Electronic Supplementary Information

Mechanistic investigation of CO₂ 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(SO₄) (circles) and 5(SO₄) (squares) determined by ¹H 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-H]⁺ is given by eq (ii).

\[
\frac{d[HCOOH]}{dt} = k_2PCO_2[[Ru-H]^+] \tag{i}
\]

\[
\frac{d[[Ru-H]^+]}{dt} = k_1PH_2[[Ru-OH_2]^{2+}] - k_1[[Ru-H]^+] - k_2PCO_2[[Ru-H]^+] \tag{ii}
\]

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

\[
[[Ru-H]^+] = \frac{k_1PH_2[[Ru-OH_2]^{2+}]}{(k_1 + k_2PCO_2)} \tag{iii}
\]

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

\[
[[Ru-OH_2]^{2+}] = [[Ru-OH_2]^{2+}]_0(k_1 + k_2PCO_2)/(k_1PH_2 + k_2PCO_2) \tag{iv}
\]

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

\[
\frac{d[HCOOH]}{dt} = k_1k_2[[Ru-OH_2]^{2+}]_0PH_2PCO_2/(k_1PH_2 + k_2PCO_2) \tag{v}
\]
**Fig. S3** Time-dependent TONs for the hydrogenation of CO$_2$ ($P_{H_2}/P_{CO_2} = 5.5/2.5$ MPa) catalysed by 6(SO$_4$) at 40 °C at pH 3.0 in H$_2$O 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$_3$CN of 3(PF$_6$) (a), 4(PF$_6$) (b), 7(PF$_6$) (c) and 8(PF$_6$) (d).