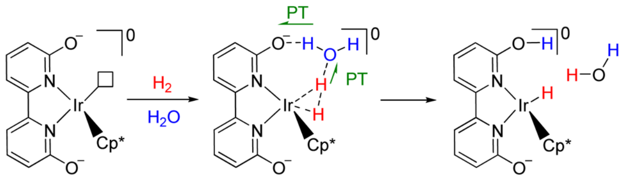
MECHANISTIC STUDIES

As we previously reported, the CO_2 hydrogenation first proceeds through the heterolysis of H_2 (assisted by a pendent base in complexes **2** and **3**) to form an Ir−H species.[20,21] This is followed by CO_2 insertion into the Ir−H bond to give a formato complex. The dissociation of formate is accompanied by the addition (via heterolysis) of H_2 to reinitiate the catalytic cycle. The Ir−H species of **2** and **4** were detected with ^1H NMR ($\delta = -10.56$ and -10.32 ppm, respectively) by adding high-pressure H_2 under basic conditions (see the Supporting Information, Figure S2). To gain further mechanistic insight, we investigated the kinetic isotope effect with our catalysts. To our knowledge, a deuterium kinetic isotope effect in the hydrogenation has not yet been reported. This may be due to the fact that the D_2/CO_2 gas mixture is not readily available. Because our complexes not only serve as catalysts for hydrogenation of CO_2 to formate, but also can catalyze the reverse reaction—the reaction of formic acid (under slightly acidic conditions)—we have recently reported a convenient method to obtain D_2/CO_2 gas mixtures from the decomposition of DCO_2D in D_2O with our 4DHBP catalyst **1**.[40] Consequently, this method of D_2/CO_2 generation was employed to study the deuterium isotope effect in the hydrogenation of CO_2. The D_2/CO_2 (1/1) mixture was generated from a degassed DCO_2D/D_2O solution of 4DHBP catalyst **1** in a stainless autoclave (see the Supporting Information). The pressure of the gas mixture was controlled by adjusting the temperature to change the dehydrogenation rate. The released gases were analyzed by GC, which indicated that the ratio of D_2 to CO_2 is 1:1 and the purity of D_2 is up to 98% (2% HD, see the Supporting Information, Figure S3). The gas generation system was connected to a hydrogenation system in which the pressure was adjusted by a backpressure regulator (1 MPa). The hydrogenation was carried out in 2 M bicarbonate solution (10 mL) with complexes **1**, **2**, and **4** (0.2 μmol) at 50 °C for 1 h. The reaction results are listed in Table 2. The product concentration was detected by HPLC and confirmed by ^1H NMR using DSS (sodium 3-(trimethylsilyl)-1-propanesulfonate) as an internal standard (see the Supporting Information, Figure S4). By comparing the concentration determined by ^1H NMR and HPLC, the main product was identified. DCO_2K in entry 2 and HCO_2K in entry 3 were found to be less than 5%.

As shown in Table 2, when D_2/CO_2 (entry 3) was used instead of H_2/CO_2 (entry 1), the rate of the reaction in an aqueous solution of $KHCO_3$ decreased markedly (KIE = 1.19, 1.07, 1.37 for complexes **1**, **2**, and **4**, respectively; Table 2, entry 3). The observed KIEs represent a composite of the individual isotope effects for both heterolysis of D_2 to form Ir−D and CO_2 insertion into Ir−D to generate Ir−ODCO. Therefore, it is not possible to identify the rate-determining step by analysis of the KIE on the TOF alone. Since the rate-determining step has been previously predicted by DFT calculations[20] to be the heterolytic cleavage of H_2, we expect the heterolysis of D_2 to contribute largely to the observed KIE. Interestingly, we found a special effect of D_2O for different complexes when D_2O was used in reaction with H_2/CO_2 or D_2/CO_2. Heavy water had almost no effect on the reaction rate when 4DHBP complex **1** was used (entries 1 vs 2, and entries 3 vs 4 for complex **1**) In contrast, it showed a remarkable influence on the reaction rate when complexes **2** and **4** were used. The reaction was significantly inhibited by replacing H_2O with D_2O in either reaction using H_2/CO_2 or D_2/CO_2 (entries 1 vs 2, and entries 3 vs 4, for complexes **2** and **4**, respectively). In addition, the reaction rate decreased markedly with an increase in the D fraction in the reaction solution (see the Supporting Information, Figure S5). When the reaction was carried out with D_2/CO_2 in $KDCO_3/D_2O$, we obtained the lowest TOF, which indicates the dual effect of deuterated gas and solvent. Comparing the KIE data for **1** with those for **2** and **4**, we can conclude that heavy water is involved in the rate-limiting heterolysis of dihydrogen for complex **2** and **4** but not for 4DHBP complex **1**.

The assistance of water on the splitting of H_2 has been predicted computationally.[41−44] Our previous studies have demonstrated that the rate-determining step of the CO_2 hydrogenation is the heterolysis of H_2, and it was significantly enhanced by the pendent base through a second-coordination-sphere effect.[20] As our KIE experiments described above suggest, the solvent effect of D_2O has a remarkable influence on the reaction rate, most likely through participation in the rate-determining step. Accordingly, we propose that a solvent molecule (i.e., H_2O) may form hydrogen bonds with the pendent base and the approaching H_2 along the reaction coordinate for heterolysis and participate in the proton transfer to the pendent base heterolysis (Scheme 1). The participation of H_2O could stabilize the transition state and facilitate the heterolysis of H_2, which is further demonstrated by DFT calculations.

Scheme 1. Proposed Mechanism for H_2 Heterolysis Assisted by the Pendent Base and Water Molecule through a Proton Relay[a]



[a] The green arrows indicate the movement of protons via a proton relay. The open square indicates a vacant coordination site.

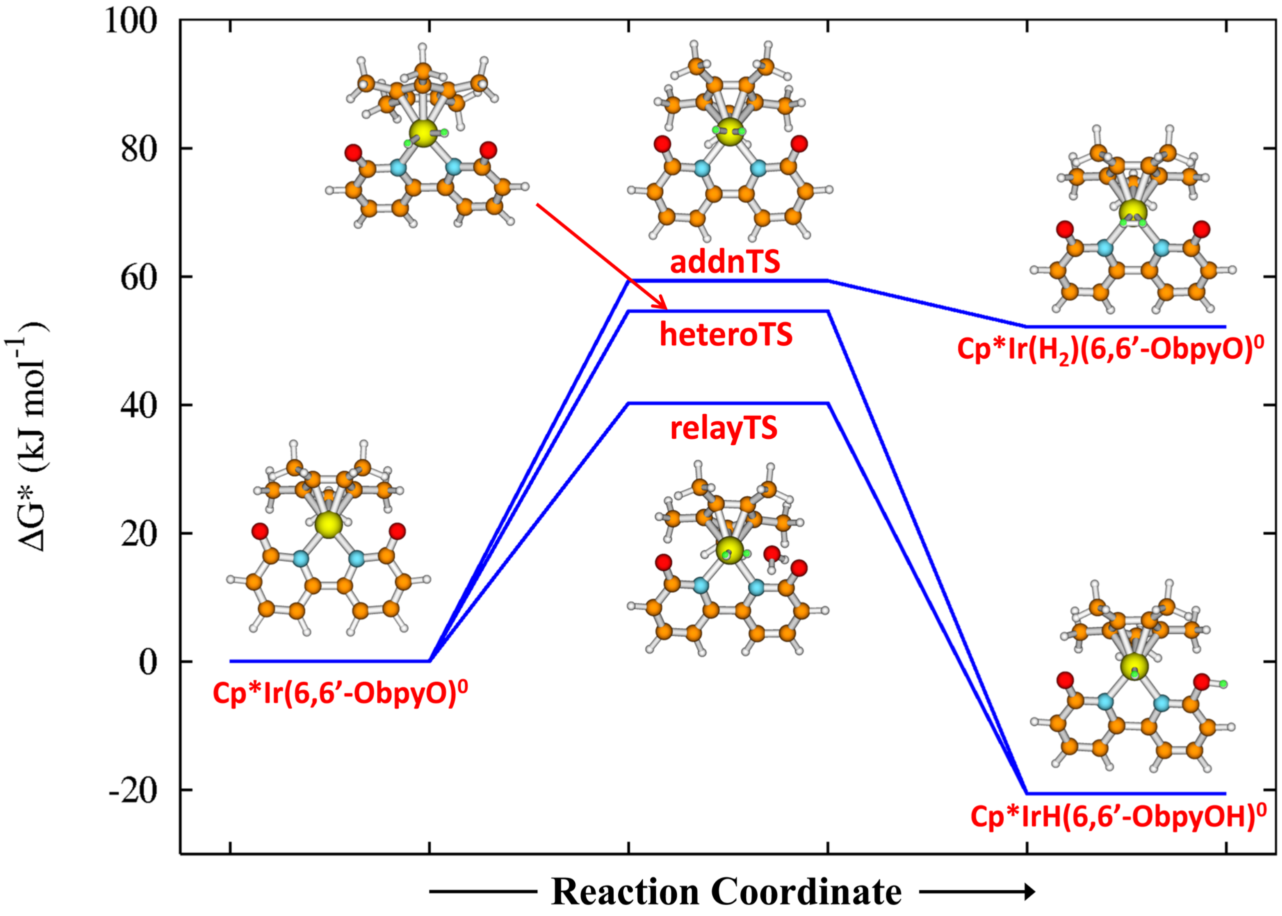


Figure 1. The relative free-energy profiles for H_2 addition to the Ir center to form a dihydrogen complex via the "addnTS" transition state, H_2 heterolysis to form the Cp*IrH(6,6′-ObpyOH) complex via the "heteroTS" transition state, and water-assisted H_2 heterolysis to form the Cp*IrH(6,6′-ObpyOH) complex via the "relayTS" transition state. The hydrogen atoms corresponding to the reactant H_2 are tinted green. Larger pictures of the structures are presented in Figure S6 of the the Supporting Information.

THEORETICAL STUDIES OF THE REACTION MECHANISM

The reactant H_2 molecule was assigned a gas-phase standard state, and the participating H_2O molecule was assigned the standard state of the pure liquid (see the Supporting Information for details). Because it is well-known that the entropy in solution is overestimated by gas-phase calculations, the gas-phase translational entropy was omitted from the free energy of all species in solution and for the solvent H_2O.[30] This consideration has a negligible effect on the free energy of activation and reaction involving the addition of H_2 to the active form of the catalyst owing to cancellation of similar corrections, but it has a substantial effect on the free energy of $H_2O_{(liq)}$, for which the correction (correctly) removes most of its gas-phase entropy.

Using Cp*Ir(6,6′-ObpyO)^0 (the first structure in Scheme 1) as a prototype, we identified three different transition states and pathways to two reaction intermediates resulting from the reaction of Cp*Ir(6,6′-ObpyO)^0 and H_2 (Figure 1). One of these corresponded to the formation of a dihydrogen adduct to the Ir center via a dihydride transition state (addnTS). This pathway had an activation free energy of 59.3 kJ mol^{-1} and a reaction free energy of 52.1 kJ mol^{-1} relative to Cp*Ir(6,6′-ObpyO)^0 and H_2 gas. The pathway for direct heterolysis of H_2 to form Cp*IrH(6,6′-ObpyOH)^0 via a second coordination sphere interaction with the pendent base (heteroTS) was found to be more energetically favorable than the formation of a dihydrogen adduct, having an activation free energy of 54.6 kJ mol^{-1} and a reaction free energy of −20.6 kJ mol^{-1}. Moreover, the calculations predicted the water-assisted heterolysis pathway shown in Scheme 1 and Figure 1 (relayTS) to have the even lower activation free energy (relative to Cp*Ir(6,6′-ObpyO)^0, H_2 and $H_2O_{(liq)}$) of 40.3 kJ mol^{-1}. This result supports the hypothesis that solvent water is involved in the rate-determining step of H_2 heterolysis. The energetics and structures along these pathways are shown in Figure 1 (larger structures are presented in Figure S1, and key geometric parameters are listed in Table S1 of the the Supporting Information). An animation of the normal mode corresponding to the imaginary frequency (981*i* cm^{-1}) of the relayTS is available as a .pptx file in the the Supporting Information.

In summary, our experimental mechanistic studies with D_2O, D_2, and $KDCO_3$ have clearly demonstrated for the first time that water is involved in the rate-limiting step and significantly accelerates heterolysis of H_2 for complexes **2** and **4** that have pendent bases near the metal center, but not for the 4DHBP complex **1**. The theoretical studies also predict that proton transfer proceeds through a hydrogen-bonding network involving a water molecule and the pendent oxyanion and can lower the barrier for H_2 heterolysis. Comparison between mononuclear and dinuclear complexes with four hydroxyl groups (**4** and **3**, respectively) shows that the catalytic activity is not significantly affected by the number of metal centers.

Comparison between mononuclear complexes with two and four hydroxyl groups (**2** and **4**, respectively) demonstrates that more hydroxyl groups in ortho and para positions to the coordinating N atoms that donate electrons produce more effective catalysis of CO_2 hydrogenation.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental details, including KIE measurements and synthesis, Arrhenius plot of hydrogenation of CO_2, ^1H NMR charts of Ir-hydride for complexes **2** and **4**, GC analysis of D_2 gas generated from dehydrogenation of DCO_2D in D_2O, ^1H NMR of hydrogenation products, plot for hydrogenation reaction rate vs *D* fraction, computational details, calculated structures and Cartesian coordinates of key intermediates, and animation of the normal mode corresponding to the imaginary frequency ($981i$ cm^{-1}) of the relayTS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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