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Formic acid dehydrogenation catalysed by ruthenium complexes bearing the tripodal ligands triphos and NP_3†‡

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The selective formic acid dehydrogenation to a mixture of CO_2 and H_2 was achieved with moderate to good productivities in the presence of homogeneous Ru catalysts bearing the polydentate tripodal ligands 1,1,1-tris-(diphenylphosphinomethyl)ethane (triphos) and tris-[2-(diphenylphosphino)ethyl]-amine (NP_3), either made *in situ* from suitable Ru(III) precursors or as molecular complexes. Preliminary mechanistic studies highlighting subtle differences due to ligand effects in the corresponding systems under study are also presented.

Introduction

One of the most important scientific and technological challenges nowadays is finding new energy vectors, possibly derived from renewable sources that can contribute to the worldwide demand for energy in a sustainable manner with advantageous costs. In this respect, hydrogen is a promising energy carrier and is considered as a clean alternative to fossil fuels, especially if used as combustible for fuel cells. The development of efficient technologies for hydrogen generation from renewable energy sources and for hydrogen storage in a safe and reversible manner is a pre-requisite for the utilization of hydrogen on a large scale in small- and middle-size mobile or stationary devices.[1,2]

Compared to other fuels, hydrogen has a high gravimetric energy density, but its volumetric energy density at atmospheric pressure is too low for most envisioned applications. Therefore, it is necessary to obtain an improved volumetric hydrogen storage density. Currently, none of the existing methods, such as compressed gas containers, liquid hydrogen containers, or the use of interstitial hydrides and porous materials as physical adsorbents for hydrogen, are entirely satisfactory options either in terms of costs or safety for widespread use. Recently, the use of organic compounds as "chemical reservoirs", from which hydrogen can be released on-demand and safely under mild conditions, has emerged as a promising alternative to other methods.[3]

Among the different organic hydrogen storage molecules, in particular, formic acid (HCOOH) has recently received considerable attention, as it contains 4.4 wt% of hydrogen, is a cheap liquid under ambient conditions and can be handled, stored and transported safely. Following a dehydrogenation rather than a decarbonylation pathway, in the presence of suitable catalysts, HCOOH can be selectively decomposed to a mixture of CO_2 and H_2 which, upon purification, can give fuel cell grade hydrogen. In principle, by a subtle choice of the catalytic system, the reaction can be reverted and CO_2 obtained as a by-product can be re-hydrogenated to HCOOH. In this way CO_2 can be used as a renewable feedstock and a zero-carbon demand and emission catalytic cycle can be invoked, avoiding the use of fossil fuels for energy production.[4]

Various combinations of transition metals and stabilizing ligands have been tested to achieve efficient homogeneous catalysts able to promote the selective dehydrogenation of HCOOH. Among the different transition metals, such as Fe, Co, Ir, Rh, ruthenium has been so far the most widely investigated metal for this reaction, often in association with ancillary ligands such as phosphines. It is worth mentioning the results obtained by Wills,[5] Puddephatt[6] and co-workers and later on by Laurenczy *et al.* who carried out the

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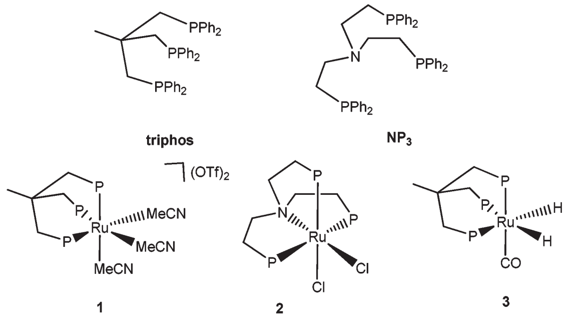
†Dedicated to Professor David Cole-Hamilton, an inspiring scientist, on the occasion of his retirement and for his outstanding contribution to transition metal catalysis.

‡Electronic supplementary information (ESI) available: Reaction profiles (gas volume *vs.* time) for selected HCOOH dehydrogenation runs; VT-NMR spectra; additional experimental details. See DOI: 10.1039/c2dt32043f



Scheme 1

dehydrogenation of HCOOH–HCOONa (9 : 1) in water using Ru sources together with the water soluble TPPTS ligand [TPPTS = tris-(*meta*-sulfonatophenyl)phosphine], obtaining a TOF of 460 h^{-1} working at 120 °C.[7] In parallel, some of us showed that the combination of Ru(η^6-arene)Cl_2 precursors and diphosphines such as dppm and dppe [dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane] in the presence of organic amines was able to give efficient HCOOH dehydrogenation at 25 °C. TON values of 260 000 were obtained, corresponding to TOF > 900 h^{-1}.[8] More recently, under optimized conditions the same catalyst system showed turnover numbers up to 800 000 and a TOF of 48 000 h^{-1} at 80 °C, setting the benchmark test for Ru catalysts for this reaction so far.[4h]

The beneficial stabilizing effect of tetradentate ligands such as PP_3 (PP_3 = tris-[2-(diphenylphosphino)ethyl]phosphine) together with $Fe(BF_4)_2\cdot6H_2O$ to promote the catalytic activation of HCOOH, originally reported in 1991,[9] was recently reinvestigated, showing an outstanding performance with TON = 92 000 and high TOF = 9425 h^{-1} at 80 °C in propylene carbonate as a solvent.[10] Interestingly, the same ligand was used together with $Co(BF_4)_2\cdot6H_2O$ for the reduction of CO_2 and bicarbonate with hydrogen to formates at 60–80 °C under a total pressure CO_2 + H_2 = 60–100 bar, giving a maximum 94% yield after 20 h.[11]

Here we report on the dehydrogenation of formic acid/amines in the presence of the facially capping 1,1,1-tris-(diphenylphosphinomethyl)ethane (triphos) and related tetradentate tris[2-(diphenylphosphino)ethyl]amine (NP_3), either used *in situ* together with $Ru(acac)_3$ as a ruthenium source or as ligands for known complexes such as [Ru(κ^3-triphos)$(MeCN)_3$]$(OTf)_2$ (**1**),[12] [Ru(κ^4-NP_3)Cl_2] (**2**)[13] and *cis*-[Ru(κ^3-triphos)(CO)$(H)_2$] (**3**,[14] see Scheme 1). The catalytic tests are complemented by $^{31}P\{^1H\}$ NMR studies based on stoichiometric reactions, which gave information on the nature of some of the species which are formed upon reaction with formate and formic acid/amine adduct, respectively, under different experimental conditions.

Results and discussion

The facially capping triphosphine 1,1,1-tris-(diphenylphosphinomethyl)ethane (triphos) and the tripodal aminotrisphosphine tris-[2-(diphenylphosphino)ethyl]amine (NP_3) have been used in the past for stabilisation of unusual transition metal moieties and geometries as well as in catalytic applications.[15] Although a variety of metal complexes with multidentate phosphine ligands have been shown to be efficient catalysts for HCOOH dehydrogenation and CO_2 hydrogenation, to the best of our knowledge, neither triphos nor NP_3 have been reported so far in combination with Ru precursors for the former reaction, whereas the use of an *in situ* catalytic system based on $Ru(acac)_3$ and triphos for the reduction of CO_2 to methanol under acidic conditions has been recently disclosed by Leitner and co-workers.[16] Thus, we decided to investigate the behaviour of such complexes and ligands for HCOOH dehydrogenation.

Catalytic formic acid dehydrogenation tests

We have tested five variations on the catalytic system for the HCOOH dehydrogenation to CO_2 + H_2, namely (i) $Ru(acac)_3$ + triphos (1 : 1); (ii) $Ru(acac)_3$ + NP_3 (1 : 1); (iii) [Ru(κ^3-triphos)$(MeCN)_3$]$(OTf)_2$ (**1**); (iv) [Ru(κ^4-NP_3)Cl_2] (**2**); [Ru(κ^3-triphos)(CO)$(H)_2$] (**3**), running the tests under atmospheric pressure, measuring the development of gas with either an automatic[17] or a manual gas-burette. Aliquots of the gas mixtures produced were analyzed off-line either by GC or FT-IR methods. The effect of the temperature on the productivity of the catalytic systems was also investigated, running the tests both at 40 °C and 80 °C, using either the azeotropic mixture HCOOH–NEt_3 (5 : 2) or the combination HCOOH–$OctNMe_2$ (11 : 10, $OctNMe_2$ = *n*-octyldimethylamine), respectively.[18]

At 40 °C using the commercial azeotrope HCOOH–NEt_3 (5 : 2), the reaction proceeds with moderate TOFs using both molecular complexes **1** and **2** (see Table 1). GC analysis of the gas mixtures showed the presence of a 1 : 1 mixture of CO_2 + H_2, hence complete selectivity for HCOOH dehydrogenation *vs.* decarbonylation is obtained as no signal corresponding to CO was detected, implying a quantity lower than 10 ppm which is the sensitivity limit for this technique. For a maximum expected gas volume of *ca.* 2.91 L, under these conditions **1** produced *ca.* 454 mL after 18 h, whereas **2** gave *ca.* 564 mL after 45 h, corresponding to final TONs of 487 and 604, respectively. Disappointingly, using the *in situ* generated catalysts prepared according to methods (i)–(ii), the reactions did not show any significant activity under the conditions described in Table 1. This suggests that under such mild conditions the metal cannot be efficiently reduced from Ru(III) to the active Ru(II) form and/or be stabilized by the ancillary ligand to form catalytically active species.

Improved catalytic performances were observed running the HCOOH dehydrogenation tests at 80 °C, in the presence of *n*-octyldimethylamine (Table 2), using HCOOH : Ru = 1000 and HCOOH : Ru = 10 000 ratios. In all cases the gas volume expected for complete conversion (630 mL) was obtained after different reaction times depending on the catalytic system used.

From Table 2, it can be concluded that the best catalytic system under the conditions applied was complex **1**, as would

Table 1 Formic acid dehydrogenation catalysed by complexes **1** and **2** in the presence of NEt_3 at 40 °C

Entry	Catalyst	Vol (mL) after 180 min	TON after 180 min	Max vol (mL) [*t*(h)]	Final TON	Final conversion (%)
1	**1**	65	69	454 [18]	487	16
2	**2**	20	21	564 [45]	604	19

Reaction conditions: catalyst, 19.1 μmol; HCOOH–NEt_3 (5 : 2), 5 mL; HCOOH : catalyst = 3117; gas measured *via* automatic burette and analyzed by GC (H_2 : CO_2 = 1 : 1).

Table 2 Formic acid dehydrogenation catalysed by Ru/L_n (L_n = tripodal ligand: triphos, NP_3) and **1–3** in the presence of $OctNMe_2$ at 80 °C

Entry	Catalyst	Vol (mL) after 60 min	TON after 60 min	Max vol (mL) [*t*(min)]	Final TON
1	**i**[a]	210	314	630 [180]	1000
2	**ii**[a]	70	105	630 [490]	1000
3	**1**[b]	630	1000	630 [60]	1000
4	**1**[c]	100	1504	630 [320]	10 000
5	**2**[b]	130	204	630 [230]	1000
6	**2**[c]	60	902	630 [420]	10 000
7	**3**[b]	250	373	630 [220]	1000

Reaction conditions: [a] $Ru(acac)_3$, 12.9 μmol; ligand, 12.9 μmol; HCOOH–$OctNMe_2$ (11 : 10), 2.73 mL (density at 25 °C = 0.894 mg mL^{-1}); HCOOH : catalyst = 1000; 80 °C. Gas measured *via* a manual gas burette and analyzed *via* FT-IR spectroscopy. [b] As above, preformed catalyst 12.9 μmol. [c] As above, preformed catalyst 1.29 μmol.

Table 3 Recycling tests for formic acid dehydrogenation catalysed by **1** in the presence of $OctNMe_2$ at 80 °C

Cycle	Vol (mL) after 60 min	TOF (h^{-1}) after 60 min	Max vol (mL) [*t*(min)]	Final TOF (h^{-1})
I	630	1000	630 [60]	1000
II	600	944	630 [65]	923
III	430	676	630 [90]	666
IV	350	550	630 [110]	545
V	340	535	630 [120]	500
VI	330	519	630 [130]	461
VII	300	472	630 [140]	428
VIII	240	377	630 [150]	400

Reaction conditions: complex **1**, 12.9 μmol; HCOOH–$OctNMe_2$ (11 : 10), 2.73 mL (density at 25 °C = 0.894 mg mL^{-1}); HCOOH : catalyst = 1000; 80 °C; from run 2, 12.9 mmol of neat HCOOH were added by microsyringe for each run. Gas measured *via* a manual gas burette and analyzed *via* FT-IR spectroscopy.

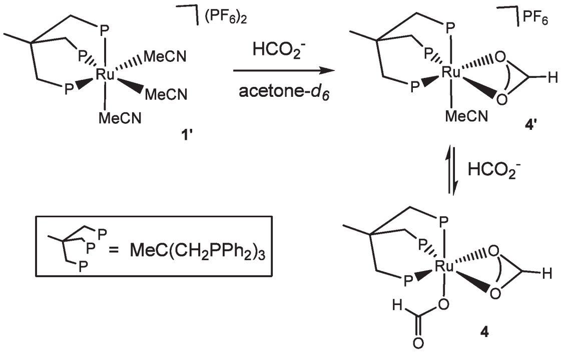
be expected for a Ru(II) species bearing a strongly coordinating tripodal polyphosphine and three labile solvent ligands, able in principle to make up to three coordination sites available for substrate coordination and activation. In contrast to the results reported by Leitner and co-workers for the Ru(triphos)-catalysed CO_2 hydrogenation to methanol under acidic conditions, which were however run at higher temperature (140 °C),[16] the system based on *in situ* formation of the putative active catalyst (run 1) did not perform as efficiently as complex **1**. Complete conversion of HCOOH was reached only after 3 h instead of 1 h as for the molecular Ru-triphos complex **1**. In the case of the NP_3-based system, both methods gave more sluggish conversions than triphos (Table 2, runs 2 and 5; see also reaction profiles in Fig. S1–2, ESI‡). Both complexes **1** and **2** were active at higher substrate to catalyst ratios, reaching final TONs of 10 000 after 320 and 420 min, respectively.

Interestingly, a few nicely shaped crystals formed at the end of a catalytic experiment using $Ru(acac)_3$ and triphos. $^{31}P\{^1H\}$ and ^1H NMR spectra of the crystals dissolved in $CDCl_3$ showed unequivocally that the complex formed under these conditions was the known $[Ru(\kappa^3\text{-triphos})(CO)(H)_2]$ (**3**).[14] Thus, we thought it could be of interest to synthesise **3** (see ESI‡ for details) and test it as the preformed catalyst for HCOOH dehydrogenation under the same conditions. Indeed, also this complex was endowed with catalytic activity that closely resembles that observed for an *in situ* generated Ru-triphos system (*cf.* runs 1 and 7, Table 2, and Fig. S3 in ESI‡). This observation may in turn suggest that either **3** is formed under the conditions applied in run 1 or that both $Ru(acac)_3$/triphos and **3** evolve toward the same (or at least very similar) catalytically active species, perhaps $[Ru(\kappa^3\text{-triphos})(H)(\eta^2\text{-}H_2)]^+$ upon loss of CO and protonation of one hydrido ligand. This species has already been proposed in the literature as an active catalyst for hydrogenation reactions.[19] However, **3** was neither observed to be formed during the HCOOH dehydrogenation tests when complex **1** was used as a pre-catalyst, nor during NMR mechanistic studies starting from an analogue of **1** as a ruthenium source (*vide infra*).

Recycling experiments using the best catalyst found in this study, *i.e.* complex **1**, were also carried out. After evolution of the gas volume expected in the first run (630 mL), neat HCOOH (1000 equiv. to Ru originally used) was added to the thermostated reaction vessel kept at 80 °C and the next run was started. In this way, it was possible to recycle the mixture containing the catalyst and the amine for up to eight consecutive runs (Table 3, Fig. S5‡ for reaction profile). As can be seen from Table 3, complete conversion of the substrate was invariably reached after each recycle, albeit with a decrease of TOFs already noticeable after 1 h.

VT-NMR mechanistic studies on model reactions

In order to gain a better insight into the mechanism of substrate activation and pre-catalyst modifications during the catalytic cycle, we decided to test the reactivity of complexes **1** and **2** with formate and formic acid/amine. At first, the behaviour of complex **1** was studied. Prior to the mechanistic studies, anion metathesis on **1** was carried out to exchange the potentially coordinating triflate with hexafluorophosphate



Scheme 2

(Experimental section), obtaining the new complex [Ru(κ^3-triphos)(MeCN)$_3$](PF$_6$)$_2$ (**1′**).

A series of variable temperature (VT) NMR experiments involving **1′** was carried out as follows. In the first experiment, 2.58 mg of HCOONHEt$_3$ (0.1 mL of a solution of 25.8 mg of reagent dissolved in 1.0 mL of acetone-d$_6$), freshly prepared by the reaction of HCOOH and NEt$_3$ in a 1 : 1 ratio, were added under nitrogen to a solution of **1′** (20 mg, 1.76×10^{-2} mmol) in 0.6 mL of acetone-d$_6$ at 233 K. The first ^{31}P{^{1}H} NMR spectrum recorded at this temperature immediately after mixing the reagents showed that the original singlet due to **1′** at 27.2 ppm was now accompanied (*ca.* 1 : 1 ratio) by a new AM$_2$ system at 42.7 ppm (d, $^2J_{PP}$ = 42 Hz) and 29.5 ppm (t), which we assigned to the diformato complex [Ru(κ^3-triphos)(η^1-OOCH)(η^2-OOCH)] (**4**) (Scheme 2). In keeping with formate coordination, the corresponding ^{1}H NMR spectrum showed a broad resonance at 8.34 ppm, at chemical shift values expected for Ru-coordinated formate.[20] The appearance of a new singlet at 2.18 ppm confirms that MeCN has been partially released in solution. Complex **4** may arise from stepwise ligand substitution from putative species such as [Ru(κ^3-triphos)(MeCN)(η^2-OOCH)] (**4′**) depending on the Ru/formate stoichiometry.[21]

In keeping with this hypothesis, addition of 1 equiv. of neat HCOOH at 233 K caused the complete disappearance of the signal due to **1′**, while maintaining the pattern due to **4**. The VT NMR experiment was continued by raising gradually the temperature up to 313 K, and a broadening of the signals corresponding to **4** was observed, to eventually collapse at 313 K. A close inspection of the corresponding ^{1}H NMR spectra showed that no hydride species were formed throughout the heating sequence.

In a second experiment, **1′** was mixed with 2 equiv. of HCOONHEt$_3$ at 233 K before starting the VT NMR sequence. The initial ^{31}P{^{1}H} NMR spectrum measured upon mixing of the reagents gave the same picture observed for experiment 1, except that **1′** was much less abundant (*ca.* 8% left), supporting the hypothesis discussed above. The addition of HCOOH caused the complete disappearance of **1′** accompanied by release of MeCN in solution as observed in the ^{1}H NMR spectra. By increasing the temperature, at 273 K two singlets at 42.3 ppm and 42.0 ppm appeared, reaching a maximum concentration at 293 K. The situation at 313 K showed that the pattern due to **4** was still present, together with a broad hump at *ca.* 41.0 ppm. This behaviour again suggests a rapid formate exchange at higher temperatures.

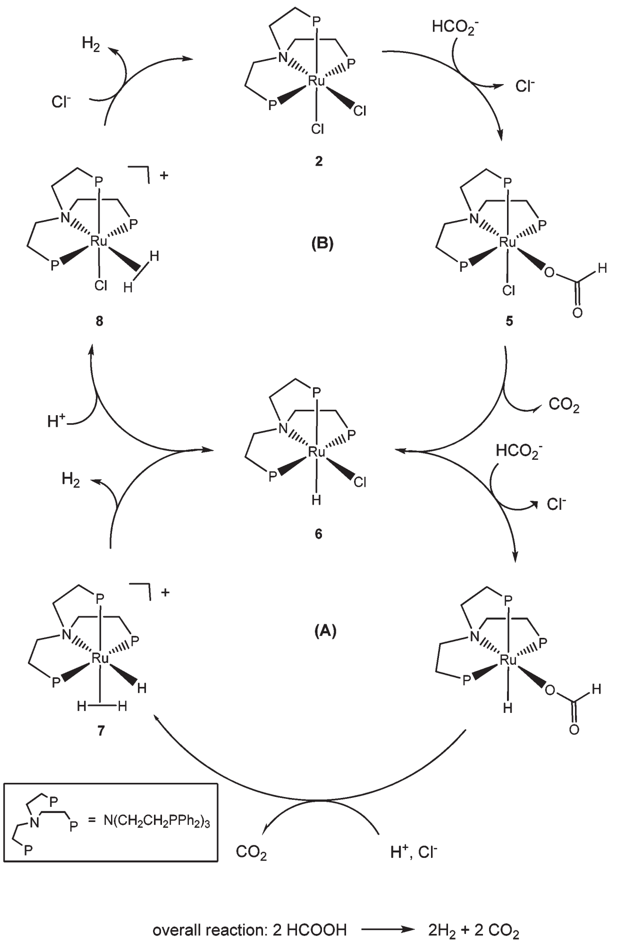
^{13}C{^{1}H} NMR spectra in acetone-d$_6$ of a mixture of **1′** with 2 equiv. of HCOONHEt$_3$ and 1 equiv. of HCOOH, taken at 233 K, showed a small singlet at 178.7 ppm, at values expected for coordinated formate.[20a] Finally, FT-IR spectra of the final solution at room temperature showed ν_{CO} formate stretching modes at 1697 and 1546 cm^{-1}, in the range expected for η^1-O(O)CH and η^2-O(O)CH coordination, respectively.[20,22] These spectroscopic investigations, although preliminary, suggest the presence of Ru-coordinated formate species equilibrating between η^2- to η^1-fashion in this system. Attempts to isolate **4** by carrying out the reactions at preparative scale have unfortunately failed so far due to decomposition of the complex during workup.

During all experiments, no ^{31}P{^{1}H} signals at negative chemical shift values attributable to triphos partial de-chelation (*i.e.* κ^3- to κ^2-coordination switch), proposed by some authors to occur during catalytic reactions,[23] were visible throughout the experiments. Moreover, complex **3** was never observed to be formed during the VT NMR experiments. We could safely rule out the presence of Ru carbonyl species such as [Ru(κ^3-triphos)(MeCN)$_x$(CO)$_y$]$^{2+}$ (x = 0–2; y = 1–3; $x + y = 3$) by comparison with NMR spectra obtained by saturating an acetone-d$_6$ solution of **1′** with CO gas at 1 atmosphere (see ESI‡).

Although at this stage the experiments described above do not allow a full interpretation of the mechanism responsible for the catalytic dehydrogenation of HCOOH promoted by **1**, on the basis of all the evidence so far obtained it can be concluded that for these systems triphos behaves as a κ^3-P facial ligand, and that any metal-hydrido species which may form are quickly converted on an NMR timescale in the temperature range 233–313 K using **1′** as a starting complex.

A VT-NMR study was also carried out starting from complex **2**. By dissolving **2** in CD$_2$Cl$_2$, a first ^{31}P{^{1}H} NMR spectrum showed the expected AM$_2$ spin system with the P$_A$ triplet at 45.7 ppm ($^2J_{PP}$ = 30 Hz) and the P$_M$ doublet at 26.6 ppm. To this solution, HCOONHEt$_3$ (1 equiv.) was added under nitrogen at 233 K. The corresponding ^{31}P{^{1}H} NMR spectrum showed the appearance of a new set of signals at 47.8 ppm (t, $^2J_{PP}$ = 29 Hz, P$_A$) and 25.8 ppm (d, P$_M$). The corresponding ^{1}H NMR spectrum showed a new singlet at 8.41 ppm which can be attributed to coordinated formate. Based on chemical shift and coupling constant values, we propose for the new species the tentative formula [Ru(κ^4-NP$_3$)Cl(η^1-OOCH)] (**5**). This species reached a 1 : 1 ratio with **2** at 253 K. At 273 K a new AM$_2$ system, showing a doublet at 42.4 ppm ($^2J_{PP}$ = 18 Hz) and a triplet at 29.3 ppm, slowly increased at the expense of **5**. This species was identified by comparison with literature data[24] as the hydrochloride complex [Ru(κ^4-NP$_3$)Cl(H)] (**6**), as confirmed by the presence of the Ru–H resonance at −6.56 ppm (dt, $J_{HP(trans)}$ = 97 Hz; $J_{HP(cis)}$ = 26 Hz, 1H, RuH) in the corresponding ^{1}H NMR spectrum. At 283 K the ratio between **2**, **5** and **6** reached 7 : 3 : 1, while at 273 K a further decrease in the concentration of **5** was accompanied by an increase of **6** (ratio **2** : **5** : **6** = 3 : 1.5 : 1). At 273 K a new octahedral species characterized by a doublet at 56.4 ppm (d, $^2J_{PP}$ = 16 Hz, 2P, P_M) and a triplet at 51.6 ppm (P_A) slowly increased. A broad singlet at −9.99 ppm appeared in the corresponding ^{1}H NMR spectrum. This new species was identified as the highly fluxional complex $[Ru(\kappa^4\text{-}NP_3)(\eta^2\text{-}H_2)(H)]^+$ (**7**) by comparison with previous data obtained in our laboratories.[25] At this point, a second equivalent of $HCOONHEt_3$ was added. As expected, this caused an increase in the concentration of **5** and a decrease of **2**. Raising the temperature to 293 K a further increase of **6** and **7** was observed, together with a decrease of **2** and **5**. The probe was then cooled to 233 K and 1 equiv. of HCOOH was added. This in turn caused the complete disappearance of **2** and **5**, leaving **7** and a new AM_2 set of signals with a P_A triplet at 50.0 ppm ($^2J_{PP}$ = 33 Hz) and a P_M doublet at 25.5 ppm. At 293 K the latter (**8**) was the main species present in the $^{31}P\{^1H\}$ NMR spectrum, with only a small residue of **7**. The broad singlet at −9.99 ppm in the ^{1}H NMR spectrum, typical of $Ru(\eta^2\text{-}H_2)$ moiety, increased in intensity.

The $^{31}P\{^1H\}$ and ^{1}H NMR variable temperature experiments were repeated reacting **1′** and **2** with the azeotrope $HCOOH–NEt_3$ (5 : 2) which was used for the catalytic tests, using a 5 : 1 ratio to the complexes, and the observations previously described were consistent with these experiments.



Scheme 3

In order to assign the signals due to **8**, a close inspection of the VT NMR experiment sequence (Fig. S6 and S7 in ESI‡) suggested that species such as **2** and **5**, having Cl^- *trans* to apical P, were characterized by ^{31}P NMR patterns bearing the triplet at lower (*i.e.* more deshielded) and the doublet at higher fields, whereas this order reverts in the case of **6** and **7**. As the former pattern (deshielded triplet) was observed also for **8**, we reasoned that this species could be structurally related to **2** and **5**. For this reason, compound **6** was prepared and isolated as described in the literature,[24] and reacted at 233 K with HCOOH on an NMR tube scale using CD_2Cl_2 as a solvent. The corresponding $^{31}P\{^1H\}$ NMR and ^{1}H NMR spectra showed unequivocally the formation of **8**, to which we assign the formula $[Ru(\kappa^4\text{-}NP_3)Cl(\eta^2\text{-}H_2)]^+$, as a major product. Interestingly, by leaving the NMR tube at room temperature and collecting another set of spectra after 1 h at 293 K, formation of **2** was observed to form at the expense of **8**. From these experiments it can be proposed that the stable complex **6** may follow two different activation pathways, shown in Scheme 3. In path A, chloride exchange with formate in **6** leads to an (unobserved) hydrido-formate species $[Ru(\kappa^4\text{-}NP_3)H(\eta^1\text{-}OOCH)]$ which rapidly evolves upon protonation to **7**, which then regenerates **6** by hydrogen release and chloride coordination, in line with the mechanism reported for the Fe/PP_3 system.[10] In path B, protonation of **6** leads to **8**, which then gives back **2** releasing hydrogen. The coexistence of these two pathways may have an implication in the lower activity of **2** compared to **1** observed in formic acid dehydrogenation tests.

Conclusions

The activity of Ru(II) complexes containing the tripodal phosphine triphos and the amino(tris)phosphine NP_3 in the selective catalytic dehydrogenation of formic acid to carbon dioxide and hydrogen has been assessed under different conditions. The complex $[Ru(\kappa^3\text{-triphos})(MeCN)_3](OTf)_2$ (**1**) showed superior performances with a TON of 10 000 after 6 h using 0.01 mol% of the catalyst and allowed for recycling up to eight times (0.1 mol% catalyst) giving a total TON of 8000 after *ca.* 14 h of continuous reaction at 80 °C in the presence of $OctNMe_2$. Preliminary mechanistic NMR studies using $Ru(\kappa^3\text{-triphos})(MeCN)_3](PF_6)_2$ (**1′**) and $[Ru(\kappa^4\text{-}NP_3)Cl_2]$ (**2**) are presented demonstrating that the NP_3 ligand helps to stabilise Ru-hydrido species. This kind of intermediate must be short-lived in the triphos-based system. Further work is currently being carried out to establish a rationale for such behaviour, also by means of DFT theoretical calculations.

Experimental

General methods and materials

Complexes **1** and **2** were prepared according to literature procedures.[12,13] Formic acid and *N*,*N*-dimethyloctylamine were distilled in vacuum prior to use and stored under nitrogen. The formic acid to amine ratio was determined by ^1H NMR spectroscopy on a Bruker Avance 400 spectrometer. $Ru(acac)_3$ and the $HCOOH–NEt_3$ (5 : 2) mixture were purchased from commercial suppliers and used without further purification. Deuterated solvents for NMR measurements were purchased from commercial suppliers and stored onto activated 4A molecular sieves under N_2 before use. The variable temperature ^1H and $^{31}P\{1H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400.13 and 100.61 MHz, respectively). Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ NMR were referenced to 85% H_3PO_4, with the downfield shift taken as positive.

Catalytic tests

All catalytic experiments were carried out under an inert argon or nitrogen atmosphere in a flask heated either by oil bath or by external heating liquid circulation. The flask was connected to a reflux condenser, which was connected either to a setup of two manual burettes or to an automatic burette to measure the amounts of gas generated. The mixture of gas produced during the catalytic runs was either analyzed by FTIR-ATR Shimadzu IRAffinity-1 with a gas cell (path length 10 cm) or by GC using a gas chromatograph HP 6890N (permanent gases: Carboxen 1000, TCD, external calibration; amines: HP Plot Q, 30 m, FID) and a hydrogen sensor (Hach Ultra Analytics GmbH).

Typical procedure for the HCOOH dehydrogenation tests: A solution of HCOOH–amine (2.5 mL) was pre-warmed to 80 °C ($HCOOH–OctNMe_2$ 11 : 10) in a three-necked round bottomed flask with a thermostated oil bath. The flask was purged with argon or nitrogen before the starting reaction by addition of the solid catalyst. In the case of experiments run at 40 °C (using the mixture $HCOOH–NEt_3$ 5 : 2), the automatic burette setup previously described was used.[17]

Typical procedure for recycling experiments at 80 °C: As soon as the gas volume evolution reached the theoretical value expected for 100% HCOOH conversion, the apparatus was flushed with nitrogen to remove any traces of hydrogen and carbon dioxide. The remaining reaction mixture containing the catalyst and the amine, kept at 80 °C, was reutilized as such for the following run by addition of neat HCOOH (0.49 mL, 12.9 mmol) through a syringe.

Variable temperature NMR experiments

Typically, the NMR tube samples were prepared at 233 K (acetone–liquid nitrogen bath) under nitrogen by dissolving 20 mg of the Ru complex in 0.70 mL of deuterated solvent and adding either 1 to 2 equiv. of HCO_2NHEt_3, followed by 1 equiv. of neat HCOOH, or 5 equiv. of $HCOOH–NEt_3$ (5 : 2). The NMR spectra were collected in the temperature range 233–313 K in the case of **2** (CD_2Cl_2) or 233–323 K in the case of **1** (acetone-d_6).

Synthesis of $[Ru(\kappa^3\text{-triphos})(MeCN)_3](PF_6)_2$ (1′). Complex **1** (1.0 mmol, 1.15 g) was dissolved under nitrogen in warm MeCN (20 mL), to which a solution of NH_4PF_6 (2.3 mmol, 0.38 g) in warm EtOH (20 mL) was added. After 15 min stirring at room temperature, the mixture was concentrated under vacuum and cold EtOH was added to induce precipitation.

The desired complex $[Ru(\kappa^3\text{-triphos})(MeCN)_3](PF_6)_2$ (**1′**) was obtained in almost quantitative yield, recrystallised from MeCN–EtOH (1 : 1) giving a white microcrystalline product (1.06 g, 0.93 mmol).

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