Electronic Supplementary Information

Mechanistic investigation of CO_2 hydrogenation by Ru(II) and Ir(III) aqua complexes under acidic conditions: two catalytic systems differing in the nature of the rate determining step

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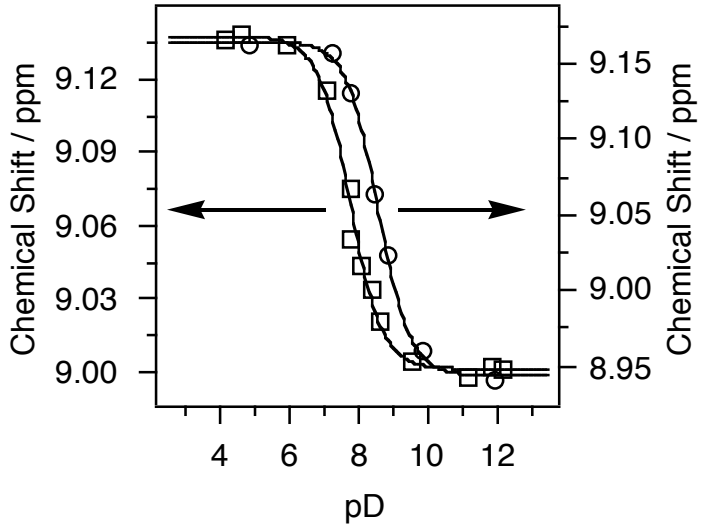

Fig. S1 pD-dependent chemical shift changes of the protons on 6-positions of the bpy ligands of **1**(SO_4) (circles) and **5**(SO_4) (squares) determined by ^{1}H NMR.

Derivation of eq 2 (S2) According to Fig. 3, the rate for the product formation including the formate complex is given by eq (i). The rate of formation of $[Ru\text{-}H]^+$ is given by eq (ii).

$$d[HCOOH]/dt = k_2 P_{CO_2}[[Ru\text{-}H]^+] \quad \text{(i)}$$

$$d[[[Ru\text{-}H]^+]/dt = k_1 P_{H_2}[[Ru\text{-}OH_2]^{2+}] - k_{-1}[[Ru\text{-}H]^+] - k_2 P_{CO_2}[[Ru\text{-}H]^+] \quad \text{(ii)}$$

Under the steady state conditions, $d[[[Ru\text{-}H]^+]/dt \approx 0$, from which eq (iii) is derived.

$$[[Ru\text{-}H]^+] = k_1 P_{H_2}[[Ru\text{-}OH_2]^{2+}]/(k_{-1} + k_2 P_{CO_2}) \quad \text{(iii)}$$

Since $[[Ru\text{-}OH_2]^{2+}]_0 = [[Ru\text{-}OH_2]^{2+}] + [[Ru\text{-}H]^+]$, eq (iii) is rewritten by eq (iv).

$$[[Ru\text{-}OH_2]^{2+}] = [[Ru\text{-}OH_2]^{2+}]_0(k_{-1} + k_2 P_{CO_2})/(k_{-1} + k_1 P_{H_2} + k_2 P_{CO_2}) \quad \text{(iv)}$$

Eq (i) is then written by eq (v) by using eq (iii) and eq (iv).

$$d[HCOOH]/dt = k_1 k_2[[Ru\text{-}OH_2]^{2+}]_0 P_{H_2} P_{CO_2}/(k_{-1} + k_1 P_{H_2} + k_2 P_{CO_2}) \quad \text{(v)}$$

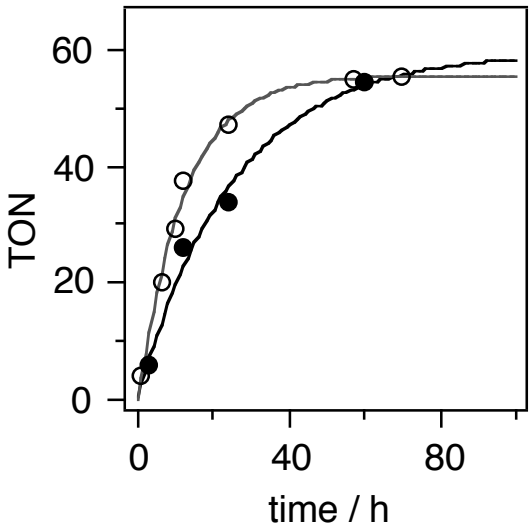

Fig. S3 Time-dependent TONs for the hydrogenation of CO_2 {P_{H_2/CO_2} = 5.5/2.5 MPa} catalysed by **6**(SO_4) at 40 ˚C at pH 3.0 in H_2O with a citrate buffer (filled circles) or without the buffer (unfilled circles).

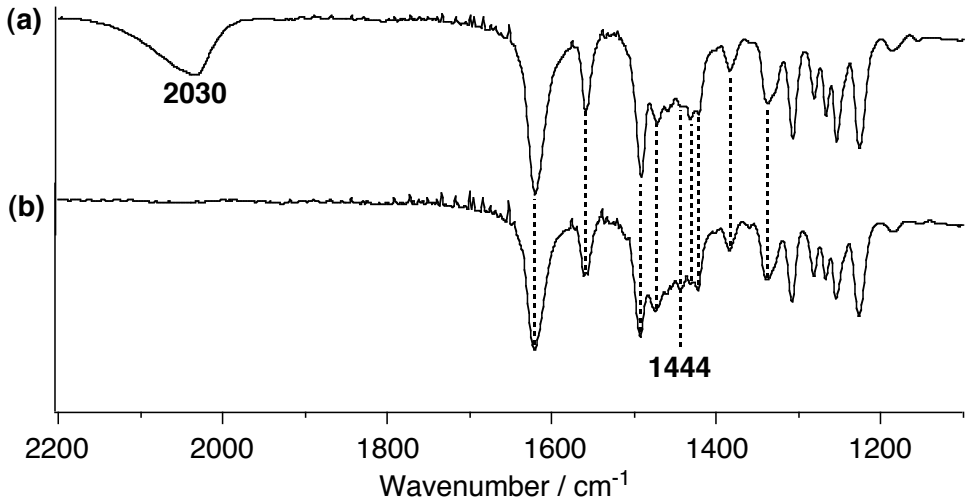

Fig. S4 IR spectra as KBr disks of **8**(PF_6) (a) and D-labeled **8**(PF_6) (b).

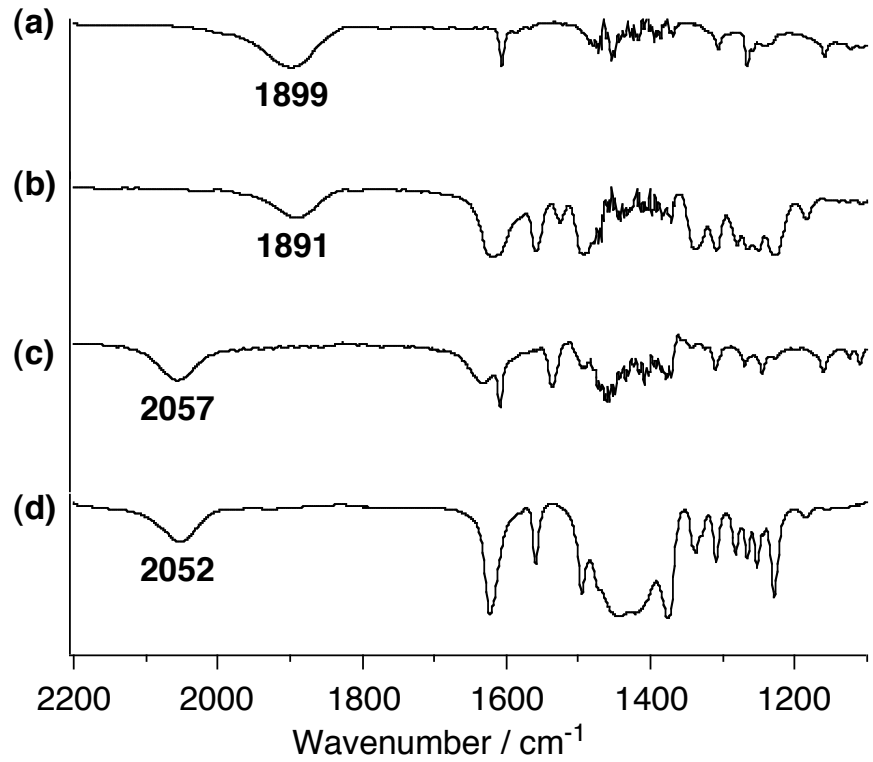

Fig. S5 IR spectra in CH_3CN of **3**(PF_6) (a), **4**(PF_6) (b), **7**(PF_6) (c) and **8**(PF_6) (d).