Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Direction to Practical Production of Hydrogen by Formic Acid Dehydrogenation with Cp*Ir Complexes Bearing Imidazoline Ligands

Naoya Onishi,[a] Mehmed Z. Ertem,[b] Shaoan Xu,[a] Akihiro Tsurusaki,[a,c] Yuichi Manaka,[c,d] James T. Muckerman,[b] Etsuko Fujita,[b] and Yuichiro Himeda*[a,c,d]

[a] National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan

[b] Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000, United States

[c] Renewable Energy Research Centre, National Institute of Advanced Industrial Science and Technology, 2-2-9 Machiikedai, Koriyama, Fukushima, 963-0298, Japan

[d] CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Experimental section

General. Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques or in a glovebox, and all aqueous solutions were degassed prior to use. The pH values were measured by an Orion 3-Star pH meter with a glass electrode after calibration with standard buffer solutions. The amount of released gases was measured by a wet gas meter (Shinagawa Corp., W-NK-05; test limit: 1 mL) which is of the volumetric positive displacement type. The pressure of the gases generated from the dehydrogenation of FA in a closed system was monitored by a Swagelok pressure transducer (S model, PTI-S-MG16-22AQ). The content of the released gases was analyzed by a 490 Micro GC (Agilent Tech.). CO was detected using an FID equipped by a GL Science GC-390 gas chromatograph with a methanizer using a Porapak Q 80/100 column at 50 °C. Formate concentrations were monitored by an HPLC on an anion-exclusion column (Tosoh TSK gel SCX(H^+)) using aqueous H_3PO_4 solution (20 mM) as eluent and a UV detector ($\lambda = 210$ nm). Water used in the reactions was obtained from a Simplicity water purification system. Complexes **C1-C2**,[1] **C3**,[2] **C4-6**[3] were synthesized according to the previous reports.

General procedure for catalytic dehydrogenation of FA/formate: A freshly prepared 5 mM solution of catalyst (200 μL) was added to a deaerated aqueous HCO_2H (FA)/HCO_2Na (SF) solution, and the mixture was stirred at the desired temperature. The volume of released gases was determined by a wet gas meter. The TOF was determined according to the released gases. The average TOF of the initial 10 min was adopted for the initial TOF. After the reaction completed, the residual FA in the solution was quantified with HPLC. The TON was calculated based on the catalyst loading and concentration of residual FA or formate. Their errors are less than 5% under the same conditions of temperature and atmospheric pressure.

Procedure for durability test of complex C4: A freshly prepared 10 mM solution of **C4** (1.0 mL, 10 μmol) was added to a deaerated 10 M aqueous FA solution (1 L, 10 mol FA), and the mixture was stirred at 50 °C. After 114 h, when the volume of released gases exceeded 408 L, the reaction solution was cooled in an ice bath to suspend the dehydrogenation. A degassed aqueous solution of FA (460 g) in 100 mL of water was added to the reaction solution. The mixture solution was warmed to 50 °C, and the gas release restarted. After 363 h, FA was not detected in the reaction solution by HPLC. Finally, 1.018 m^3 of gases was evolved and afforded a total TON of 2,000,000.

Procedure for catalytic dehydrogenation of FA in a closed system: A high-pressure glass cylinder (Hiper Glass Cylinder, Taiatsu Techno Co., 100 mL, Max. 3 MPa) equipped with a pressure transducer and a back pressure valve (set at 1 MPa) was charged with **C4** (2 μmol) and a freshly degassed 8 M FA solution (80 mL). The apparatus was flushed with Ar and sealed. After it was transferred into a water bath of 60 °C, the reaction was started by vigorously stirring. The internal pressure was recorded automatically. The induction period is due to the slowly increasing temperature of the reaction solution. After the pressure reached to 1 MPa, the volume of the released gases through the back pressure valve was measured by a wet gas meter. At the end of the reaction, the residual FA in the solution was quantified with HPLC.

General Procedure for NMR study of Ir-H complex: To **C4** (2.0 mg, 3.4 μmol) solid in a NMR tube under Ar was added the 1.4 mL of SF solution in D_2O (3.6 mM) in an ice bath. After 1 hr, the mixture was measured by a ^1H NMR spectrum. After the appearance of the peak derived from an Ir-H complex was confirmed, 100 μL of D_2SO_4 solution in D_2O (2 M) was added to the **C4**/SF solution, and then a ^1H NMR measurement was taken.

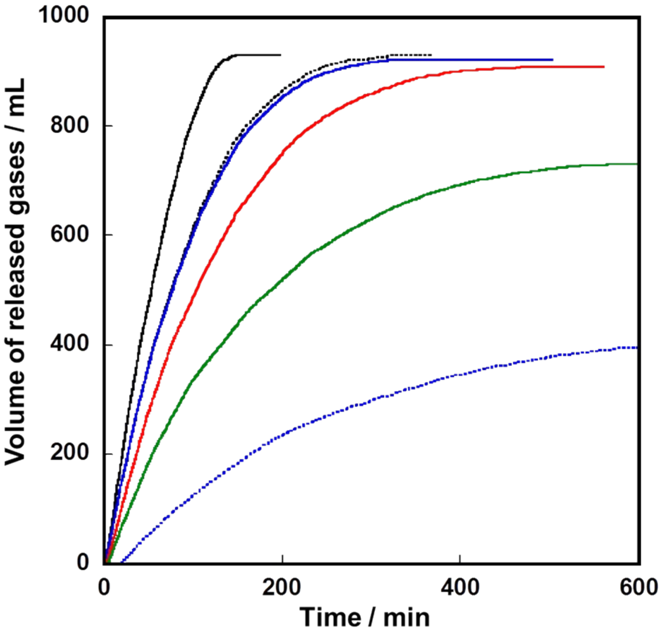


Figure S1. Time courses of released gas volume for the dehydrogenation of FA (1 M) with **C4** (50 μM) at various pH. (Black dotted line; pH 1.0, Black solid line; pH 1.7, Blue solid line; pH 2.2, Red solid line; pH 2.5, Green solid line; pH 2.8, Blue dotted line; pH 3.5).

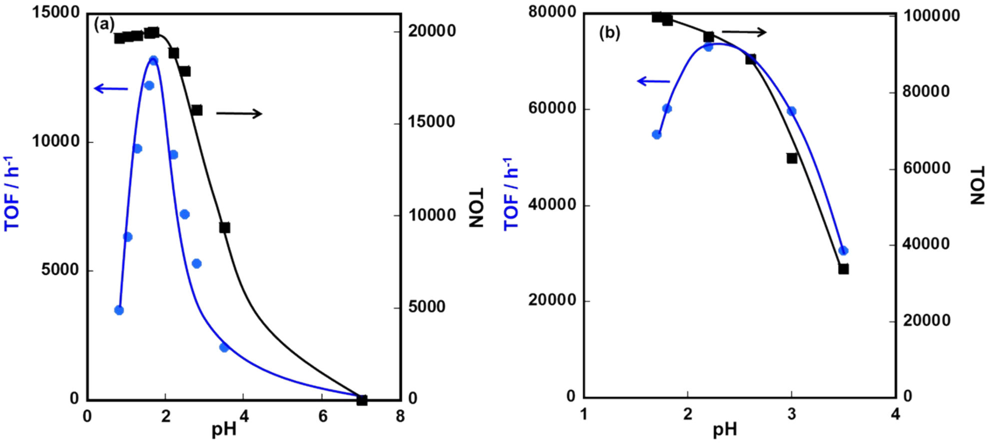


Figure S2. pH dependence of FA dehydrogenation at 60 °C using (a) complex **C4** (50 μM) in 1 M FA/SF solution (pH 1.7-7.0) or 1 M FA containing H_2SO_4 (pH 0.8-1.6), and (b) complex **C6** (10 μM) in 1 M FA/SF solution. The pH of the solution is adjusted by changing the ratio of FA and SF while keeping their total concentration constant or adding H_2SO_4. (Blue solid line, TOF; Black solid line, TON)

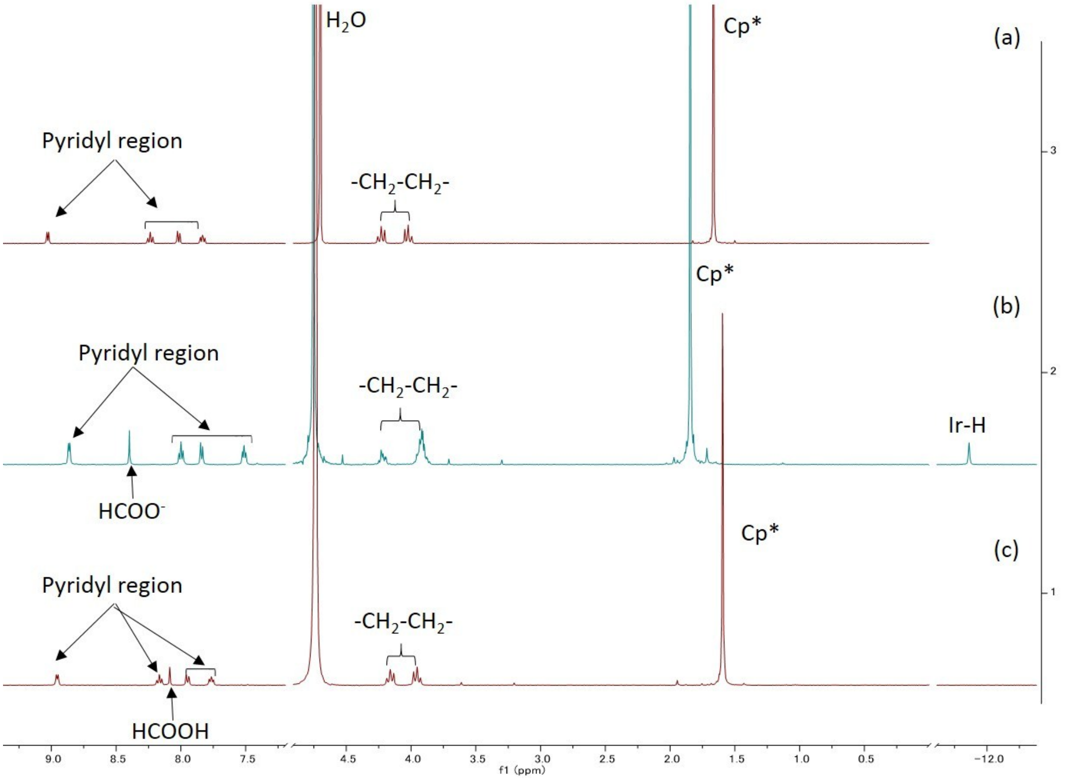


Figure S3. ^{1}H NMR spectrum for Ir-H study of **C4**. (a) **C4** in D_2O, (b) **C4** with 3 eq. SF in D_2O, and (c) D_2SO_4 addition to (b).

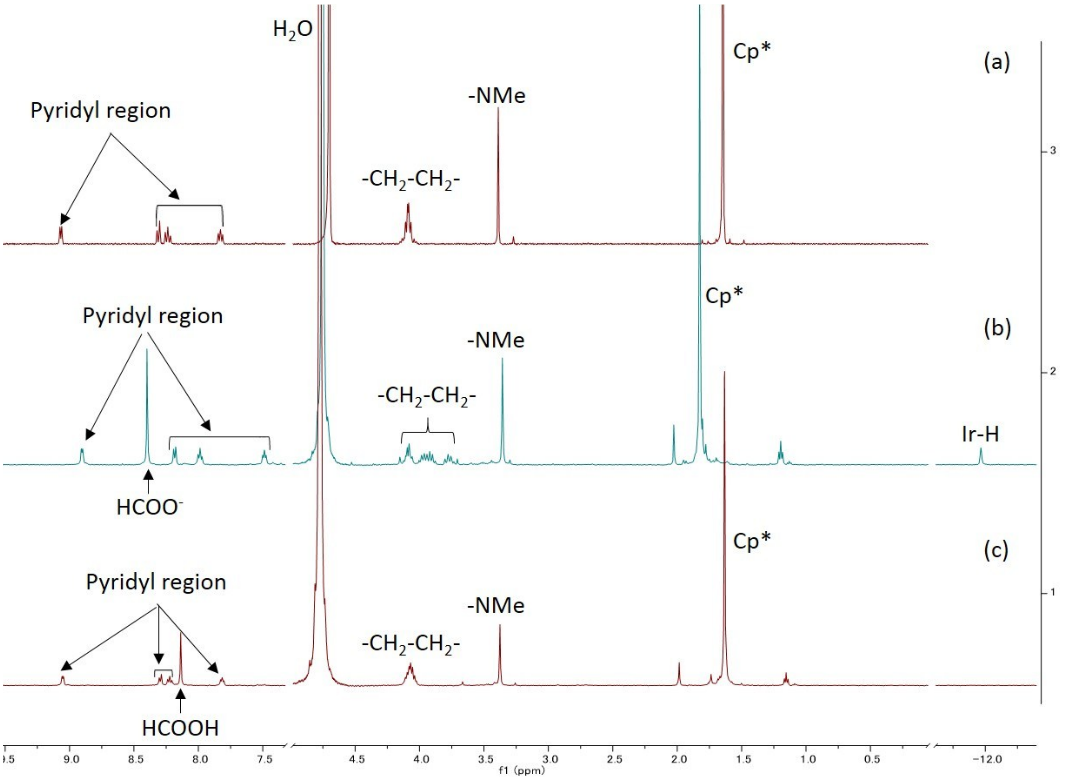


Figure S4. ^{1}H NMR spectrum for Ir-H study for **C5**. (a) **C5** in D_2O, (b) **C5** with 3eq. SF in D_2O, and (c) D_2SO_4 addition to (b).

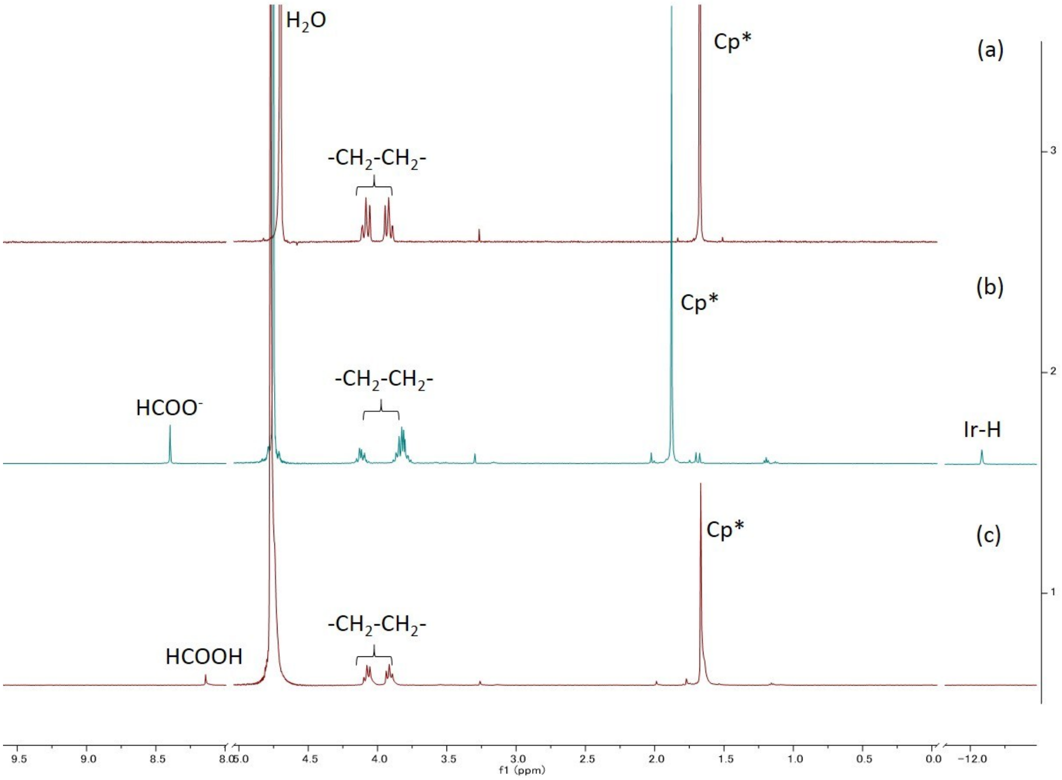


Figure S5. ^1H NMR spectrum for Ir-H study of **C6**. (a) **C6** in D_2O, (b) **C6** with 3 eq. SF in D_2O, and (c) D_2SO_4 addition to (b).

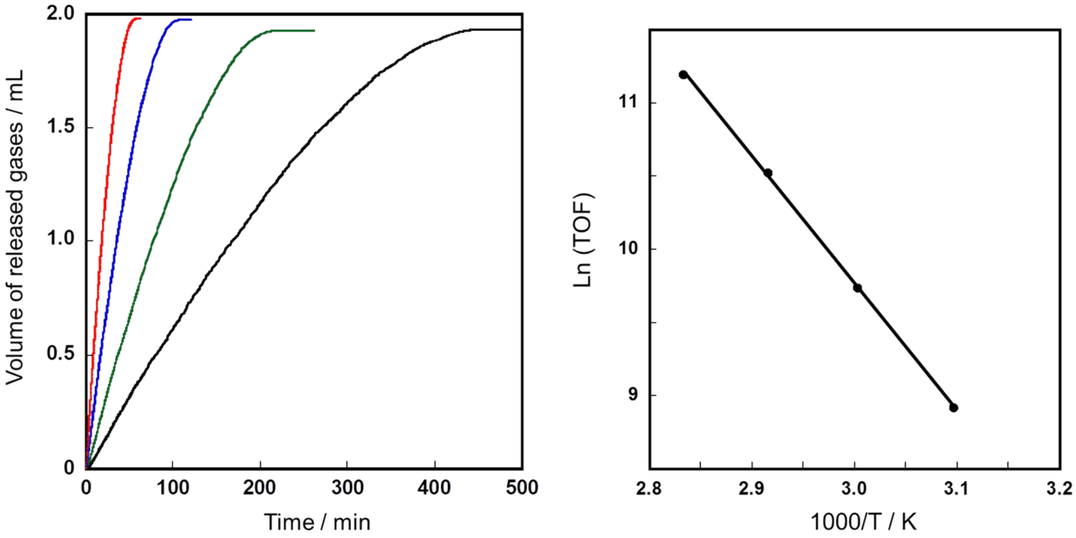


Figure S6. (a) Time course of volume of released gas in the dehydrogenation of FA with **C4** under various temperature conditions. (Conditions: [FA] = 2 M, [cat] = 50 µM, red; 80 °C, blue; 70 °C, green; 60 °C, black; 50 °C). (b) Arrhenius plot of TOF values for dehydrogenation of FA by **C4**. The activation energy is calculated to be 72.0 kJ mol^{-1}.

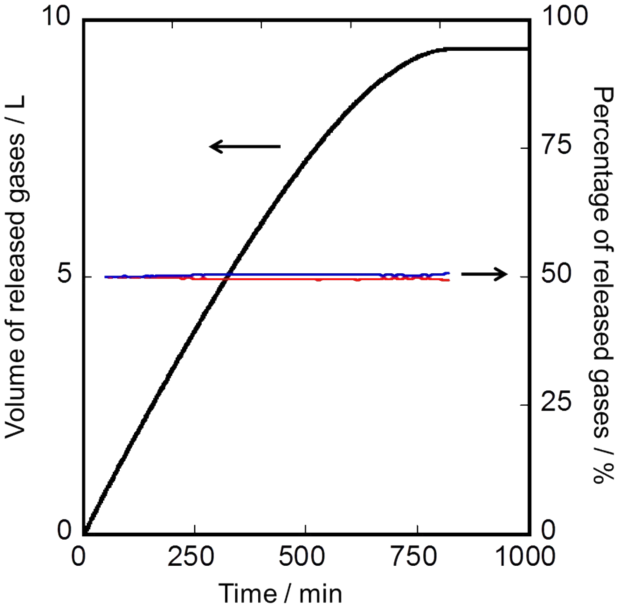


Figure S7. Time course of percentage of released gases (red: H_2, blue: CO_2) and volume of released gases (black) for the dehydrogenation of FA in an aqueous 4 M FA solution using **C4** (20 µM) at 60 ^{o}C.

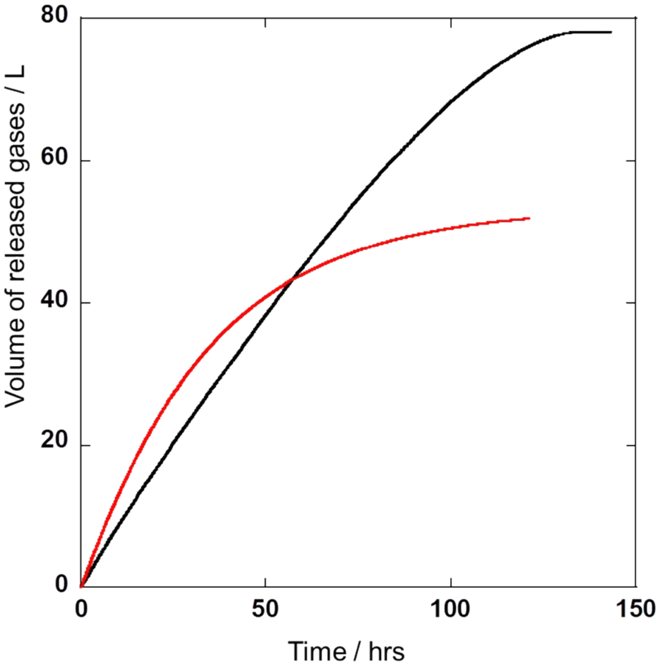


Figure S8. Time course of volume of released gases for the dehydrogenation of FA at 60 ^{o}C in 8 M FA solution (200 mL) using 1 µmol of **C4** (black) and **C6** (red).

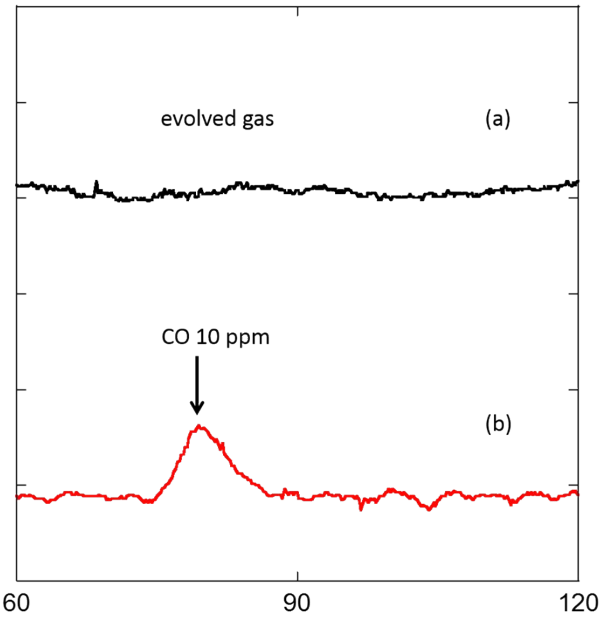


Figure S9. Gas chromatogram of the released gases from the reaction using **C4** and CO containing gas using a FID with methanizer. (a) 1 mL of the released gases under 1 MPa, (b) 1 mL of 10 ppm of CO gas, was injected.

Table S1. pH dependence of the dehydrogenation of FA by **C4**.[a]

pH	Time / h	TOF[b] / h^{-1}	Volume / mL	TON	Residual FA conc.[c] / M
0.8	20	3480	878	19,700	0.017
1.0	10	6350	925	19,800	0.01
1.3	6	9760	930	19,850	0.007
1.6	3	12,200	931	19,990	0.0003
1.7	2.5	13,200	931	20,000	0
2.2	6	9540	923	18,880	0.053
2.5	7	7230	909	17,900	0.103
2.8	10	5290	761	15,800	0.21
3.5	12	2040	400	9400	0.53
7	-	0	0	0	1

[a] The reaction was carried out using **C4** (50 μM) at 60 °C in 20 mL of aqueous 1 M FA/SF solution (pH 1.7-7) or 1 M FA solution adjusted by H_2SO_4 (pH 0.8-1.6). [b] The average value of the first 10 min. [c] Analyzed by HPLC.

Table S2-1. Kinetic isotope effect in the dehydrogenation of FA using by **C4**.[a]

Substrate/ Solvent	TOF[b] / h^{-1}	KIE[c]	Substrate/Additive/ Solvent	TOF[b] / h^{-1}	KIE[c]
HCO_2H / H_2O (**pH 1.7**)	13,600	-	HCO_2H / H_2SO_4 / H_2O (**pH 1.0**)	6200	-
HCO_2H / D_2O	6690	2.03	HCO_2H / D_2SO_4 / D_2O	3500	1.77
DCO_2D / H_2O	8530	1.59	DCO_2D / H_2SO_4 / H_2O	2690	2.30
DCO_2D / D_2O	3860	3.52	DCO_2D / D_2SO_4 / D_2O	1220	5.08

[a] The reaction was carried out in 10 mL of aqueous 1 M FA solution or 1 M FA solution containing 0.05 M sulfuric acid using **C4** (100 μM) at 60 °C. [b] Average TOF over the initial 10 min. Each reaction was repeated twice with an error less than 5%.

Table S2-2. Kinetic isotope effect in the dehydrogenation of FA using by **C6**.[a]

Substrate/ Solvent	TOF[b] / h^{-1}	KIE[c]	Substrate/Additive /Solvent	TOF[b] / h^{-1}	KIE[c]
HCO_2H / H_2O (**pH 1.7**)	20,100	-	HCO_2H / HCO_2Na / H_2O (**pH 3.5**)	20,860	-
HCO_2H / D_2O	12,650	1.59	HCO_2H / HCO_2Na / D_2O	5030	4.15
DCO_2D / H_2O	6500	3.09	DCO_2D / DCO_2Na / H_2O	13,250	1.57
DCO_2D / D_2O	4790	4.20	DCO_2D / DCO_2Na / D_2O	4170	5.00

[a] The reaction was carried out in 10 mL of aqueous 1 M FA solution or 1 M FA/SF (1/1) solution using **C6** (50 μM) at 50 °C. [b] Average TOF over the initial 10 min. Each reaction was repeated twice with an error less than 5%.

Table S3. Comparison of DFT calculated $\Delta G^{\ddagger}$ values (in kcal/mol) for β-hydride elimination and

H_2 production for complexes **C4** and **C6** at 333.15 K.

	Complex **C4**		Complex **C6**	
pH	$\Delta G^{\ddagger}_{\beta\text{-elim}}$	$\Delta G^{\ddagger}_{H2}$	$\Delta G^{\ddagger}_{\beta\text{-elim}}$	$\Delta G^{\ddagger}_{H2}$
0.0	19.3	17.5	20.4	18.8
1.0	17.8	17.5	18.9	17.3
1.7	16.7	17.5	17.8	17.3
2.1	16.1	17.5	17.2	17.3
2.5	15.5	17.5	16.6	17.3
2.8	15.0	17.5	16.2	17.3
3.5	15.0	17.5	15.1	17.3

Table S4. Temperature dependence of the dehydrogenation of FA by **C4**.[a]

Temp, °C	1/T K	TOF,[b] h^{-1}	ln(TOF)	Volume, L
50	0.003096	7490	8.9213	1.93
60	0.003003	16,900	9.7351	1.93
70	0.002916	37,200	10.524	1.97
80	0.002833	72,500	11.191	1.98

[a] The reaction was carried out using 50 µM of **C4** in 20 mL of aqueous 2 M FA solution. For all reactions, FA was completely decomposed confirmed by HPLC, and TONs were 20,000. [b] The average value of the first 10 min.

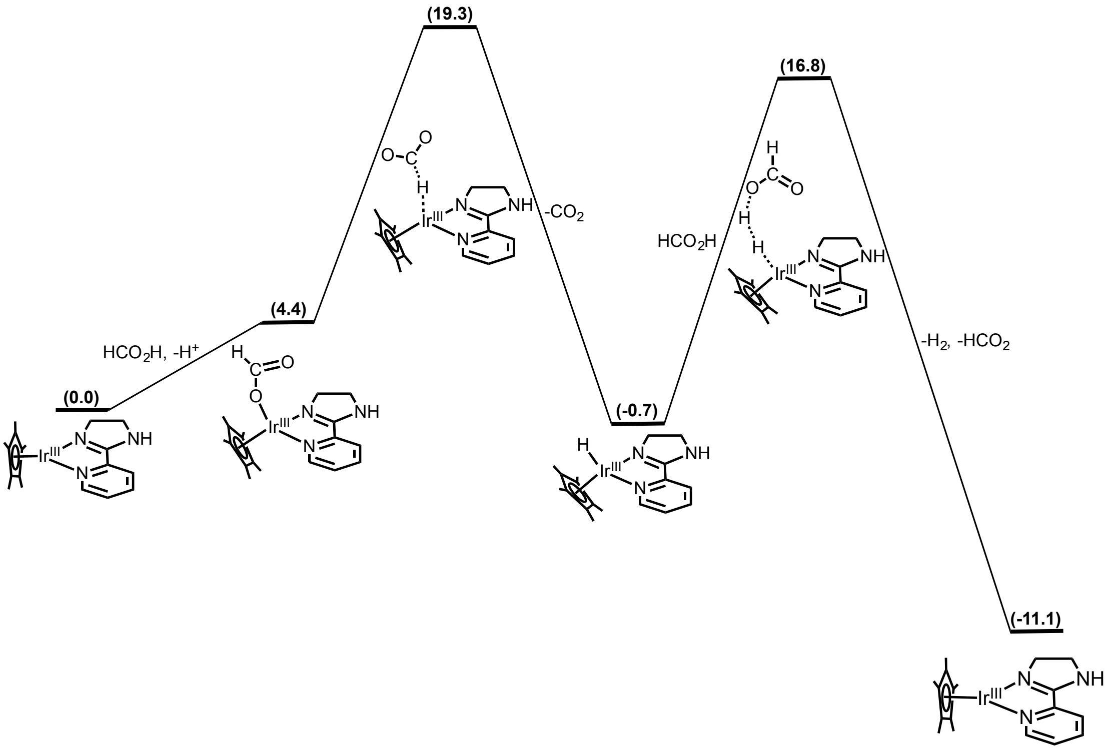
Table S5. FA concentration dependence of the dehydrogenation of FA by **C4**.[a]

FA, M	Time / h	TOF[b] / h^{-1}	Volume / L	TON
1	2.5	13,200	0.91	20,000
2	4	16,900	1.9	40,000
3	6	17,700	2.9	60,000
4	13	19,900	3.9	80,000
6	14	19,800	5.7	120,000
8	17	19,700	7.8	160,000
12	18	14,400	11	240,000
20	62	5050	19	404,000

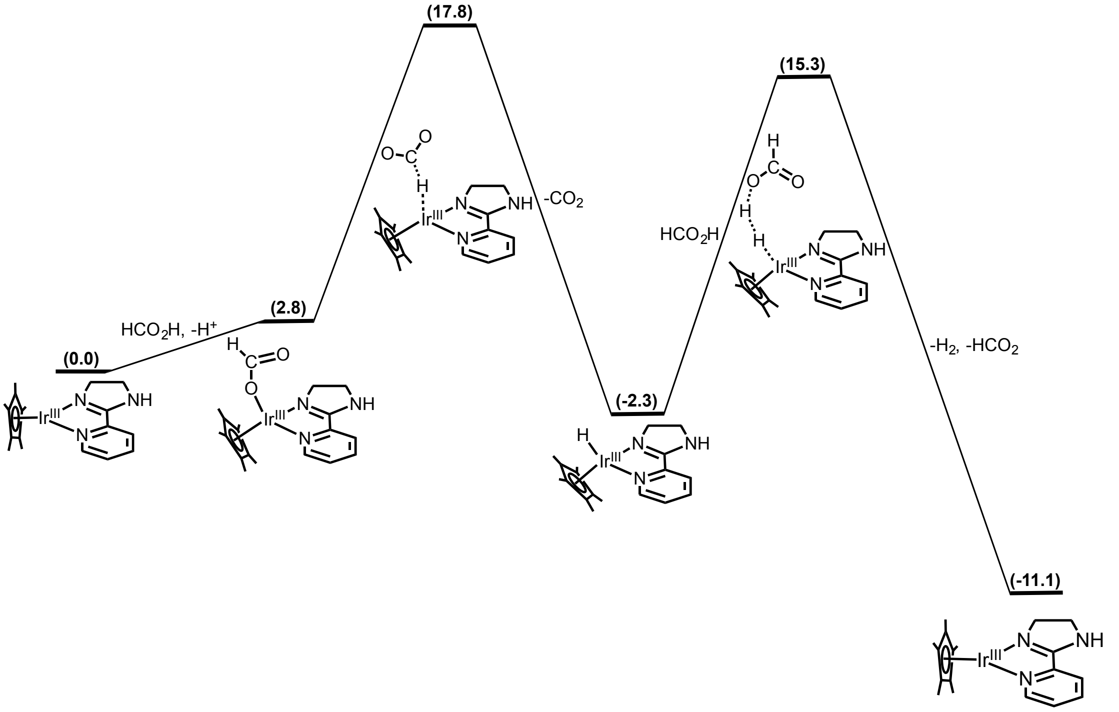
[a] The reaction was carried out using 50 µM of **C4** at 60 °C in 20 mL of aqueous FA solution. For all reactions, FA was completely decomposed confirmed by HPLC. [b] The average value of the first 10 min.

COMPUTATIONAL METHODS

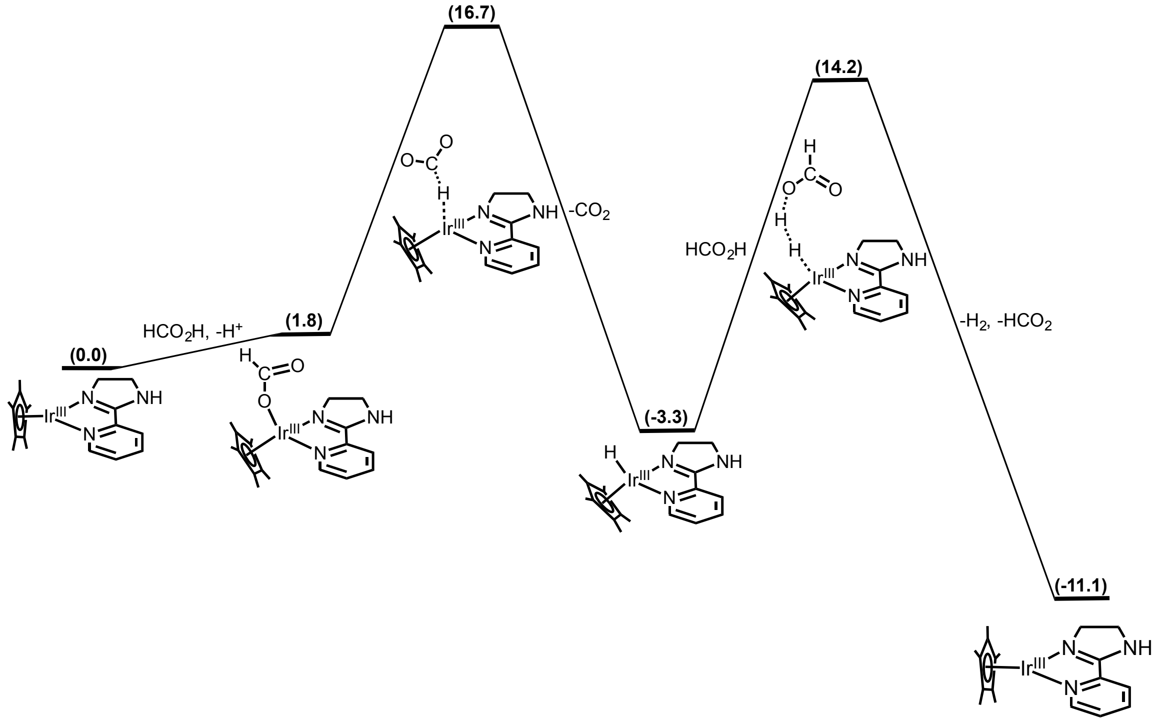
All geometries were fully optimized at the M06 level of density functional theory[4-6] with the SMD aqueous continuum solvation model[7] using the Stuttgart [8s7p6d2f | 6s5p3d2f] ECP60MWB contracted pseudopotential basis set[8] on Ir and the 6-31G(d,p) basis set[9] on all other atoms. Non-analytical integrals were evaluated using the integral=grid=ultrafine option as implemented in the Gaussian 09 software package.[10] The nature of all stationary points was verified by analytic computation of vibrational frequencies, which were also used for the computation of zero-point vibrational energies, molecular partition functions (with all frequencies below 50 cm^{-1}, with the exception of the imaginary frequency of transition states, replaced by 50 cm^{-1} when computing free energies), and for determining the reactants and products associated with each transition-state structure.[11] Partition functions were used in the computation of 333 K thermal contributions to the free energy employing the usual ideal-gas, rigid-rotator, harmonic oscillator approximation.[11] Free-energy contributions were added to single-point, SMD-solvated M06 electronic energies computed at the optimized geometries obtained with the initial basis with the SDD basis set on Ir and the larger 6-311++G(2d,p) basis set[9] on all other atoms to arrive at final, composite free energies. As mentioned above, solvation effects associated with water as the solvent were accounted for using the SMD aqueous continuum solvation model.[7] For all non-gas species, a 1 M standard state was used for all species in solution, thus, an adjustment for the 1 atm to 1 M standard-state concentration change of $RT\ln(24.5)$, (1.89 kcal/mol at 298 K) was added to the computed gas-phase free energies. In the case of the water solvent, the 1 atm gas-phase free energy is adjusted by the sum of a 1 atm to 1 M standard-state concentration change (1.89 kcal/mol), the experimental 1 M to 55.4 M self-solvation free energy (–6.32 kcal/mol) and a 55.4 M to 1 M standard-state concentration change (2.38 kcal/mol) yielding an overall correction of –2.05 kcal/mol to the gas-phase free energy. The 1 M to 1 M solvation free energy of the proton was taken from experiment as –265.9 kcal/mol.[12-15]



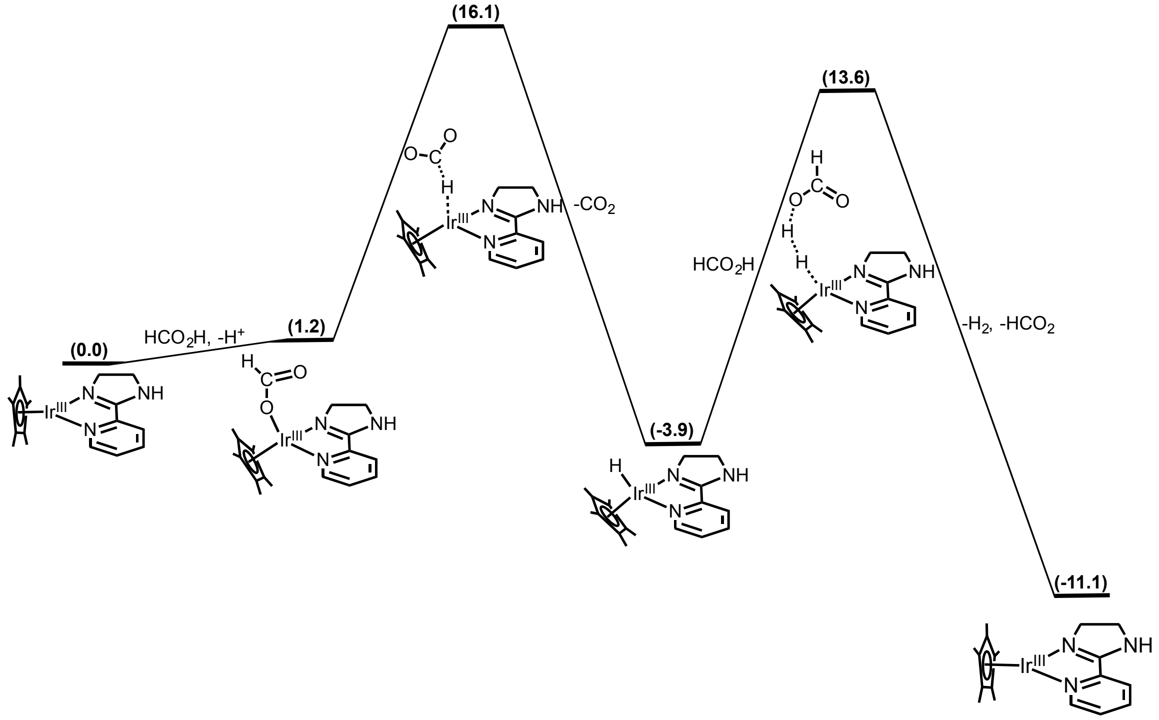
Scheme S1. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 0.0 and 333.15 K. The relative free energies are reported in units of kcal/mol.



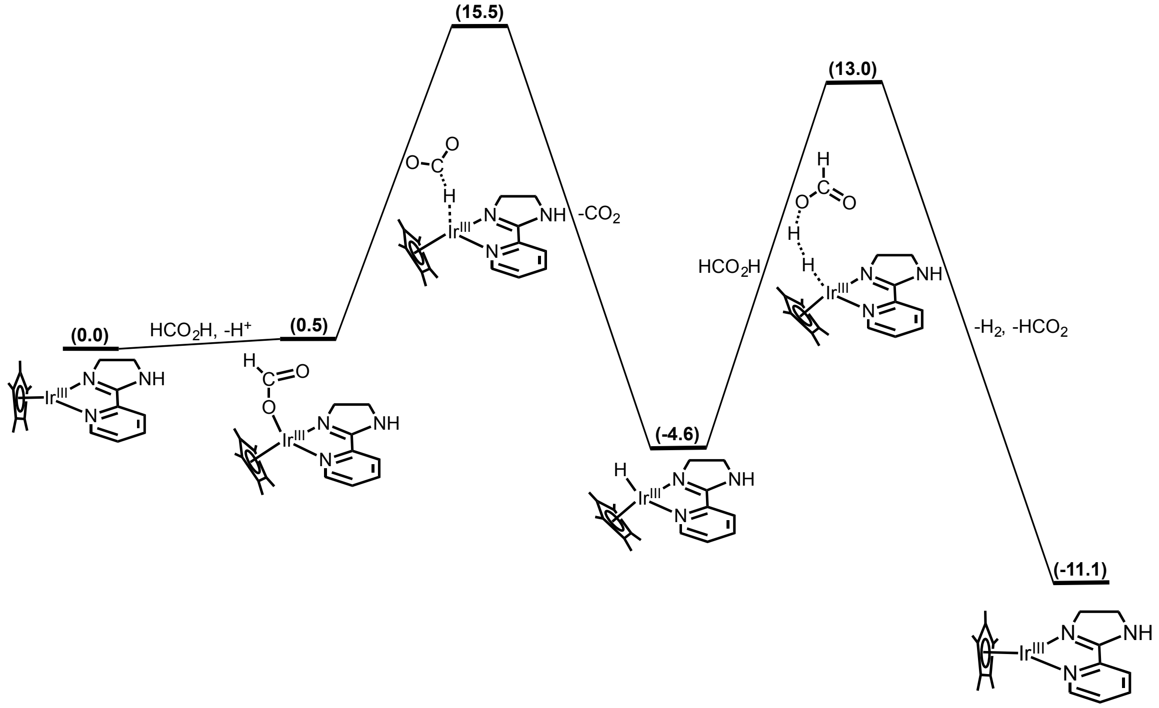
Scheme S2. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 1.0 and 333.15 K. The relative free energies are reported in units of kcal/mol.



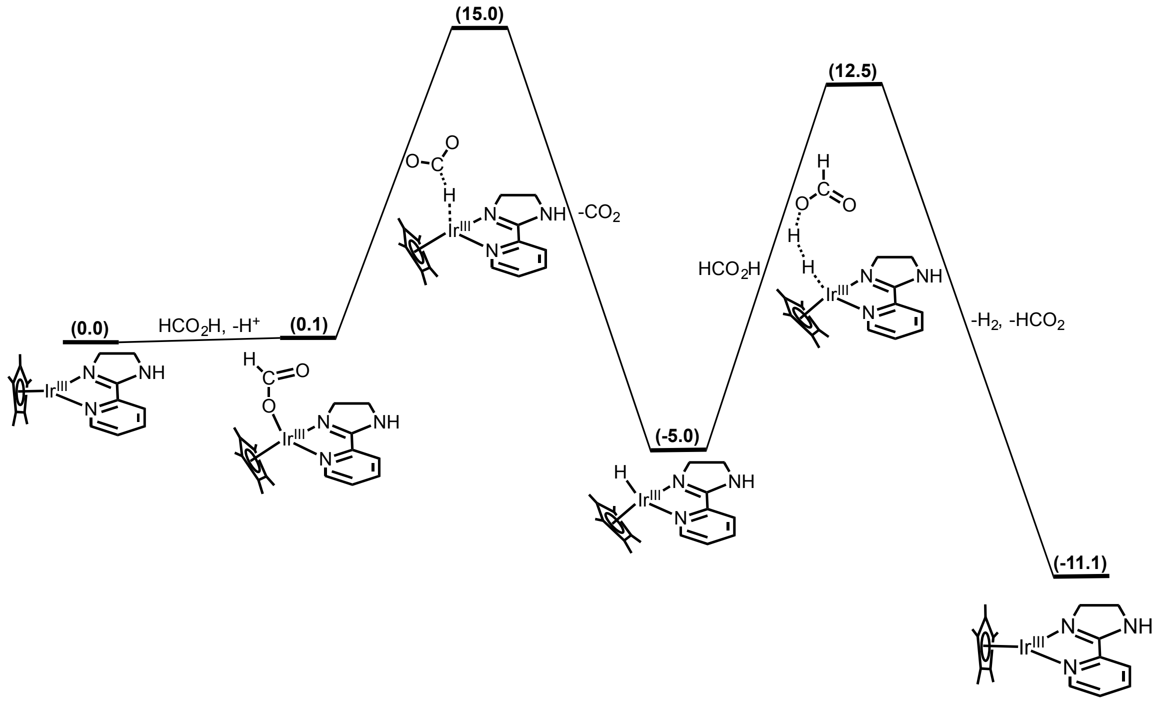
Scheme S3. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 1.7 and 333.15 K. The relative free energies are reported in units of kcal/mol.



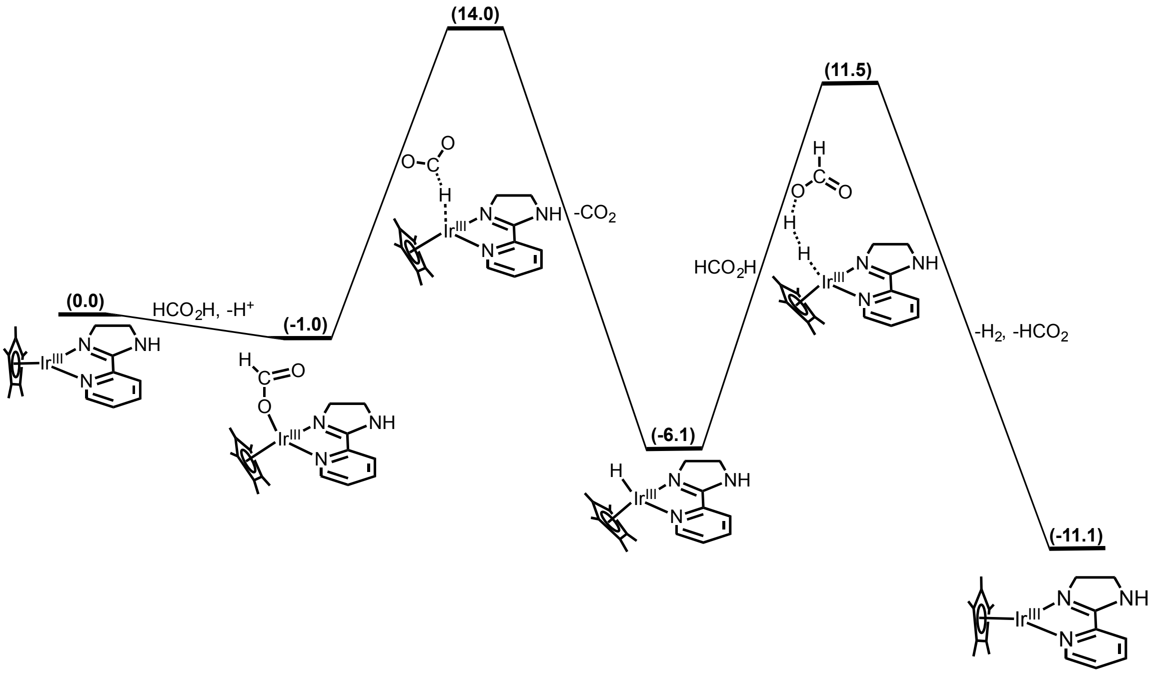
Scheme S4. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 2.1 and 333.15 K. The relative free energies are reported in units of kcal/mol.



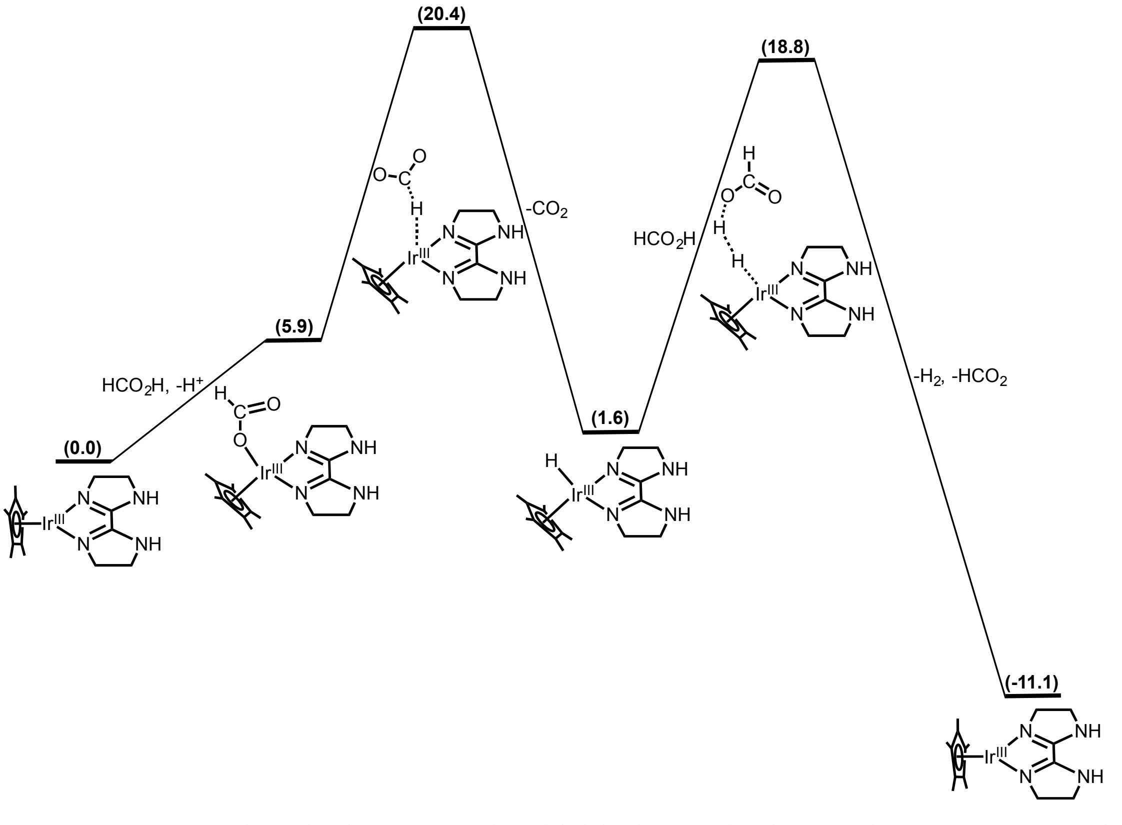
Scheme S5. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 2.5 and 333.15 K. The relative free energies are reported in units of kcal/mol.



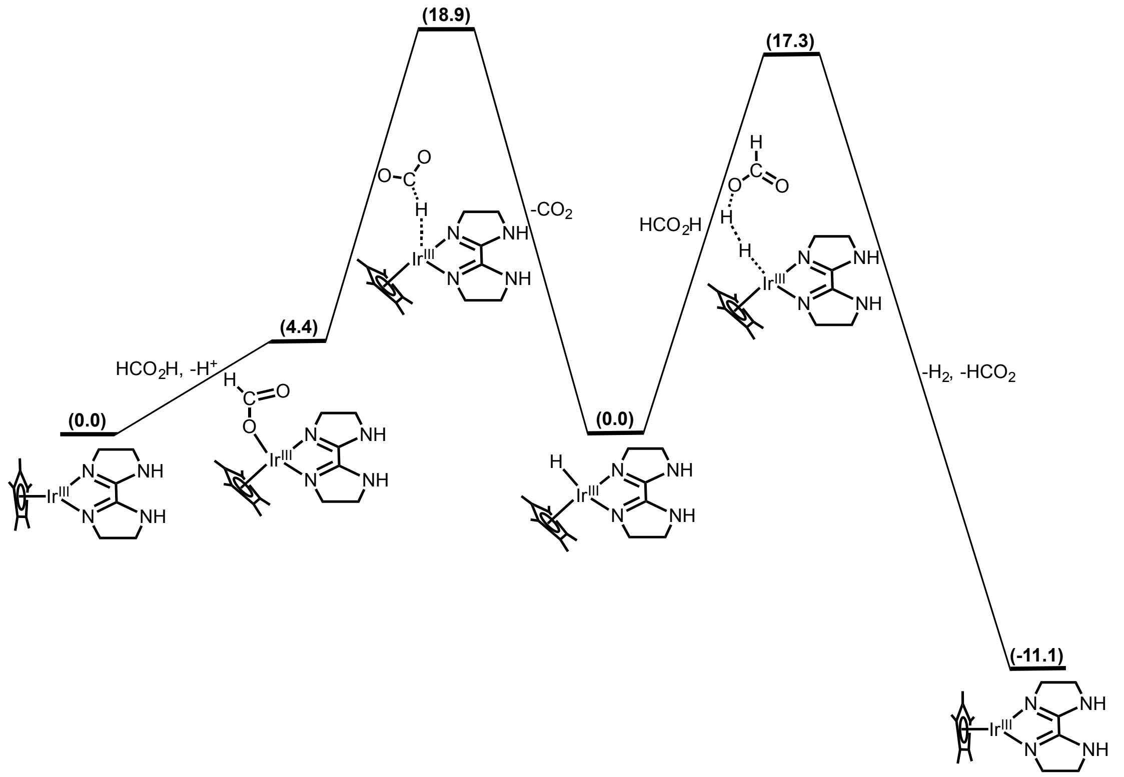
Scheme S6. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 2.8 and 333.15 K. The relative free energies are reported in units of kcal/mol.



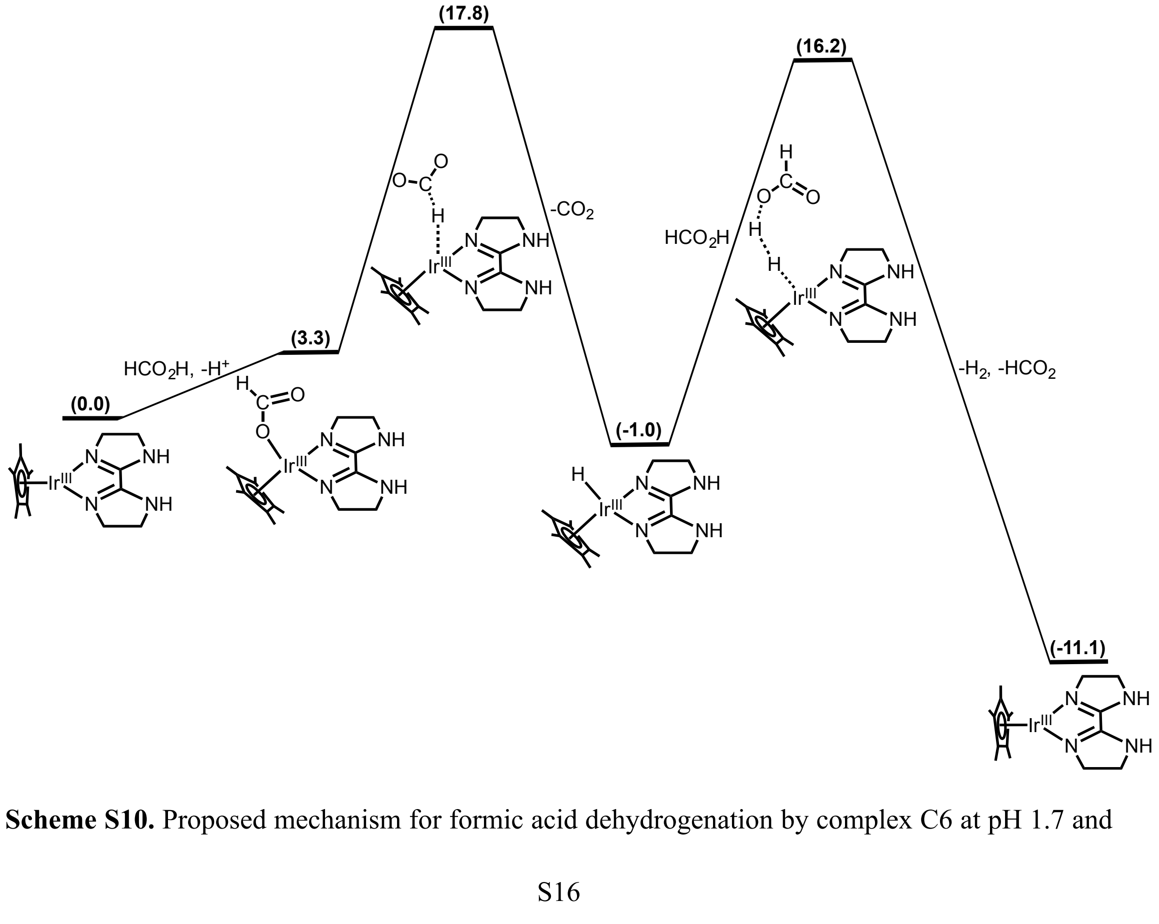
Scheme S7. Proposed mechanism for formic acid dehydrogenation by complex **C4** at pH 3.5 and 333.15 K. The relative free energies are reported in units of kcal/mol.



Scheme S8. Proposed mechanism for formic acid dehydrogenation by complex **C6** at pH 0.0 and 333.15 K. The relative free energies are reported in units of kcal/mol.

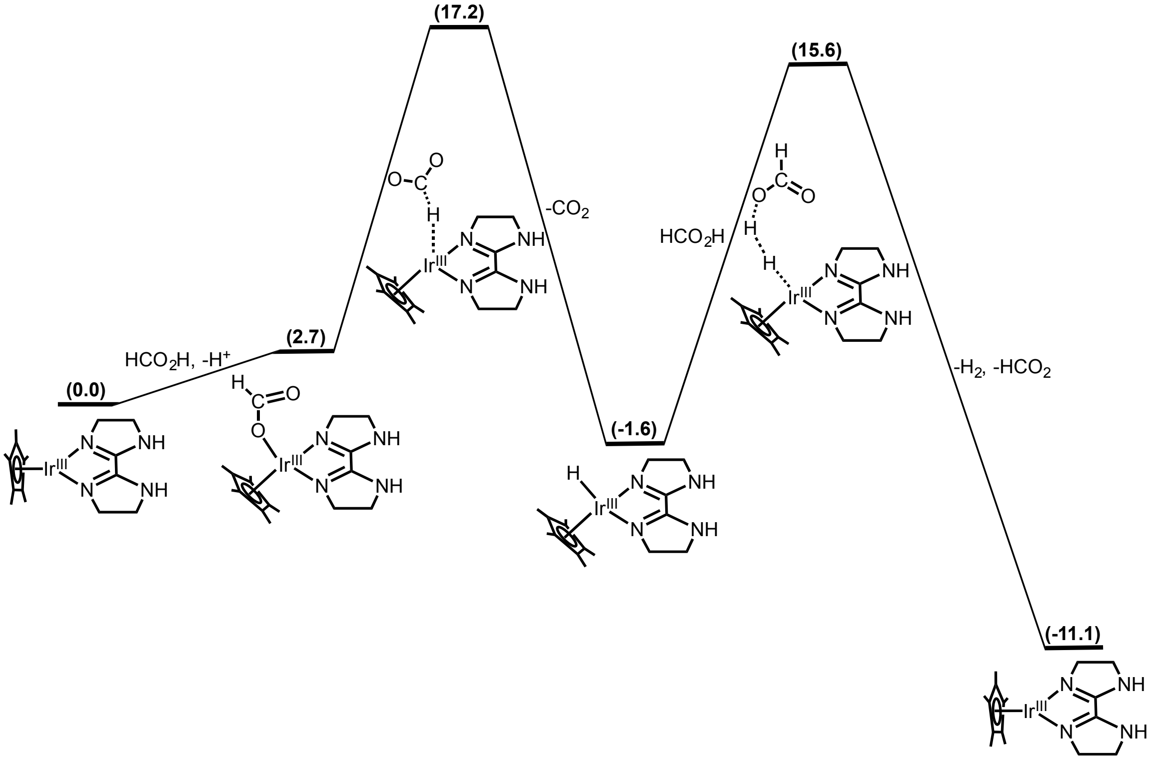


Scheme S9. Proposed mechanism for formic acid dehydrogenation by complex **C6** at pH 1.0 and 333.15 K. The relative free energies are reported in units of kcal/mol.

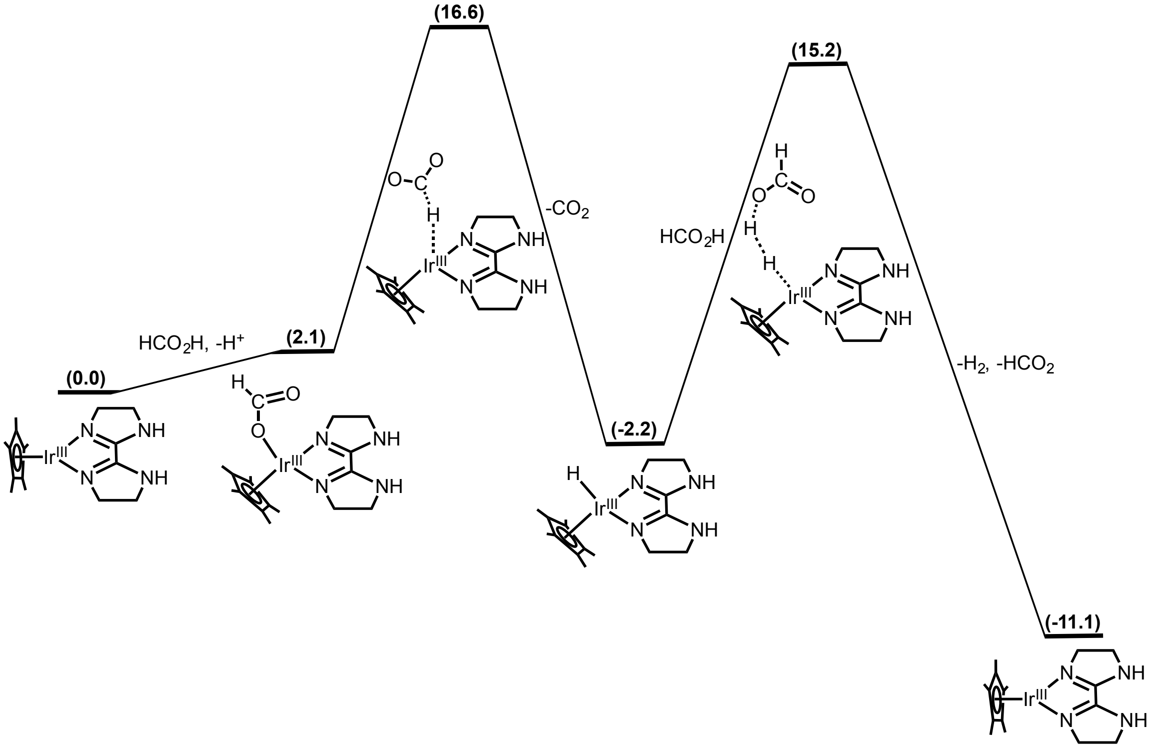


Scheme S10. Proposed mechanism for formic acid dehydrogenation by complex C6 at pH 1.7 and

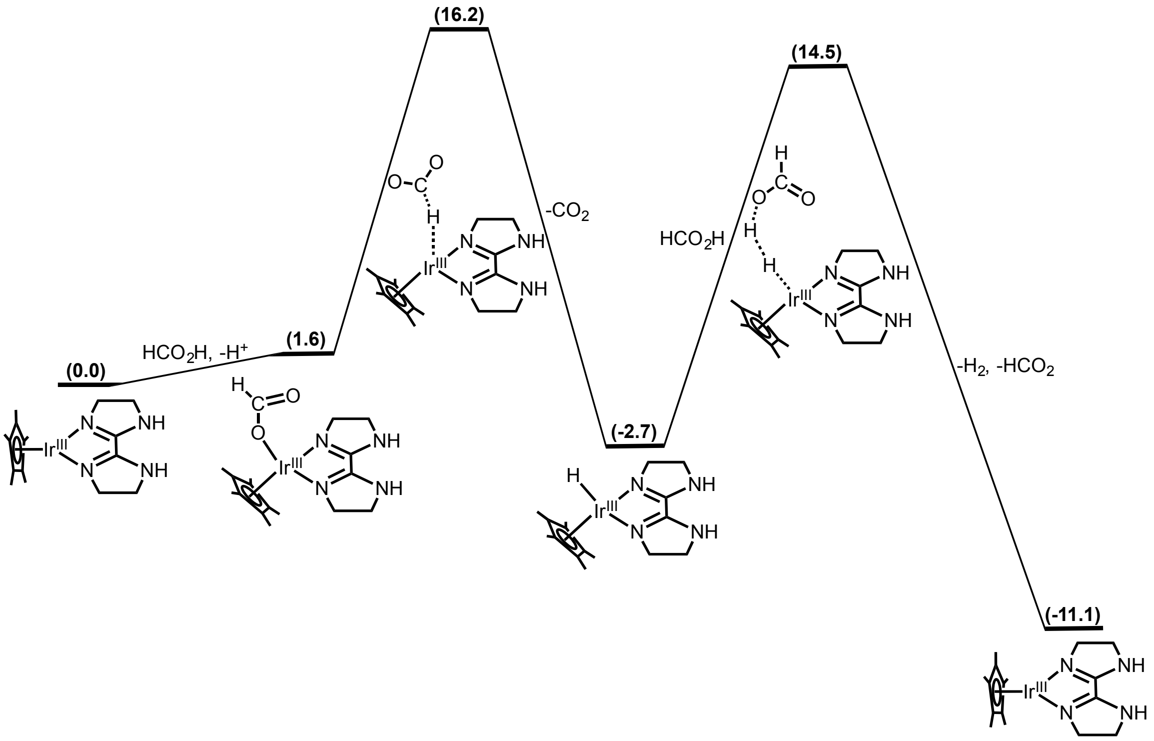
333.15 K. The relative free energies are reported in units of kcal/mol.



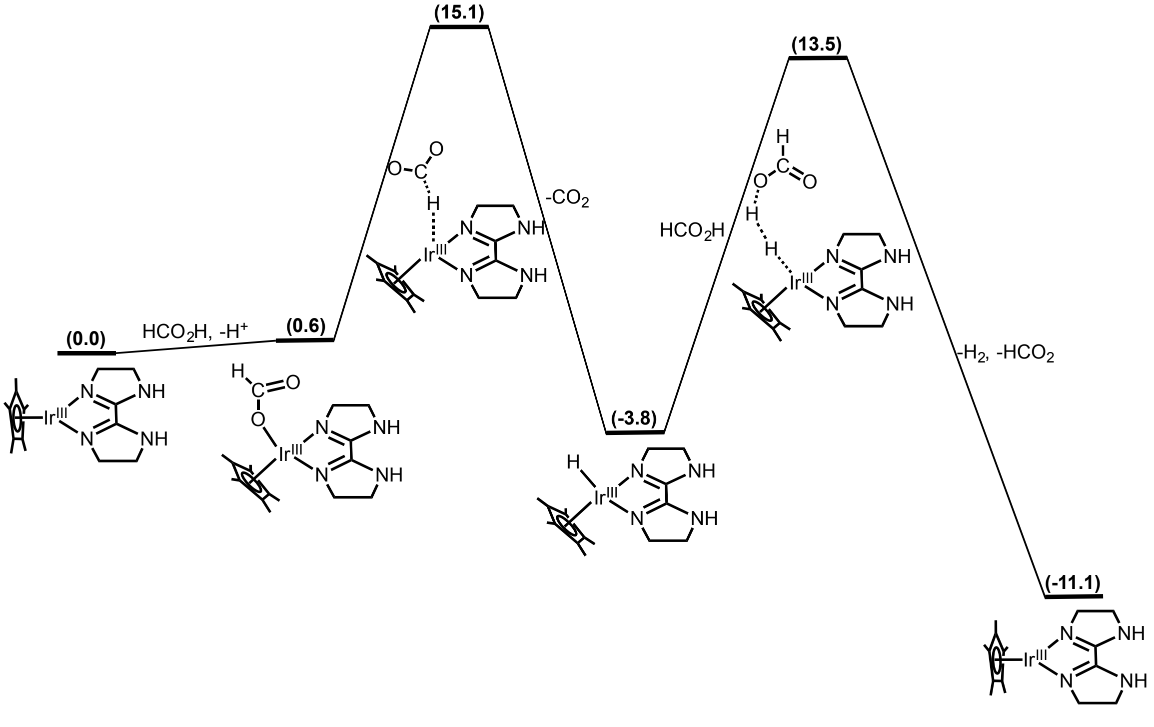
Scheme S11. Proposed mechanism for formic acid dehydrogenation by complex **C6** at pH 2.1 and 333.15 K. The relative free energies are reported in units of kcal/mol.



Scheme S12. Proposed mechanism for formic acid dehydrogenation by complex **C6** at pH 2.5 and 333.15 K. The relative free energies are reported in units of kcal/mol.



Scheme S13. Proposed mechanism for formic acid dehydrogenation by complex **C6** at pH 2.8 and 333.15 K. The relative free energies are reported in units of kcal/mol.



Scheme S14. Proposed mechanism for formic acid dehydrogenation by complex **C6** at pH 3.5 and 333.15 K. The relative free energies are reported in units of kcal/mol.

Optimized Coordinates and Energies

[Cp*Ir(4)]$^{2+}$

E = -968.179534965 a.u.

77	0.380067	0.000790	-0.066641
6	2.027923	-0.044293	1.277180
6	2.294818	0.928990	0.242123
6	1.924676	-1.352059	0.659562
6	2.074091	-1.185925	-0.744586
6	2.298495	0.229665	-1.004949
6	1.921552	0.236838	2.727223
1	1.270403	-0.487776	3.225996
1	1.530461	1.243443	2.908565
1	2.914464	0.171917	3.191777
6	2.530037	2.379653	0.462369
6	1.684828	-2.615578	1.403741
1	1.916448	2.761757	1.285266
1	0.891558	-2.494195	2.150376
1	2.307756	2.966598	-0.433839
1	1.406036	-3.434582	0.734221
1	3.581359	2.552285	0.724060
1	2.596465	-2.913252	1.936660
6	2.010315	-2.240638	-1.787146
6	2.491363	0.825837	-2.348095
1	1.480919	-1.884081	-2.677277
1	1.891834	0.307054	-3.103033
1	1.503997	-3.138984	-1.421866
1	2.221964	1.886623	-2.358574
1	3.023534	-2.525864	-2.097836
1	3.545107	0.740617	-2.644229
6	-2.285527	1.184547	-0.015296
6	-2.362303	3.459702	-0.120688
6	-0.917575	2.975474	0.046265
1	-2.557899	3.861369	-1.121011
1	-2.653407	4.205766	0.620473
1	-0.514672	3.218239	1.037752
1	-0.242904	3.390064	-0.707121
7	-3.116386	2.212833	0.066718
1	-4.123483	2.139561	-0.011240
7	-1.010608	1.513550	-0.084510
6	-2.639686	-0.237591	-0.006183
6	-3.923020	-0.743211	-0.052090
6	-4.087224	-2.129062	-0.063207
1	-4.782645	-0.080202	-0.088956
6	-1.706900	-2.362472	0.017095
6	-2.969742	-2.946087	-0.029846
1	-5.084504	-2.556319	-0.103497
1	-0.801484	-2.963560	0.038246
1	-3.058254	-4.027174	-0.042703
7	-1.547993	-1.038222	0.033272

[Cp*Ir(4)(HCO$_2$)]$^{+}$

E = -968.908237723 a.u.

77	-0.395976	0.011695	-0.327308
7	1.101245	1.495635	-0.170824
6	2.335882	1.111805	-0.042155
1	4.183829	1.972626	-0.193733
6	-1.743604	0.324240	1.481790

6	-1.671712	-1.061421	1.201353
6	-2.235100	0.988505	0.284764
6	-2.537367	-0.014686	-0.693852
6	-2.134132	-1.290306	-0.157863
6	-1.402649	1.007539	2.759751
1	-0.944304	1.987356	2.582799
1	-0.707737	0.414806	3.363485
1	-2.304354	1.177690	3.363103
6	-1.204812	-2.129625	2.124557
6	-2.520292	2.446238	0.172837
1	-0.534136	-1.735989	2.895413
1	-1.779133	3.041689	0.718372
1	-0.676502	-2.924918	1.586477
1	-2.516983	2.776277	-0.871566
1	-2.060058	-2.596744	2.629869
1	-3.505930	2.680943	0.595911
6	-3.180751	0.216112	-2.017154
6	-2.358452	-2.622317	-0.787310
1	-2.878012	-0.540576	-2.748054
1	-2.301937	-2.562860	-1.879604
1	-2.923602	1.200298	-2.422085
1	-1.616853	-3.356116	-0.452294
1	-4.273110	0.169630	-1.919889
1	-3.349184	-3.017698	-0.525646
7	3.238556	2.111800	0.147826
1	-0.044529	0.083700	-1.918294
6	2.538692	3.355355	-0.222053
1	2.759280	3.616944	-1.264561
1	2.836414	4.186663	0.419540
6	1.072908	2.955488	-0.041707
1	0.405175	3.402691	-0.783826
1	0.696390	3.216723	0.957805
6	2.597573	-0.317984	-0.056053
6	3.850383	-0.899983	0.067881
6	3.947515	-2.285246	0.049598
1	4.732056	-0.275903	0.182660
6	1.570106	-2.389107	-0.228701
6	2.789506	-3.038276	-0.101465
1	4.914227	-2.769075	0.151033
1	0.644182	-2.942996	-0.363883
1	2.819136	-4.122861	-0.124074
7	1.465008	-1.053261	-0.197228

[Cp*Ir(4)(HCO_2)]$^+$ β-hydride elimination TS

E = -1157.39873917 a.u.

77	-0.450437	0.058585	0.048043
7	1.061718	-1.173823	-0.723735
6	2.285480	-0.738997	-0.691879
1	4.164525	-1.544564	-0.693110
6	-2.041024	-0.160632	-1.476172
6	-1.877371	1.224922	-1.177757
6	-2.392919	-0.850105	-0.249590
6	-2.501694	0.144830	0.787936
6	-2.154908	1.416466	0.234005
6	-1.863614	-0.801413	-2.806422
1	-1.564529	-1.850417	-2.710046
1	-1.105308	-0.284577	-3.404296
1	-2.806175	-0.776315	-3.368047
6	-1.507824	2.305091	-2.130872
6	-2.726386	-2.295730	-0.119852
1	-1.010629	1.903359	-3.019465
1	-2.169833	-2.900951	-0.843719
1	-0.834796	3.035114	-1.666001

1	-2.490899	-2.670522	0.881708
1	-2.401799	2.848908	-2.462158
1	-3.795972	-2.466436	-0.298983
6	-2.916883	-0.103366	2.193782
6	-2.214720	2.724276	0.942669
1	-2.475017	0.629260	2.876795
1	-1.847195	2.644763	1.971882
1	-2.632017	-1.105234	2.529841
1	-1.626791	3.490810	0.426559
1	-4.008554	-0.022624	2.276052
1	-3.249879	3.086607	0.988227
7	3.226998	-1.635323	-1.068265
6	0.789721	-1.685460	2.222657
1	0.160450	-0.408591	1.580971
8	-0.140694	-2.369419	2.531234
8	1.965737	-1.472587	2.204870
6	2.572891	-2.956973	-1.051371
1	2.820520	-3.486707	-0.123758
1	2.894650	-3.567316	-1.897462
6	1.085090	-2.585020	-1.119319
1	0.462642	-3.179508	-0.441037
1	0.675238	-2.687883	-2.133048
6	2.496060	0.637623	-0.269022
6	3.725980	1.273969	-0.215442
6	3.773712	2.593325	0.217951
1	4.628201	0.745393	-0.510540
6	1.396971	2.522383	0.513257
6	2.592165	3.224392	0.585088
1	4.722061	3.119452	0.269063
1	0.455328	2.977930	0.807853
1	2.584116	4.253458	0.928990
7	1.341371	1.252592	0.093102

[Cp*Ir(4)(H)]$^+$

E = -968.908237723 a.u.

77	-0.395976	0.011695	-0.327308
7	1.101245	1.495635	-0.170824
6	2.335882	1.111805	-0.042155
1	4.183829	1.972626	-0.193733
6	-1.743604	0.324240	1.481790
6	-1.671712	-1.061421	1.201353
6	-2.235100	0.988505	0.284764
6	-2.537367	-0.014686	-0.693852
6	-2.134132	-1.290306	-0.157863
6	-1.402649	1.007539	2.759751
1	-0.944304	1.987356	2.582799
1	-0.707737	0.414806	3.363485
1	-2.304354	1.177690	3.363103
6	-1.204812	-2.129625	2.124557
6	-2.520292	2.446238	0.172837
1	-0.534136	-1.735989	2.895413
1	-1.779133	3.041689	0.718372
1	-0.676502	-2.924918	1.586477
1	-2.516983	2.776277	-0.871566
1	-2.060058	-2.596744	2.629869
1	-3.505930	2.680943	0.595911
6	-3.180751	0.216112	-2.017154
6	-2.358452	-2.622317	-0.787310
1	-2.878012	-0.540576	-2.748054
1	-2.301937	-2.562860	-1.879604
1	-2.923602	1.200298	-2.422085
1	-1.616853	-3.356116	-0.452294
1	-4.273110	0.169630	-1.919889

1	-3.349184	-3.017698	-0.525646
7	3.238556	2.111800	0.147826
1	-0.044529	0.083700	-1.918294
6	2.538692	3.355355	-0.222053
1	2.759280	3.616944	-1.264561
1	2.836414	4.186663	0.419540
6	1.072908	2.955488	-0.041707
1	0.405175	3.402691	-0.783826
1	0.696390	3.216723	0.957805
6	2.597573	-0.317984	-0.056053
6	3.850383	-0.899983	0.067881
6	3.947515	-2.285246	0.049598
1	4.732056	-0.275903	0.182660
6	1.570106	-2.389107	-0.228701
6	2.789506	-3.038276	-0.101465
1	4.914227	-2.769075	0.151033
1	0.644182	-2.942996	-0.363883
1	2.819136	-4.122861	-0.124074
7	1.465008	-1.053261	-0.197228

$[Cp^*Ir(4)(H)(HCO_2H)]^+$ H_2 formation TS

E = -968.908237723 a.u.

77	-0.395976	0.011695	-0.327308
7	1.101245	1.495635	-0.170824
6	2.335882	1.111805	-0.042155
1	4.183829	1.972626	-0.193733
6	-1.743604	0.324240	1.481790
6	-1.671712	-1.061421	1.201353
6	-2.235100	0.988505	0.284764
6	-2.537367	-0.014686	-0.693852
6	-2.134132	-1.290306	-0.157863
6	-1.402649	1.007539	2.759751
1	-0.944304	1.987356	2.582799
1	-0.707737	0.414806	3.363485
1	-2.304354	1.177690	3.363103
6	-1.204812	-2.129625	2.124557
6	-2.520292	2.446238	0.172837
1	-0.534136	-1.735989	2.895413
1	-1.779133	3.041689	0.718372
1	-0.676502	-2.924918	1.586477
1	-2.516983	2.776277	-0.871566
1	-2.060058	-2.596744	2.629869
1	-3.505930	2.680943	0.595911
6	-3.180751	0.216112	-2.017154
6	-2.358452	-2.622317	-0.787310
1	-2.878012	-0.540576	-2.748054
1	-2.301937	-2.562860	-1.879604
1	-2.923602	1.200298	-2.422085
1	-1.616853	-3.356116	-0.452294
1	-4.273110	0.169630	-1.919889
1	-3.349184	-3.017698	-0.525646
7	3.238556	2.111800	0.147826
1	-0.044529	0.083700	-1.918294
6	2.538692	3.355355	-0.222053
1	2.759280	3.616944	-1.264561
1	2.836414	4.186663	0.419540
6	1.072908	2.955488	-0.041707
1	0.405175	3.402691	-0.783826
1	0.696390	3.216723	0.957805
6	2.597573	-0.317984	-0.056053
6	3.850383	-0.899983	0.067881
6	3.947515	-2.285246	0.049598
1	4.732056	-0.275903	0.182660

6	1.570106	-2.389107	-0.228701
6	2.789506	-3.038276	-0.101465
1	4.914227	-2.769075	0.151033
1	0.644182	-2.942996	-0.363883
1	2.819136	-4.122861	-0.124074
7	1.465008	-1.053261	-0.197228

[Cp*Ir(6)]$^{2+}$

E = -947.347962386 a.u.

77	0.316075	-0.005371	-0.006117
7	-1.323042	1.295558	-0.031878
6	-2.507466	0.738706	-0.001836
6	2.082720	-0.294344	-1.168458
6	2.102678	-1.226050	-0.074018
6	2.087202	1.055616	-0.629092
6	2.072052	0.954122	0.791993
6	2.064891	-0.460549	1.137162
6	2.077642	-0.642963	-2.608504
1	1.570337	0.123499	-3.202834
1	1.585621	-1.605162	-2.784215
1	3.109891	-0.721855	-2.974578
6	2.140712	-2.708217	-0.186420
6	2.083782	2.298466	-1.444114
1	1.652625	-3.049468	-1.105055
1	1.385454	2.217197	-2.284663
1	1.644792	-3.188975	0.663020
1	1.800449	3.169663	-0.845806
1	3.179263	-3.060462	-0.210158
1	3.082605	2.481980	-1.859205
6	2.045021	2.068802	1.772488
6	2.036988	-1.001718	2.516605
1	1.359585	1.851773	2.599309
1	1.473569	-0.347859	3.189838
1	1.732264	3.006638	1.303827
1	1.590012	-2.000639	2.545350
1	3.043970	2.218976	2.201105
1	3.060617	-1.079254	2.906076
6	-3.032238	2.943880	-0.093001
1	-3.468586	3.596492	0.665111
1	-3.298748	3.326692	-1.083516
6	-1.515602	2.749309	0.079527
1	-1.165522	3.081390	1.064291
1	-0.934190	3.273486	-0.683547
6	-2.515047	-0.734690	-0.014202
6	-3.071769	-2.930422	0.095978
6	-1.553901	-2.758883	-0.088078
1	-3.337115	-3.304631	1.090079
1	-3.522137	-3.580996	-0.655736
1	-1.214463	-3.110226	-1.069461
1	-0.975783	-3.281144	0.678988
7	-3.534692	1.567947	0.053096
1	-4.504621	1.289327	-0.042975
7	-3.555488	-1.548972	-0.054283
1	-4.519285	-1.255527	0.057482
7	-1.337396	-1.306497	0.003362

[Cp*Ir(6)(HCO$_2$)]$^{+}$

E = -1136.59486594 a.u.

77	-0.369283	0.062798	-0.041350
7	1.330029	1.345295	-0.171284

6	2.503501	0.818505	-0.000450
1	4.465833	1.304161	-0.354355
6	-1.610002	1.242003	1.243937
6	-1.653436	-0.129098	1.661020
6	-2.117055	1.313029	-0.114662
6	-2.512923	-0.015115	-0.496957
6	-2.210829	-0.916580	0.577149
6	-1.157756	2.390588	2.072420
1	-0.822050	3.228576	1.453164
1	-0.336132	2.106411	2.738602
1	-1.985491	2.749366	2.697326
6	-1.246376	-0.662174	2.987423
6	-2.295467	2.542716	-0.934061
1	-0.465497	-0.045610	3.444611
1	-1.634310	3.347814	-0.597073
1	-0.871102	-1.688142	2.905919
1	-2.081016	2.349243	-1.991064
1	-2.106463	-0.677105	3.669076
1	-3.327948	2.908763	-0.865153
6	-3.080098	-0.372687	-1.822788
6	-2.497694	-2.376148	0.643202
1	-2.921842	-1.427184	-2.064291
1	-2.692093	-2.797044	-0.347300
1	-2.633489	0.233267	-2.618739
1	-1.659040	-2.926616	1.085752
1	-4.160105	-0.178244	-1.826223
1	-3.379899	-2.562589	1.268968
7	3.551740	1.660618	-0.097084
6	0.170214	-1.595551	-2.545510
1	0.593721	-1.698071	-3.567301
8	-0.433324	-2.544714	-2.037438
8	0.395708	-0.440883	-2.030554
6	3.030073	2.890035	-0.723490
1	3.249243	2.881819	-1.797709
1	3.477570	3.780664	-0.279213
6	1.525079	2.774692	-0.445392
1	0.906869	3.092702	-1.290308
1	1.221985	3.353341	0.437842
6	2.507714	-0.604876	0.329741
6	1.562536	-2.583560	0.702141
6	3.064082	-2.688633	0.979697
1	0.943628	-2.995774	1.503862
1	1.283331	-3.076517	-0.239633
1	3.524419	-3.567463	0.525728
1	3.283871	-2.685214	2.054575
7	1.341409	-1.137916	0.546563
7	3.560785	-1.444133	0.365781
1	4.484584	-1.091133	0.592470

[Cp*Ir(6)(HCO$_2$)]$^+$ β-hydride elimination TS

E = -1136.56417884 a.u.

77	-0.434959	0.048081	0.044916
7	1.274164	-0.915710	-0.805960
6	2.402528	-0.270209	-0.769493
1	4.395334	-0.700182	-0.718590
6	-2.065028	0.052028	-1.470661
6	-2.223338	1.175481	-0.600509
6	-2.117187	-1.144214	-0.651559
6	-2.346622	-0.749574	0.702829
6	-2.382238	0.697331	0.750733
6	-1.922728	0.080406	-2.951280
1	-1.272330	-0.727242	-3.306390
1	-1.503262	1.030578	-3.297247

1	-2.899771	-0.049537	-3.435220
6	-2.227526	2.604580	-1.010633
6	-2.024353	-2.539455	-1.160410
1	-1.600869	2.773018	-1.892833
1	-1.343721	-2.609719	-2.016183
1	-1.870953	3.253779	-0.204012
1	-1.670205	-3.227334	-0.385271
1	-3.248446	2.919747	-1.261586
1	-3.009807	-2.889601	-1.493730
6	-2.545005	-1.659837	1.862075
6	-2.678447	1.532724	1.947074
1	-2.175786	-1.214062	2.791467
1	-2.367478	1.030002	2.868713
1	-2.035357	-2.617547	1.715878
1	-2.160365	2.496720	1.898782
1	-3.614695	-1.867661	1.994388
1	-3.754620	1.735960	2.023872
7	3.503721	-0.969831	-1.122662
6	1.392835	-1.360569	2.133570
1	0.330991	-0.395882	1.511031
8	0.780130	-2.355071	2.381613
8	2.400509	-0.718870	2.149278
6	3.099145	-2.389347	-1.079939
1	3.389930	-2.829988	-0.117750
1	3.566647	-2.959064	-1.884709
6	1.575844	-2.292714	-1.221200
1	1.040377	-3.013620	-0.595909
1	1.246527	-2.432682	-2.259592
6	2.304708	1.115821	-0.343088
6	1.195307	2.927941	0.339056
6	2.700778	3.179668	0.476479
1	0.755573	3.508338	-0.483091
1	0.633236	3.148601	1.250976
1	3.029825	3.116625	1.520961
1	3.009196	4.142955	0.067075
7	1.112162	1.500011	0.005762
7	3.268755	2.060656	-0.300209
1	4.233083	1.780811	-0.153462

[Cp*Ir(6)(H)]$^+$

E = -948.072712076 a.u.

77	-0.329032	-0.017511	-0.303308
7	1.356527	1.267706	-0.160512
6	2.533130	0.723711	-0.049282
1	4.483990	1.307767	-0.214943
6	-1.660097	0.332837	1.513943
6	-1.832504	-0.993643	1.025446
6	-1.980134	1.232759	0.426837
6	-2.414573	0.461847	-0.698694
6	-2.295387	-0.935991	-0.343005
6	-1.256416	0.741077	2.888160
1	-0.601718	1.620773	2.870685
1	-0.723185	-0.064271	3.404551
1	-2.133206	1.000339	3.496975
6	-1.595489	-2.247708	1.790722
6	-1.965701	2.718586	0.517393
1	-0.787989	-2.131259	2.522050
1	-1.160359	3.072900	1.170743
1	-1.338473	-3.078934	1.125229
1	-1.838001	3.182540	-0.466314
1	-2.501977	-2.536101	2.338407
1	-2.912974	3.081299	0.937456
6	-2.959767	1.000656	-1.976403

6	-2.721632	-2.100318	-1.171370
1	-2.784338	0.312541	-2.809733
1	-2.667180	-1.868494	-2.240378
1	-2.502700	1.962030	-2.233385
1	-2.083768	-2.973165	-0.989284
1	-4.043355	1.157668	-1.896203
1	-3.755984	-2.391869	-0.945548
7	3.571697	1.577098	0.139914
1	0.067352	-0.116481	-1.885222
6	3.043926	2.914090	-0.193228
1	3.288253	3.167188	-1.232251
1	3.460016	3.679793	0.463859
6	1.537875	2.716023	-0.000901
1	0.930293	3.270657	-0.720878
1	1.212533	2.998586	1.010813
6	2.535306	-0.726262	-0.068825
6	1.554406	-2.720975	-0.236569
6	3.027936	-2.917574	0.125407
1	0.870376	-3.282689	0.405738
1	1.344670	-2.993591	-1.280847
1	3.517628	-3.682890	-0.478904
1	3.153116	-3.168474	1.186057
7	1.354064	-1.274176	-0.087341
7	3.586034	-1.579303	-0.146171
1	4.458902	-1.311466	0.297003

$[Cp^{*}Ir(6)(H)(HCO_2H)]^{+}$ H_2 formation TS

E = -1137.73795240 a.u.

77	-0.254553	-0.225341	-0.016396
6	-0.933420	-1.683469	1.433552
6	-1.439826	-2.049577	0.122178
6	-2.276563	-0.991914	-0.343603
6	-1.498666	-0.402582	1.768033
6	-2.303330	0.046771	0.668857
6	-1.281126	0.340381	3.034932
1	-2.078657	0.088586	3.745646
1	-0.325101	0.079091	3.499950
1	-1.310072	1.423316	2.875170
6	-3.118394	1.290633	0.625570
1	-4.098920	1.117881	1.088042
1	-2.633001	2.106865	1.171662
1	-3.289662	1.620910	-0.404192
6	-3.004007	-0.936853	-1.637859
1	-4.049064	-1.239054	-1.493239
1	-3.002938	0.078894	-2.048174
1	-2.558989	-1.608255	-2.378606
6	-1.153310	-3.324172	-0.586838
1	-1.894604	-4.082658	-0.305380
1	-1.197158	-3.200015	-1.673642
1	-0.164900	-3.716037	-0.325163
6	-0.082479	-2.531143	2.310299
1	0.541134	-1.919977	2.971016
1	-0.705073	-3.179097	2.940425
1	0.578145	-3.176052	1.720779
1	-0.048085	0.658597	-1.597872
6	-1.712076	3.174003	-1.926283
1	-2.116355	4.206523	-1.796107
8	-2.316596	2.399141	-2.686091
8	-0.655809	2.931937	-1.258550
1	-0.332309	1.442983	-1.334779
6	2.690134	-0.247292	-0.461793
6	3.510104	-1.799959	-1.874263
1	4.648293	-0.138507	-1.061172

6	2.073424	-2.139824	-1.467485
1	3.559756	-1.387560	-2.889274
1	4.186765	-2.652965	-1.805394
1	2.033336	-2.996718	-0.780219
1	1.421398	-2.352459	-2.318756
6	2.460137	0.952503	0.337695
6	2.592325	2.980136	1.316836
1	4.235873	1.977003	0.310499
6	1.209048	2.358165	1.537526
1	3.031959	3.376756	2.233282
1	2.567380	3.773990	0.560532
1	0.384614	3.024883	1.269580
1	1.068010	2.037091	2.578229
7	1.627453	-0.939437	-0.745943
7	1.223915	1.168122	0.675505
7	3.364719	1.830203	0.809569
7	3.860507	-0.755492	-0.893032

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