An efficient binuclear catalyst for decomposition of formic acid

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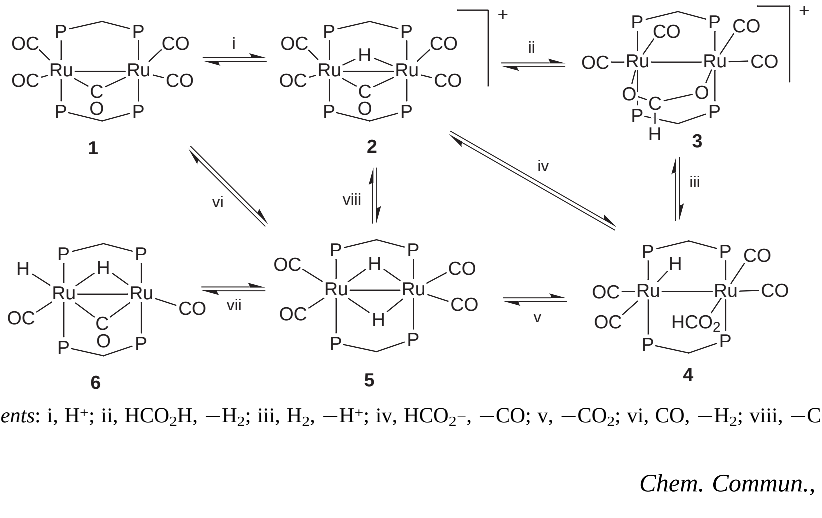
The complex [Ru_2(μ-CO)(CO)$_4$(μ-dppm)$_2$] is more active than mononuclear ruthenium complexes as a catalyst for decomposition of formic acid to CO_2 and H_2; under conditions of highest activity, a coordinatively unsaturated diruthenium dihydride [Ru_2H(μ-H)(μ-CO)(CO)$_2$(μ-dppm)$_2$] is present and can be isolated from solution.

This paper reports the first study of the decomposition of formic acid to hydrogen and carbon dioxide using a locked binuclear catalyst and presents evidence that this is an unusual catalytic reaction in which two metals can act cooperatively to give enhanced activity.† The reversible reaction between HCO_2H and H_2 + CO_2 has been the subject of considerable interest, either for catalytic transfer hydrogenation using formic acid or for utilization of CO_2 as a reagent in organic synthesis.[1,2]

The reaction of [Ru_2(μ-CO)(CO)$_4$(μ-dppm)$_2$] **1**,[3] dppm = $Ph_2PCH_2PPh_2$, in acetone (5×10^{-3} м) with formic acid (10^{-1} м) in a closed tube at 20 °C was monitored by NMR. The products were H_2 [$\delta(^1H)$ 4.5] and CO_2 [$\delta(^{13}C)$ 125.8] only and the reaction was complete in 0.3 h, corresponding to a mean turnover rate of *ca.* 70 h^{-1}, and considerably higher activity was observed when the reaction was carried out in an unsealed vessel, for reasons discussed below. The activity is significantly higher than for comparable mononuclear ruthenium complex catalysts: for example, [RuHBr(CO)(PEt$_2$Ph)$_3$] gives a turnover rate of *ca.* 4 h^{-1} in refluxing acetic acid (117 °C).[1a]

The high catalytic activity of **1** prompted a more detailed study and some important features of the binuclear catalysis have been elucidated. The catalysis is more efficient in the dipolar aprotic solvent acetone than in solvents such as toluene or dichloromethane. The catalytic reaction is strongly or completely inhibited by the presence of excess CO; in a sealed vessel, CO dissociates from **1** at intermediate stages of reaction and then acts as inhibitor, whereas, in a vessel in which evolved gases sweep CO from the system, this effect cannot occur and so the catalysis is faster. The reaction appears not to be wholly intramolecular since decomposition of either HCO_2D or DCO_2H leads to formation of a mixture of H_2, HD and D_2 rather than HD alone, but the conclusion is weakened by the observation that decomposition of HCO_2H in the presence of D_2 gives both H_2 and HD. The final product mixture from decomposition of HCO_2D or DCO_2H is approximately that expected from statistical considerations (H_2 : HD : D_2 = 1 : 2 : 1, determined by MS) but in the very early stages of reaction H_2 is predominant. Under these reaction conditions, there was no evidence for reversibility which would lead to isomerization between HCO_2D and DCO_2H. Decomposition of $H^{13}CO_2H$ gave only H_2 and $^{13}CO_2$, with no free or coordinated ^{13}CO detectable by either IR or ^{13}C NMR.

There were interesting changes in the ruthenium complexes present at various stages of the catalytic reaction and several of these could be isolated or identified spectroscopically. When the reaction was carried out in a sealed tube, the only ruthenium complex present when reaction was complete was unchanged **1** but other complexes were present during catalysis (Scheme 1). The first complex formed at −30 °C was [Ru_2(μ-H)(μ-CO)(CO)$_4$(μ-dppm)$_2$]$^+$ **2**, as the formate salt.‡ This complex is formed by protonation of the Ru–Ru bond of **1** and the same cation is formed by protonation with other acids such as H[BF_4].[4] Next to be formed was the cation [Ru_2(μ-HCO_2)(CO)$_4$(μ-dppm)$_2$]$^+$ **3** (also as the formate salt), whose spectroscopic properties‡ are very similar to the known μ-acetate analogue;[4,5] the first formation of H_2 could be detected at this stage. When most formic acid was consumed, two more complexes were formed transiently. The major complex was characterized as [Ru_2H_2(CO)$_4$(μ-dppm)$_2$] **5**, by the following spectroscopic data.‡[6] In the ^1H NMR spectrum, a hydride resonance at $\delta(^1H)$ −9.25 [qnt, J(PH) 9 Hz] integrated for two protons and a single resonance at $\delta(CH_2P_2)$ 4.6 were observed, in the ^{13}C NMR spectrum a single terminal carbonyl resonance was observed at δ(CO) 196.8, and in the ^{31}P NMR spectrum a singlet was observed at δ(P) 34.3. These data indicate structure **5**, having D_{2h} symmetry; a less symmetrical but fluxional structure is also possible[6] though no change in the NMR spectra was observed at −70 °C. The second transient complex was tentatively identified as [$Ru_2H(HCO_2)$(CO)$_4$(μ-dppm)$_2$] **4**.‡ It is characterized in the ^1H NMR by resonances at δ −6.7 (br s, 1H, RuH) and at δ 8.5 (s, 1H, HCO_2), in the ^{13}C NMR (in a reaction using $H^{13}CO_2H$) by δ 165 (s, CH, HCO_2) (the concentration of **4** was never great enough to allow identification of the metal carbonyl resonances even using ^{13}C enriched starting material **1**) and in the ^{31}P NMR by a single resonance at δ 39.8.[5] If structure **4** is correct, it is required to be fluxional in order to give a single resonance in the ^{31}P NMR spectrum.[4] Further



Scheme 1 *Reagents*: i, H^+; ii, HCO_2H, $-H_2$; iii, H_2, $-H^+$; iv, HCO_2^-, −CO; v, $-CO_2$; vi, CO, $-H_2$; viii, −CO; viii, H^+, CO, $-H_2$.

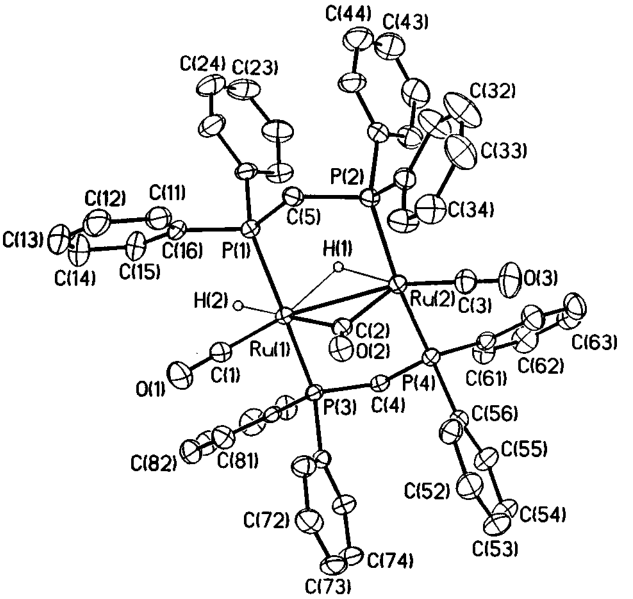
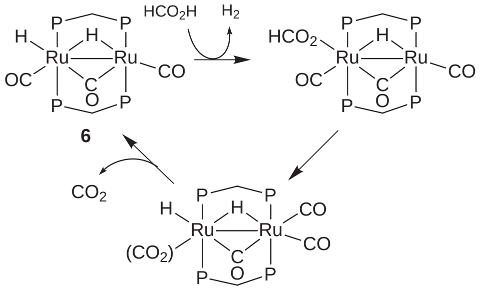


Fig. 1 A view of the structure of $[Ru_2H(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$. Distances (Å): Ru(1)–Ru(2) 2.8769(5), Ru(1)–C(1) 1.857(5), Ru(1)–C(2) 2.198(5), Ru(2)–C(2) 2.006(4), Ru(2)–C(3) 1.841(5). The hydride H-atoms were located but not refined; approximate distances Ru(1)–H(1) 2.16, Ru(2)–H(1) 2.16, Ru(1)–H(2) 1.66.

study indicated that the concentration of **5** with respect to **2** was pH dependent, since addition of Et_3N led to an increase in the relative concentration of **5**. Overall then, at high $[HCO_2H]$, complex **1** reacted to give **2** and **3** and, as HCO_2H was consumed, the concentrations of these complexes decreased and the transient complexes **4** and **5** appeared, quickly followed by reformation of **1**. These observations are readily rationalized since **5** is expected to be very reactive towards formic acid, and formate probably dissociates easily from **4** in the presence of formic acid to give the less nucleophilic anion $[H(O_2CH)_2]^-$; hence the concentration of these complexes **4** and **5** only builds up to detectable levels when the concentration of formic acid is low.

When the reaction was carried out in an unsealed vessel, the initial reactions were similar but a new complex $[Ru_2H(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2]$, **6**, was formed in the later stages rather than **4** or **5**. Complex **6** is a unique example of a coordinatively unsaturated binuclear ruthenium dihydride;[4,6] it could be crystallized from the reaction mixture and was fully characterized by an X-ray structure determination (Fig. 1) as well as by spectroscopic methods.‡ Complex **6** was stable in the solid state but in solution it was stable only in the presence of hydrogen and in the complete absence of oxygen; it reacted rapidly with CO to give **1** with loss of H_2. Clearly, this high reactivity of **6** with CO explains why no **6** is formed when the reaction is carried out in a sealed tube; **6** reacts with one equivalent of CO to give **5** and then with a second equivalent of CO to give **1** and H_2. Solutions containing the coordinatively unsaturated complex **6** were particularly active for further catalytic decomposition of formic acid.

It is interesting to speculate on why the binuclear system described above is so reactive for decomposition of formic acid. The key steps in the initial catalytic reaction are likely to be the overall oxidative addition of formic acid to ruthenium(0) to give a hydrido(formato) complex and then probably a ß-elimination from the formate to give a transient dihydrido(CO_2) complex which ultimately yields H_2 and CO_2. Both of these proposed steps require a vacant coordination site, and the necessary dissociation of two CO ligands is probably easier to accomplish in the binuclear system. There is some independent evidence for CO labilization *cis* to the bridging hydride ligand in complex **2**. Thus, exposure of **2** to ^{13}CO led to carbonyl exchange but the substitution in the terminal carbonyl sites *cis* to the μ-H ligand [$\delta(^{13}C)$ 198.6] was much faster (exchange detected in < 1 h) than in the *trans* terminal [$\delta(^{13}C)$ 200.8] or bridging [$\delta(^{13}C)$ 278.6] carbonyl sites (exchange detected after one day).§ While the reactions of Scheme 1 provide a viable route for the catalytic reaction in the presence of CO, the data suggest that CO-deficient complexes, such as **6**, are most active and it is likely that other key intermediates are too short-lived to be detected. A reasonable catalytic cycle involving **6** is shown in Scheme 2.



Scheme 2 A possible mechanism of catalysis.

In summary, this article describes a novel binuclear catalytic system for formic acid decomposition, in which the major ruthenium complexes in solution are dependent on both reaction conditions and the stage of the catalytic reaction. It suggests that binuclear and cluster complexes, especially those that can easily achieve coordinative unsaturation, may have distinct advantages over mononuclear transition metal catalysts for this and related catalytic reactions.[7]

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Notes and references

† Binuclear complexes have been identified in formic acid decomposition previously but were not thought to be involved in the catalytic cycle.[1c]

‡ *Selected spectroscopic data*: **2**: $\delta(^1H)$ −8.9 [qnt, 1H, J(PH) 9 Hz, $Ru_2(\mu\text{-}H)$]; $\delta(^{13}C)$ 199, 201 (terminal CO), 278.6 (μ-CO); $\delta(^{31}P)$ 27.8 (dppm). Preliminary X-ray data on the $[BF_4]^-$ salt gives d(Ru–Ru) 2.960(3) Å compared to 2.903(2) Å in **1**. **3**: $\delta(^{13}C)$ 188, 206 (terminal CO); 181 (HCO_2); $\delta(^{31}P)$ 30.9 (dppm). **4**: $\delta(^1H)$ −6.7 (m, 1H, RuH), 8.5 (s, 1H, HCO_2); $\delta(^{13}C)$ 165 (HCO_2); $\delta(^{31}P)$ 39.9 (dppm). **5**: $\delta(^1H)$ −9.2 (qnt, 2H, RuH) $\delta(^{13}C)$ 197 (terminal CO); $\delta(^{31}P)$ 34.3 [dppm]. **6**: $\delta(^1H)$ −9.3 [t, 1H, RuH], −9.6 [quint, 1H, $Ru_2(\mu\text{-}H)$]; $\delta(^{31}P)$ = 42.5, 46.5 (m, dppm). *Crystal data* for **6**: monoclinic, space group $P\bar{2}_1/n$, a = 11.583(1), b = 28.557(3), c = 16.783(2) Å, β = 97.817°, V = 5499(1) Å^3, T = 296 K, μ = 7.1 cm^{-1}, 7115 reflections, R_1 = 0.0466, wR_2 = 0.0918. CCDC 182/1033.

§ The assignments are based on the observation of J(CC) coupling between the mutually *trans* bridging and terminal carbonyl ligands in the fully ^{13}CO enriched complex.

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