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Insights into Hydrogen Generation from Formic Acid Using Ruthenium Complexes

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The decomposition of a HCO_2H/Et_3N azeotrope to a mixture of hydrogen and carbon dioxide may be catalyzed by a number of Ru(III) and Ru(II) complexes with high efficiency at ca. 120 °C. Evidence that suggests that the precatalyst may in each case be a common ruthenium dimer has been obtained through ^1H NMR and X-ray crystallographic studies of the complexes formed in situ and of analysis of the gases generated in the reaction using FTIR and gas chromatography methods.

There is currently a high level of interest in the use of hydrogen as an energy vector; since the only byproduct of its combustion is water, it represents a clean power source.[1,2] Currently, hydrogen is generated from fossil fuel sources using steam reforming and related processes.[3] Heterogeneous catalytic systems have been investigated for hydrogen generation from biomass, and this continues to be an important area for future research work.[4]

Formic acid (FA) may be regarded as a source of, and storage material for, hydrogen.[5–12] FA will decompose to H_2/CO_2 in a thermodynamically favored process (Scheme 1),[5k] although highly elevated temperatures are required.[5a–c] The process may be catalyzed by a number of metal complexes. Publications from the 1950s through to the present day[5d–q] describe the use of various metals including Au/Pd,[5d,5e] Ag,[5f] Ni,[5f,5g,5i] Cu,[5g,5i] Pt,[5h,5p,5q] Ru,[5h,5o] Ir,[5h] Ti, V, Cr, Mn, Fe, Co,[5h] W,[5j] Rh,[5k,5n] Pt,[5l] and Cd.[5m] Formate salts may also be used as effective sources of hydrogen, including ammonium and metal formates.[6] The reverse reaction, i.e., the hydrogenation of carbon dioxide, has been demonstrated to be a practical and viable method of making FA.[7] Fuel cells based on FA have been developed and are being commercialized.[8] The intermediacy of FA in the water gas shift reaction presents the possibility of making hydrogen from water and carbon monoxide, via FA.[9] Hence, there is significant potential for the development of a viable "joined up" system of hydrogen

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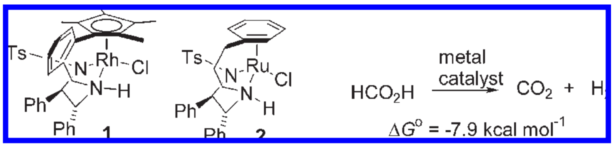
Scheme 1



generation, storage, and transport based on the use of FA, which is safer to use than high-pressure hydrogen gas.

Despite extensive prior research work, the rate at which hydrogen may be generated by the FA decomposition reaction still remains unoptimized. Recent papers, published during the course of our own studies, have highlighted this issue and presented potential solutions to it in the form of highly active homogeneous Ru catalysts.[10,11] Laurenczy has reported a continuous-injection system in which a FA/sodium formate solution is degraded to CO_2 and H_2 (without CO contamination) using $[Ru_2(H_2O)_6(OTs)_2]$ with a water-soluble phosphorus ligand. The best results were achieved at 120 °C.[11] Beller[10] chose to investigate the formation of hydrogen from FA-amine adducts (FA/triethylamine (FA/TEA) is known to form a stable 5:2 azeotrope[12]). Using a series of Ru(III) and Ru(II) catalysts, with tertiary amines, the combination of $[RuCl_2(PPh_3)_3]$ and Et_3N emerged as the best. At 40 °C, a TOF (turnover frequency; moles hydrogen/moles catalyst/h) of 3630 h^{-1} (first 20 min) was achieved and represents the highest reported activity for FA decomposition at this temperature.[10] While this is likely to remain unchallenged for the 40 °C reaction, in this paper we describe a catalyst system for hydrogen generation from FA with TOFs of up to 1.80×10^4 h^{-1} at 120 °C.

We have studied the process of asymmetric transfer hydrogenation (ATH) with Ru and Rh catalysts,[13-15] using FA/TEA as the hydrogen source, a process first reported by Noyori et al.[13] During the course of our studies on closely related but highly active *tethered* catalysts such as **1** and **2**, we frequently observed *substantial* gas generation (at rt) from FA/TEA during the course of the reaction. This was also noted to be hydrogen gas by Noyori in his 1995 paper[14b] and subsequently by other researchers in this area.[15] We also have established that the gas produced by **1**, **2**, and other catalysts we have studied is a mixture of H_2 and CO_2 (see Experimental Section and Supporting Information).

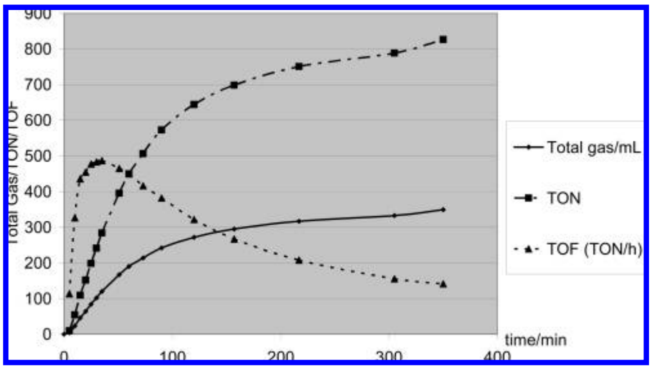
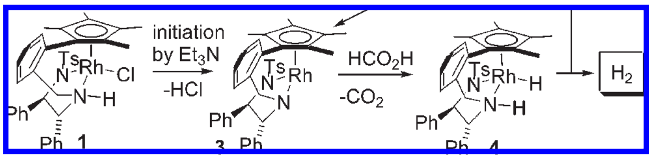


Figure 1. Hydrogen and carbon dioxide generation using catalyst **1** (6.3 mg in 2.5 mL 5:2 FA/TEA, 0.0088 mmol), at rt (20 °C).

Scheme 2. Proposed Mechanism of Hydrogen Generation from FA by Catalyst 1



Given the resurgence of interest in FA as a hydrogen-carrying vector,[5e,10,11] we elected to study this reaction further. The rate of hydrogen generation from 5:2 (molar) FA/triethylamine azeotrope (FA/TEA) was accurately determined using a gas syringe to directly measure the volume produced in the reaction (see Supporting Information). The turnover number (TON: moles hydrogen/moles catalyst) and turnover frequency (TOF) could thus be readily calculated. The results obtained from using catalyst **1** are shown in Figure 1. The maximum TOF was ca. 490 h^{-1} after ca. 35 min, and the volume of consumed FA at the end of the reaction was 7.3 mmol (335 mg, 0.28 mL); hence only ca. 20% had been consumed. This indicated that either catalyst deactivation is taking place or the ratio of FA to triethylamine must be above a minimal level for the catalyst to be active. Although this clearly indicates a limitation, the maximum TOF was very high for a catalytic decomposition of FA at *room temperature*.

Control reactions were carried out in order to determine whether the full catalyst structure was required for hydrogen generation (see Supporting Information). It was also observed that FA alone does not work; a basic additive is required, in accord with Beller's findings.[10] Aqueous FA and sodium formate were tested and gave no evolution of gas. The analogous ruthenium(II) catalyst **2** was less active in this application.

Our proposed mechanism of the hydrogen formation is anticipated to be closely related to that of ATH of ketones[13] (Scheme 2). In the first step, HCl is eliminated from **1** to furnish the 16-electron species **3**, which abstracts two hydrogen atoms from FA[13] to form ruthenium hydride complex **4**. In the absence of substrate, to which hydrogen would normally be transferred, competitive hydrogen elimination operates instead. The rate of gas evolution decreases sharply in the presence of a ketone substrate.

In view of the observed results, we speculated that other rhodium and ruthenium complexes containing a heteroatom adjacent to the metal may be able to operate through a similar process and thus generate hydrogen from FA/TEA. After a survey of a range of candidate organometallic complexes, we found that the commercially available complex $[RuCl_2(DMSO)_4]$ (**5**) was capable of the production of hydrogen from FA with a very high TOF (up to ca. 1.80×10^4 h^{-1}) and TON (2.50×10^4 after 4 cycles of FA replenishment) and without deactivation, at 120 °C. Other metal complexes (TONs in parentheses), including $Rh_2(OAc)_4$

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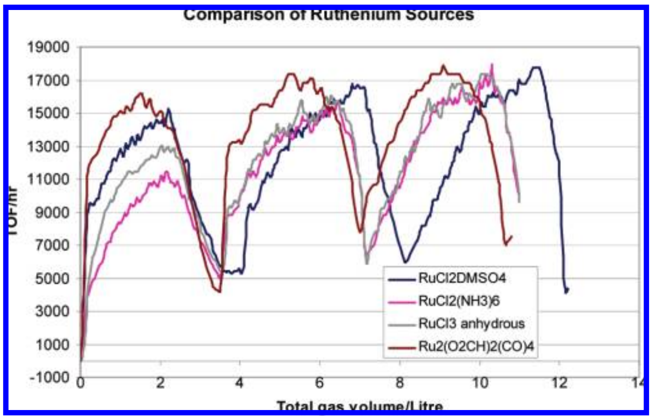

Figure 2. Hydrogen and carbon dioxide generation using Ru(II) and Ru(III) catalysts (TEA/FA, 120 °C, oil bath; see Supporting Information for full data). Maximum TOFs are 1.78×10^4 [$Ru_2Cl_2(DMSO)_4$], 1.80×10^4 [$RuCl_2(NH_3)_6$], 1.74×10^4 [$RuCl_3$], 1.78×10^4 [$Ru_2(HCO_2)_2(CO)_4$].

(17), $RhCl_3$ (17), $IrCl_3$ (434), $PdCl_2$ (4), $CoCl_2$ (3), $FeCl_3$ (3), $FeCl_2$ (3), $NiCl_2$ (3), and $(EN)_2PtCl_2$ (14), were much less effective, although $(NH_3)_2OsCl_6$ (1.30×10^3) showed some promise (see Supporting Information). The results of a typical experiment with complex **5** are shown in Figure 2, which illustrates the instantaneous TOF for the reaction. Illustrating the progress of the reaction in this way gives an immediate picture of the efficiency of the catalyst at any moment in the catalytic cycle. After an initial induction period[10] the TOF increased rapidly, before decreasing after a maximum of ca. 1.50×10^4 h^{-1} as FA was consumed. Several further aliquots of FA (calculated to replace the volume lost by gas formation) were added at the minimum-TOF point in the cycle, and in each case the TOF pattern was repeated, in each cycle rising to a higher maximum level. These results suggest that the catalyst is undergoing further activation in each cycle. The average TOF over this reaction period is ca. $(1.0-1.2)\times 10^4$ h^{-1}. If a continuous feed system were to be established, i.e., to keep the TOF at the highest point, then the average TOF has the potential to exceed 1.60×10^4 h^{-1}.

Over the course of the above reaction, each portion of added FA released ca. 3.5−4 L of total gas, i.e., 1.75−2 L of hydrogen. In the runs in Figure 2, each 3.5−4 L gas cycle was completed in ca. 20 min. Careful checks were conducted using cooled tubing to ensure that temperature changes were not giving false positive readings. It was found that the addition of extra DMSO (20 equiv) had no effect on the reaction; however the use of TEA was essential.[10] Other amines, for example, dimethyloctylamine, may be used, but provide no advantage over TEA.[10] An NMR investigation was conducted by sampling the liquid from the reaction over the course of one reaction cycle (see Supporting Information). The graph of these results revealed that the ratio of FA to TEA remained above the theoretical value for that part of the cycle, with an inflection that indicated that the FA:TEA ratio for the majority of the hydrogen-generation cycle was ca. 2:1. This suggests that some of the TEA may be preferentially evaporating at such a rate that the remaining liquid maintains a fairly constant FA:TEA ratio.

Further investigation also revealed that anhydrous $RuCl_3$ (max. TOF 1.74×10^4) and [$RuCl_2(NH_3)_6$] (max. TOF 1.80×10^4) performed as well as the DMSO complex in this application (also illustrated in Figure 2). Both catalysts continue to produce hydrogen over several cycles of added formic acid, without deactivation. The use of a higher concentration of catalyst results in faster generation of gas, but the TOFs were essentially unchanged (see Supporting Information), and the hydrogen gas from the reaction could be used directly in a hydrogen PEM fuel cell (see Supporting Information).

The observation of similar and increasing activity over the first three cycles indicates that a common catalyst is forming at high temperatures from each starting complex. There is evidence in the literature that dinuclear, divalent (Ru(II)Ru(III)) complexes containing bridging formate ligands are formed under similar conditions to ours.[5o,16] The complexes [$Ru_2(HCO_2)_4Cl\cdot 2H_2O$], [$Ru_2(HCO_2)_4Cl_2$]$^-$, and [$Ru_2(HCO_2)_4Cl.2H_2O$]$\cdot BF_4$ each contain four bridging formate ligands between bonded ruthenium atoms, which are formally a combination of Ru(II) and Ru(III).[16a−c] The complex [$Ru_2(HCO_2)_4Cl_2$]$^-$ has been characterized by X-ray crystallography,[16c] and the electronic structure of several such complexes has been described in detail.[16d,16f,16g] Closely related complexes containing bridging acetate ligands are also known and have been characterized.[16c,17] A diphosphine-bridged diruthenium complex, [$Ru_2(\mu\text{-}CO(CO)_4(\mu\text{-}dppm)_2$], has been reported to be active in formic acid decomposition to hydrogen and carbon dioxide.[5o,18] We speculated that a formate-bridged dimer may be formed in this process and subsequently participate in the dehydrogenation process via a formate addition intermediate. This would account for the requirement for TEA in the reaction, and, by implication, an ammonium formate salt.

In order to gain evidence to support the proposed formation of a Ru dimer, we attempted to isolate an active catalytic material from the reaction; however this proved unsuccessful. The addition of substoichiometric quantities of triphenylphosphine, however, provided some insights (Figure 3). The addition of 0.25 equiv of PPh_3 to the reaction after one cycle of formic acid consumption gave a slight increase in activity in the second cycle, analogous to the normal pattern, while addition of a second 0.25 equiv had little effect. The addition of a third 0.25 equiv, however, resulted in degradation of the rate of hydrogen production, while addition of a full equivalent of PPh_3 resulted in inhibition of the reaction.

These results are somewhat in contrast to those obtained by Beller,[10] in which the addition of a phosphine is shown to increase the rate of FA decomposition (in the presence of an amine); however it should be noted that Beller's results were obtained at a lower temperature than ours and may reflect the formation of a different catalytic species. From the reaction

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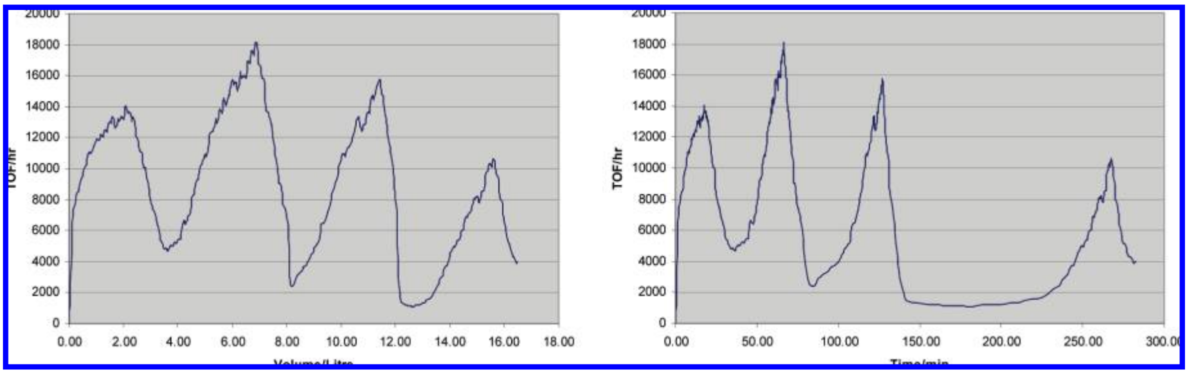

Figure 3. Observed TOFs using [$RuCl_2(DMSO)_4$] with PPh_3 added in 0.25 equiv portions after (i) 40, 80, and 150 min (10 mL FA/TEA, [$RuCl_2(DMSO)_4$] (6.5 mg, 13.4 μmol), 120 °C, oil bath).

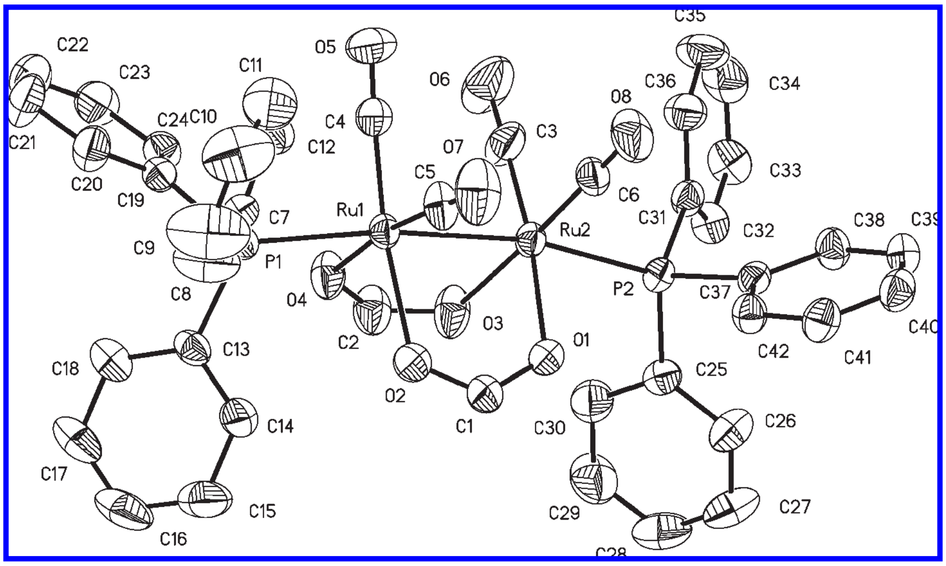

Figure 4. X-ray crystallographic structure of [$Ru_2(HCO_2)_2(CO)_4(PPh_3)_2$], **6**.

in which PPh_3 was added to [$RuCl_2(DMSO)_4$] in FA/TEA, a distinctive peak was observed in the ^{31}P NMR spectrum at δ12.6 ppm, suggesting the formation of a new complex. Triphenylphosphine oxide formation was also observed at δ 28.8 ppm in the ^{31}P NMR spectrum. A much cleaner formation of the new complex, with minimal accompanying Ph_3PO, was however achieved using ruthenium trichloride hydrate under the same conditions, and it was possible to isolate the new complex from the reaction as yellow crystals. X-ray crystallography revealed the structure of the novel complex [$Ru_2(HCO_2)_2(CO)_4(PPh_3)_2$], **6** (Figure 4); in this complex, a dimer of ruthenium with two bridging formates and a phosphine located on each metal has formed. It is also clear that decomposition of formate to carbon monoxide has taken place during the activation process in which the catalyst is formed. A related acetate-bridged system has been reported, which was formed from the reaction of [$Ru_2(CH_3CO_2)_4(CO)_4$] with trialkylphosphines;[17c] however we are not aware of a synthesis of such a complex directly from ruthenium trichloride. Complex **6** was also prepared in larger quantities, thereby permitting full characterization, via the formation of known complex [$Ru_2(HCO_2)_2(CO)_4$] (from dodecacarbonyltriruthenium)[19] followed by addition of triphenylphosphine in THF (reflux, 6 h; Supporting Information). The use of pure complex **6** for hydrogen generation from FA/TEA under the conditions described above (120 °C, oil bath) proved to be successful, although the TOF observed was lower (ca. 5.2×10^3 h^{-1}) than those seen for the phosphine-free reaction.

The isolation of an intermediate organometallic species that reflected the situation when < 1 equiv of PPh_3 was added proved to be rather more challenging. However, by adding just under 1 equiv (relative to Ru metal) of triphenylphosphine to [$Ru_2(HCO_2)_4(CO)_4$][19] at reflux in THF for 1 h, it was possible to form the novel complex [$Ru_4(HCO_2)_4(CO)_8(PPh_3)_2$], **7** (Figure 5), in which a Ru tetramer is coordinated by phosphines at the ends and contains bridging formate ligands. As was the case for **6**, two formates form a bridge between pairs of ruthenium atoms, and the structure contains a symmetrical "head to tail" bridging structure in which a "$(RuO)_2$" "square" is formed. Thus complex **7** is essentially a dimer of the complex that would be formed by loss of phosphine from **6** and contains a 2:1 ratio of ruthenium to phosphine. Complex **7** proved to be unstable and could not be characterized by mass spectrometry due to rapid disproportionation to **6** and (presumed) [$Ru_2(HCO_2)_2(CO)_4$] during ionization. This disproportionation also appears to take place in solution (followed by ^{31}P NMR),

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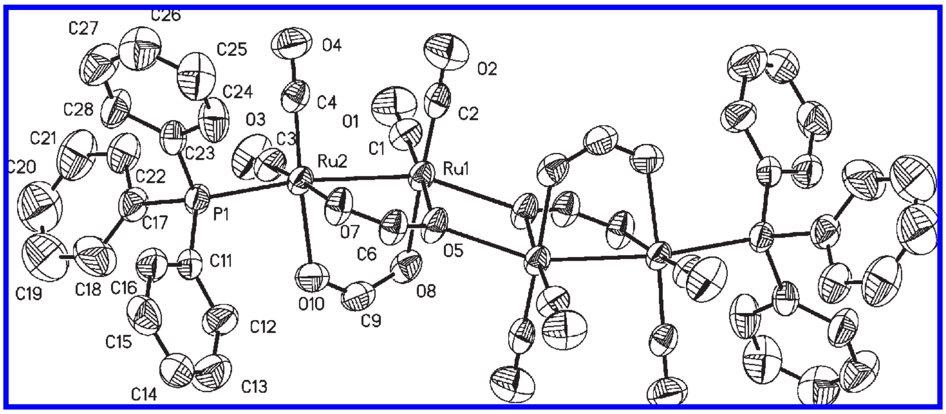


Figure 5. X-ray crystallographic structure of $[Ru_4(HCO_2)_4(CO)_8(PPh_3)_2]$, **7**.

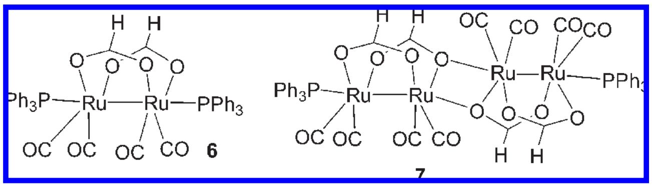
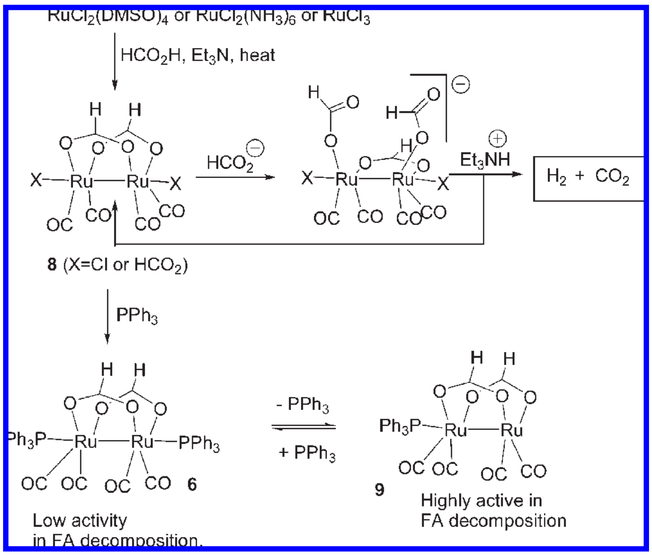


Figure 6. Ruthenium complexes formed in these studies.

Scheme 3. Proposed Catalytic Cycle in H_2 Generation from FA Using Ruthenium Complexes



and as a result, complex **7** could not be used in hydrogen generation experiments with confidence. Hence it is not possible to confirm whether **7** is an active species in the formic acid decomposition or merely an intermediate in the formation of the relatively unreactive diphosphine complex **6**. However, the complex is to our knowledge representative of a new class of ruthenium tetramer structure.

The dimeric complex $[Ru_2(HCO_2)_4(CO)_4]$ was also tested directly in the formic acid decomposition reaction (Figure 2) and gave a maximum TOF of ca. 1.78×10^4 h^{-1}. Both the maximum TOF and the pattern of TOF versus gas volume matched closely to those observed in the reactions using each of the other complexes. Although $[Ru_2(HCO_2)_4(CO)_4]$ could not be isolated directly from the reactions of $[Ru_2Cl_2(DMSO)_4]$, $[RuCl_2(NH_3)_6]$, or $[RuCl_3]$, the more stable complex **6** was isolated upon addition of triphenylphosphine. This is probably formed via trapping of $[Ru_2(HCO_2)_4(CO)_4]$ during the course of the reaction. Given the similarity of the profile of gas generation using all four ruthenium sources, we speculate that, under the conditions tested, the generation of hydrogen may be taking place through formation of a highly active common catalyst such as **8** at elevated temperature. A plausible mechanism for hydrogen generation would involve the addition of formate (i.e., from triethylammonium formate) to **8**, followed by generation of a molecule of hydrogen by the subsequent reaction with triethylammonium cation and reclosure of the formate bridge (Scheme 3). A Ru−H species, several of which are known to release hydrogen gas, may be involved at some stage in the cycle.[11,18] Addition of PPh_3 results in formation of a quantity of **6**, which is much less catalytically active due to the blocking of the ruthenium atoms by the large phosphine groups, but still retains some low reactivity, possibly through a mechanism in which the phosphine is dissociated (i.e., to give **9**).

The formation of the active catalyst *requires* heating of the reaction to over 100 °C possibly in order to promote the formation of a CO-containing complex. At this temperature there is a distinctive color change in the solution from a dull yellow to bright yellow, and rapid FA decomposition is observed. Throughout this project, and particularly in view of the formation of CO-containing complexes, efforts were made to establish the composition of the gas (full details are contained in the Supporting Information). IR spectroscopy was used to analyze the gas by taking samples at various times in the FA decomposition cycle, and this technique permitted the clear identification of carbon dioxide and carbon monoxide. Using an FT-IR method, we were able to establish that the FA decomposition gases from the $[RuCl_2(DMSO)_4]$-precatalyst reaction contained ca. 0.02 mol % CO (200 ppm). A more accurate measurement was achieved using gas chromatography (Table 1) of samples taken from the gas flows using a methaniser and FID detector system (see Supporting Information for full details). A standard of CO in CO_2 was prepared to calibrate the system. Duplicate runs were in good agreement, and the results for $[RuCl_2(DMSO)_4]$ were similar to those measured by the IR method. In all cases, the levels of CO in the gas were between 190 and 440 ppm, with $RuCl_3$ giving the lowest level and $[Ru(NH_3)_6Cl_2]$ the highest. The isolated dimer $[Ru_2(HCO_2)_2(CO)_4]$, which we speculate may be the immediate catalyst precursor, produced slightly higher levels of CO than average, but these were within the range observed. The close match in the gas composition of

Table 1. Determination of Level of CO in Gas Flow from Formic Acid Decomposition[a]

Ru source	CO rt	CO_2 rt	area CO	area CO_2	PPM CO[b]
standard ca. 136 ppm CO in CO_2	0.727	1.754	0.01281	99.98719	128
standard ca. 136 ppm CO in CO_2	0.742	1.787	0.01263	99.98737	126[c]
$[Ru_2(HCO_2)_2(CO)_4]$	0.740	1.845	0.03272	99.96728	327
$[Ru_2(HCO_2)_2(CO)_4]$	0.745	1.846	0.03274	99.96726	327
$[RuCl_2(dmso)_4]$	0.729	1.827	0.02006	99.97994	200
$[RuCl_2(dmso)_4]$	0.714	1.807	0.01899	99.98101	190
$[RuCl_3]$	0.744	1.835	0.01958	99.98042	196
$[RuCl_3]$	0.736	1.835	0.01959	99.98041	196[c]
$[Ru(NH_3)_6Cl_2]$	0.738	1.828	0.04405	99.95595	440
$[Ru(NH_3)_6Cl_2]$	0.744	1.860	0.04224	99.95776	422
$[Ru_2(PPh_3)_2(HCO_2)_2(CO)_4]$	0.738	1.825	0.02583	99.97417	258
$[Ru_2(PPh_3)_2(HCO_2)_2(CO)_4]$	0.738	1.829	0.02530	99.97470	253

[a] Using an Agilent 6890N GC fitted with a Porapak Q steel column (6 ft × 1/8 in. i.d.), methaniser, and FID detector. Oven temperature 50 °C, injector 200 °C, detector 250 °C, gas flow through column 20 mL/min, carrier gas = nitrogen. Gas flow at detector: H_2 50 mL/min, air 400 mL/min. Injections of ca. 0.1 mL. [b] Duplicates were run within 10 min of each other. [c] Duplicates were run 24 h apart.

$[Ru_2(HCO_2)_2(CO)_4]$ to the other metals suggests that this complex may be formed by each metal in the activation process.

The hydrogen produced in this investigation was fed directly to a PEM fuel cell and used to power electrical devices. Although the hydrogen would therefore require prior purification (for example via gas filtration) for long-term use in this fuel cell, the advantages of the low catalyst loading required, the high TOFs, and the long-lived nature of the catalyst make the process a practical one for large-scale hydrogen production.

We also attempted to gather evidence for the in situ formation of $[Ru_2(HCO_2)_2(CO)_4]$ by ^{13}C NMR spectroscopy. Laurenczy et al. have shown that in situ ^{1}H NMR of a Ru(II) complex used in formic acid/sodium formate solution permitted the identification of ruthenium hydride containing species.[11b] Unfortunately, we were not able to observe formation of metal hydrides in our catalytic system during the course of the reaction. We were, however, able to observe peaks at ca. δ 172 and 204 corresponding to the formate and carbon monoxide ligands, respectively, upon stirring of $[Ru_2(HCO_2)_2(CO)_4]$ in FA/TEA for 10 min at rt. After heating to 120 °C these peaks disappear, suggesting that one or more catalytically active species are formed in the reaction, for which $[Ru_2(HCO_2)_2(CO)_4]$ is a precursor. We are currently investigating this reaction in order to establish the structure of the active species.

In order to establish why the Beller system works well in the presence of triphenylphosphine (in contrast to our catalyst), we examined the complex $[RuCl_2(PPh_3)_3]$, **10**.[10] At 120 °C (i.e., the conditions used in our study) this complex gave a high initial release of gas, but this quickly subsided (in less that 5 min.). Analysis of the reaction mixture by ^{31}P NMR indicated that a complex system of free PPh_3, complex **6**, $RuCl_2(PPh_3)_3$, and other species at lower field had formed. At a lower temperature of 80 °C, however, and using DMF as a solvent in which to first form an active catalyst, followed by reaction with FA/TEA at 40 °C, there was evidence of initially rapid hydrogen and CO_2 formation.[10a] ^{31}P NMR analysis of the reaction after 2 h reaction in DMF and prior to addition of FA/TEA clearly indicated that PPh_3 had dissociated (free PPh_3 was observed at δ −6.4 ppm). Chemical shifts attributed to $[RuCl_2(PPh_3)_3]$ at δ 29.3 and 40.9 ppm were shifted to 27.4 and 54.3 ppm. Analysis of the reaction mixture at timed intervals after addition of FA/TEA indicated that a complex reaction mixture had formed where PPh_3 recoordinated to give a complex with a characteristic ^{31}P NMR peak at ca. δ 27.0 ppm. After 120 min a new peak at δ 35.2 ppm appeared, which could be attributed to the known $[RuCl_2(PPh_3)_2(CO)(DMF)]$, **11** (reported ^{31}P NMR δ 34.5 ppm).[20a] DMF-containing mononuclear Ru species have been reported,[20] and DMF is known to be converted to CO at elevated temperatures in ruthenium complexes.[20c]

Beller also reported that a similar system could be generated from $RuCl_3$ and 3 equiv of PPh_3 in DMF (80 °C/2 h) followed by addition of FA/TEA. Again we found that there was an initial fast hydrogen and CO_2 formation after an induction period. However, analysis of the reaction mixture prior to the FA/TEA addition revealed the formation of a predominant product with a characteristic ^{31}P NMR shift at δ 28.8 ppm. This species appears to be $[RuCl_3(PPh_3)_2(DMF)]$ (**12**), which was independently prepared by the treatment of $RuCl_3$ with PPh_3 in DMF (X-ray details are given in the Supporting Information). However this assignment is made with caution, as Ph_3PO also appears at δ 28.8 ppm. Hence, at lower temperatures a less active monomer complex, possibly **11** or **12**, is formed and may be responsible for FA decomposition at these temperatures.

In a paper that appeared during the preparation of the manuscript, Laurenczy et al.[11b] describe the use of a Ru(II)-based catalyst containing two *meta*-monosulfonylated triphenylphosphine (TPPMS) ligands and 3−4 water molecules for the decomposition of a formic acid/sodium formate mixture. Given that the competing conversion of formic acid to CO and H_2O will generate quantities of water in the reaction, it is possible that a closely related (i.e., aqua) complex may have been generated in the Beller system. Such a complex may also be formed under our phosphine-modified conditions described above. However, given that the Laurenczy system operated much more slowly in the absence of a phosphine, we believe that a distinct species from this is formed under our phosphine-free conditions.

In conclusion, we have found that hydrogen can be generated from FA using a number of Ru(II) and Ru(III) catalysts. Our evidence suggests that the precatalyst appears to be a bisruthenium complex containing bridging formate ligands and carbonyl ligands. The structure of the active catalyst involved in the catalytic cycle is not known. The decomposition of FA to carbon dioxide and hydrogen is very rapid and is highly selective, although low levels of CO (ca. 0.02 mol %) were detected in the outflows. Temperatures of > 100 °C are required to form the dimeric catalysts that

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were studied in this project. At lower temperatures than this, and in our hands, less active monomeric ruthenium complexes appear to be formed. In view of the close analogy of alcohol dehydrogenation process with that of FA dehydrogenation,[21] we are extending our studies to the dehydrogenation of alcohols commonly represented in biomass and waste organic materials.

Experimental Section

Evidence of Hydrogen and Carbon Dioxide Formation. In order to confirm that the gas was a combination of hydrogen and carbon dioxide, we captured samples in a gas phase cell for FT-IR spectroscopy (sample spectra are shown in the Supporting Information). The spectra showed a strong peak at ca. 2300 cm^{-1}.[22] There was evidence of carbon monoxide (2150 cm^{-1}) at low levels.[22] The presence of hydrogen was confirmed by (i) performing a reduction of an N=N double bond in the dye disperse red 13 (resulting in loss of color) using a Pd/C catalyst with the gas generated from the reaction flowed through the stirred reaction and (ii) diverting the gas into a PEM fuel cell, which was used to power an electric fan.

Procedure for Hydrogen Generation from Formic Acid. An oil bath was preheated to 131 °C, and $[Ru(DMSO)_4Cl_2]$ (6.0 mg, 12.4 μmol) was added to a flask to which FA/TEA (5:2; 10 mL) was added. The flask was connected to a condenser, which in turn was connected to a gas volume measuring kit containing two syringes and a three-way tap, which was checked carefully for leaks. The flask was lowered into the oil bath, and the stopwatch and syringes were simultaneously set to take measurements. When the internal temperature of the reaction mixture reached 120 °C (~3.5 min), the volume of expansion and any gases given off were noted with the time taken. Simultaneously, the timer was reset and times taken for each 50 mL of gas generated were recorded. Formic acid was replenished as necessary, i.e., when activity was seen to significantly decay. At this point the volume of formic acid required was calculated on the basis of the amount of gas generated. For example, 3 L of gas produced represents 3 L/48 L moles of the two gases = 62.5 mmol of formic acid consumed. Therefore, 2.88 g (2.36 mL; d = 1.22 g/mL) of formic acid was required to return the reaction mixture back to the original azeotropic ratio.

The turnover number was calculated for every 50 mL generated by

$$\mathrm{TON} = \frac{\text{moles gas produced}}{\text{moles catalyst used}}$$

$$\mathrm{TON} = \frac{(0.05\ \mathrm{L}/48\ \mathrm{mol\ L}^{-1})}{\text{moles catalyst used}}$$

This will be the same for each 50 mL gas sample in any particular run. Multiplying this by 20 × no. liters hydrogen produced overall gives the overall TON for the run. This figure will continue to increase as long as the reaction runs.

The turnover frequency was calculated by

$$\mathrm{TOF\ h}^{-1} = \frac{\mathrm{TON} \times 60}{\mathrm{time/min}}$$

The graphs therefore show "instantaneous" TOFs; in some cases the graphs (see Supporting Information) are smoothed by taking the average of the values either side of each data point, twice (denoted by "averaged twice"). In other cases, the moving average trend line (3 points) has been applied to the graph. Graphs of results obtained are given in the Supporting Information.

Identification of Complex 6 in FA Decomposition Reaction and Isolation for X-ray Analysis. Ruthenium trichloride hydrate (100 mg, 0.41 mmol) and triphenylphosphine (54 mg, 0.21 mmol) were added to 5:2 FA/TEA (25 mL), and the reaction mixture was heated to 100 °C. After 1 h, formic acid (10 mL) was replenished and the reaction mixture was stirred at 100 °C for a further hour. The crude reaction mixture was allowed to cool to room temperature and yielded a yellow crystalline material. X-ray crystallography revealed structure **6** (see Supporting Information for full data). ^{31}P NMR of the crude reaction mixture revealed the formation of a predominant species at 12.6 ppm. The method for formation of a sample for full characterization is given below.

Formation of 6 from $RuCl_2DMSO_4$ under Reaction Conditions. $[Ru(DMSO)_4Cl_2]$ (40.0 mg, 82.6 μmol) and PPh_3 (10.8 mg. 41.3 μmol) were added to TEA/FA (10 mL) and heated at 120 °C using an oil bath. The two species identified by ^{31}P NMR match the chemical shifts for $[Ru_2(O_2CH)(CO)_4(PPh_3)_2]$ (12.6 ppm) and triphenylphosphine oxide (28.8 ppm). Both sources of ruthenium (oxidation levels II and III) give the same species when treated with PPh_3 in hot TEA/FA, namely, $[Ru_2(O_2CH)(CO)_4(PPh_3)_2]$.

Formation of Precursor to Complex 6. Catena-di-μ-formatodicarbonylruthenium was prepared by methods described in the literature.[19] Dodecacarbonyltriruthenium (0.58 g, 2.72 mmol on Ru) was added to formic acid (25 mL), and the reaction mixture was heated under reflux for 6 h. Concentration under reduced pressure gave a pale orange precipitate, which was washed with ether and dried (0.44 g, 2.16 mmol on Ru, 79%). To a suspension of thus formed catena-di-μ-formatodicarbonylruthenium (0.30 g, 0.74 mmol) in THF (30 mL) was added triphenylphosphine (0.39 g, 1.48 mmol), and the reaction mixture was heated under reflux for 6 h. The reaction mixture was then cooled to rt and filtered to give a golden yellow solution. Concentration under reduced pressure and crystallization from DCM (20 mL) and MeOH (1 mL) three times gave elongated yellow crystals (0.50 g, 0.54 mmol, 73%). Ten-minute X-ray crystallography analysis gave a matched data set to **6**: mp(dec) > 153.7 °C; ν_{max}/cm^{-1} (solid) 2022.0, 1979.3, 1945.1, 1920.8, 1581.8, 1480.5, 1434.3, 1354.8; found HRMS (ESI): 930.9755 $[MH]^+$, $C_{42}H_{33}O_8P_2Ru_2$ requires 930.9732 (3.42 ppm error); m/z (ESI) $[M]^+$ 929.99; δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.36−7.44 (18H, m, ArH), 7.51−7.58 (12H, m, ArH), 8.14 (2H, s, O_2CH); δ_C (75.5 MHz; $CDCl_3$; Me_4Si) 128.3 (t, J 4.6), 129.8, 133.1 (t. J 16.4), 133.7 (t, J 5.9), 176.3 (t, J 8.2), 204.6 (t, J 4.0); δ_P (121.5 MHz; $CDCl_3$; Me_4Si) 12.6.

Formation of Complex 7. To a suspension of catena-Di-μ-formatodicarbonylruthenium (0.50 g, 1.24 mmol) in THF (60 mL) was added triphenylphosphine (0.24 g, 0.93 mmol), and the reaction mixture was heated under reflux for 1 h. The reaction mixture was then cooled to rt and concentrated under reduced pressure. Isolation by silica gradient flash column chromatography 1:9−1:0 EtOAc/hexane and crystallization

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from EtOAc (7 mL) and hexane (20 mL) gave light brown double-ended needles (0.11 g, 82.5 μmol, 9%). X-ray crystallography revealed structure **7**. δ_P (121.5 MHz; $CDCl_3$; Me_4Si) 5.8.

Formation of an Authentic Sample of Mono-Ru Complex [$RuCl_3(PPh_3)_2(DMF)$], 12. To a solution of triphenylphosphine (970 mg, 3.70 mmol) in dimethylformamide (60 mL) was added ruthenium trichloride hydrate (300 mg, 1.23 mmol). The reaction mixture was stirred at 80 °C for 2 h, concentrated under reduced pressure, and recrystallized from dimethylformamide (12 mL) twice. δ_P (121.5 MHz; $CDCl_3$; Me_4Si): 28.8 (NMR spectrum also shows free triphenylphosphine). Crude X-ray data indicated atom connectivity matched that of [$RuCl_3(PPh_3)_2(DMF)$]; however crystal decomposed during collection and the data were not of high enough quality to refine.

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Supporting Information Available: Full experimental details and graphs of experimental results. This material is free of charge via the Internet at http://pubs.acs.org.

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