



**An active, stable and recyclable Ru(II) tetraphosphine-based catalytic system for hydrogen production by selective formic acid dehydrogenation**

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## Catalysis Science &amp; Technology

## ARTICLE

## An active, stable and recyclable Ru(II) tetraphosphine-based catalytic system for hydrogen production by selective formic acid dehydrogenation

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Ru(II) well-defined and *in situ* made complexes of the linear tetraphosphine meso-1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4) proved to be effective catalysts for selective formic acid dehydrogenation with good yields and TONs in the presence of added amine, both under batch and continuous feed experimental conditions. The mechanism was studied by solution NMR and DFT calculations, highlighting the role of the *trans*-dihydrido complex [Ru(H)<sub>2</sub>(meso-P4)] as the active species in catalysis.

### Introduction

The rapid increase in the world's energy consumption associated with environmental concerns related to the combustion of fossil fuels requires the development of novel and efficient technologies for energy storage and conversion. In this respect, H<sub>2</sub> is expected to play an important role as secondary energy carrier, as it allows an efficient conversion of chemical energy into electrical energy using fuel cell technologies, producing only water as by-product.<sup>1</sup> One of the limiting factors in the development of a hydrogen economy<sup>2</sup> is associated with the storage of hydrogen. Numerous approaches for hydrogen storage have been exploited, including high pressure storage, cryogenics and chemical compounds that release hydrogen upon heating. Both compression and liquification of hydrogen are well established technologies, but the use of compressed hydrogen is limited by a very poor energy density by volume, while that of liquid hydrogen requires cryogenic storage offering very limited potential applications. Hence, current research is focused on storing hydrogen as a light weight, high density energy carrier for mobile applications.<sup>3</sup>

A number of hydrogen storage materials have been proposed, including metal hydrides,<sup>4</sup> MOFs<sup>5</sup> and hydrogen-rich organic molecules<sup>6</sup> from which molecular hydrogen can be released on-demand by selective catalytic activation. In this respect, formic acid (FA) has received much attention for its potential

as hydrogen storage material,<sup>7</sup> having a hydrogen content of 4.4 %wt, being non toxic, stable, easy-to-handle. In addition, FA catalytic dehydrogenation (DH) produces CO<sub>2</sub> as the sole by-product that, if hydrogenated back to FA, can entice a CO<sub>2</sub>-neutral hydrogen storage-release cycle.<sup>7</sup> A large number of both heterogeneous and homogeneous catalysts has been reported to date for FA dehydrogenation. Homogeneous catalysts for FA DH are typically based on ruthenium,<sup>8</sup> iridium,<sup>9</sup> and iron,<sup>10</sup> with a few examples of complexes of other metals.<sup>11</sup> Iridium complexes often resulted in outstanding catalytic activities. For example, Li and coworkers recently reported an Ir catalyst supported by an N,N'-diimine ligand, which catalyzed base-free FA DH in water with a TOF (turnover frequency) of 487500 h<sup>-1</sup> at 90 °C and TON (turnover number) of 2400000 at 80 °C, which are the highest values reported for FA DH to date,<sup>9j</sup> closely rivalled by Williams' Ir(P,N) pyridylphosphine-based system very recently reported.<sup>9k</sup> Concerning Ru catalysts, the best results were obtained with the Ru(II)/dppe system [dppe = 1,2-bis(diphenylphosphino)ethane] reported by Beller and coworkers, which gave, under optimized conditions at 80 °C, TONs up to 800000 and a TOF of 48000 h<sup>-1</sup> in a single catalytic run,<sup>8i</sup> while under FA continuous feed conditions (13 μL min<sup>-1</sup>), a constant gas evolution of 15 mL min<sup>-1</sup> was observed over 45 days, affording H<sub>2</sub> with a TOF of 1000 h<sup>-1</sup> and with excellent TON (ca. 1000000), demonstrating also the long term stability of the system.<sup>8k</sup> In view of the lower cost and higher abundance, Fe complexes are being studied with increasing interest as FA DH catalysts, although they are generally less active than Ir and Ru analogues. As an exception to this trend, Hazari *et al.* recently presented a Fe pincer-type complex which, in the presence of Lewis acids co-catalysts, promoted FA DH with extraordinary catalytic activities, reaching TON = 983642 and TOF = 196728 h<sup>-1</sup> at 60 °C, even higher than those reported for most precious metal catalysts.<sup>10e</sup>

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Electronic Supplementary Information (ESI) available: Additional figures, schemes and photos; details of NMR experiments and spectra; additional tables for catalytic tests; cartesian coordinates and calculated structures. See DOI: 10.1039/x0xx00000x

We recently reported that Fe(II) complexes bearing the linear tetraphosphine ligand 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4, Chart 1) could catalyze base- and additive-free selective FA DH in batch experiments at 60 °C with TONs up to 6061 and average TOF = 1570 h<sup>-1</sup>.<sup>10g</sup> As a major drawback, batch recycling experiments showed a severe drop in activity from the first to the third cycle, indicating catalyst deactivation. Inspired by the work of Beller *et al.*,<sup>8k</sup> and with the aim to develop more robust catalysts for FA DH, we became eager to explore the activity and long-term stability of Ru/tetraphos-1 catalysts. In the present work, we describe results on selective FA dehydrogenation to H<sub>2</sub>/CO<sub>2</sub> gas mixtures, using both *in situ* generated Ru/P4 and well-defined Ru(II) complexes bearing this ligand as catalysts. Starting from initial batch reaction tests and recycling experiments showing high stability, it was then possible to carry out FA continuous feed tests with a simple laboratory setup. Moreover, the gas mixtures produced were used directly to feed a standard PEM fuel cell and demonstrate electric power generation. The catalytic tests are complemented by mechanistic studies by experimental techniques (NMR) and theoretical calculations (DFT), highlighting the role of the Ru(II) bis-(hydrido) complex *trans*-[Ru(H)<sub>2</sub>(meso-P4)] as the active catalyst, allowing for the description of a proposed mechanism.

## Results and discussion

The linear tetraphos-1 ligand (P4, Chart 1), described initially by King *et al.*,<sup>12a</sup> exists as a mixture of *rac* (S,S;R,R) and *meso* (S,R) diastereoisomers, which can be separated by fractional crystallization.<sup>12b,13</sup>

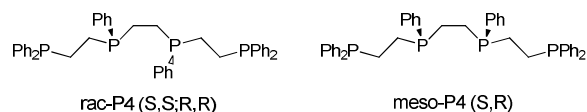


Chart 1. *rac*- and *meso*-isomers of the tetraphos-1 (P4) ligand.

Whereas the *rac*-P4 isomer typically affords *cis*- $\alpha$  complexes (albeit in principle all three configurations *cis*- $\alpha$ , *cis*- $\beta$  and *trans*- are possible), *meso*-P4 allows formation of both *trans*- and *cis*- $\beta$  complexes, with significant preference for the former.<sup>10g,13</sup> In turn, *rac*-P4 complexes with *cis*- $\alpha$  geometry offer two potentially accessible sites in *cis* position, while *trans*-complexes of *meso*-P4 favour transformations which occur on a single side of the metal centre. The reactivity of the latter complexes may thus depend significantly on the nature of the ligand in *trans* position to the reactive site.

### Catalytic FA batch dehydrogenation tests.

We started our investigation by testing FA DH with catalytic systems formed *in situ* by mixing *rac*-P4 and *meso*-P4 with suitable ruthenium(II) precursors such as [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (**A**) and [Ru(cod)(methylallyl)]<sub>2</sub> (**B**), respectively. In a first series of tests, neat FA was used as substrate without addition of an amine, and as expected from literature perusal, no activity was

observed, in contrast to Fe/P4 catalytic systems developed in our group<sup>10g</sup> or other Fe/phosphine-based protocols.<sup>10c</sup>

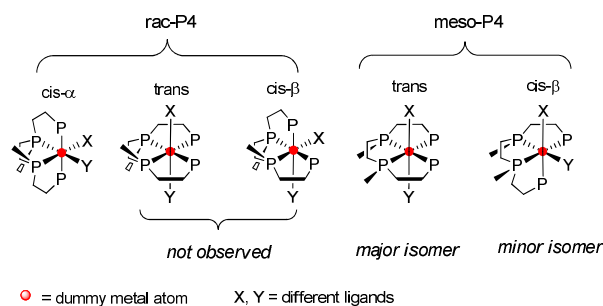


Chart 2. Allowed configurations for *rac*- and *meso*-P4 octahedral complexes.

We therefore investigated FA DH in the presence of combinations of **A**, **B** and ligand L (*meso*-P4 and *rac*-P4) as catalysts, adding N,N-dimethyloctylamine (DMOA), in a ratio FA/DMOA = 11:10, using propylene carbonate (PC, 1.0 mL) as inert solvent.<sup>8j,10g</sup> FA:catalyst, Ru:L ratios and temperature effects were also screened. Selected results, including initial TOFs (calculated after 10 min) and overall TONs (sum of all TONs upon catalyst recycling), are summarized in Table 1 (entries 1-9). TON and initial TOF values for single batch runs for each system are reported in Table S1 (see ESI).

Table 1. Formic acid dehydrogenation using *in situ* and well-defined Ru(II) precatalysts.

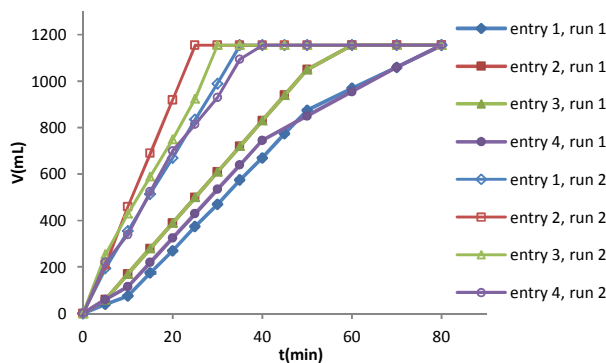
entry	Catalyst	Ru/ L	T (°C)	TOF <sub>10min</sub> run 1 (h <sup>-1</sup> ) <sup>[k]</sup>	TOF <sub>10min</sub> run 2 (h <sup>-1</sup> ) <sup>[k]</sup>	TON <sub>overall</sub> <sup>[l]</sup>	runs (n)
1 <sup>[a]</sup>	A/ <i>meso</i>	1:1	60	384	1817	11000 (7)	11
2 <sup>[a]</sup>	A/ <i>meso</i>	1:2	60	665	2354	11000 (5)	11
3 <sup>[a]</sup>	A/ <i>meso</i>	1:4	60	870	2201	11000 (5)	11
4 <sup>[b]</sup>	A/ <i>rac</i>	1:2	60	588	1740	8000 (6)	8
5 <sup>[a]</sup>	B/ <i>meso</i>	1:2	60	870	2354	11000 (5)	11
6 <sup>[b]</sup>	B/ <i>rac</i>	1:2	60	1203	2073	8000 (5)	8
7 <sup>[a]</sup>	A/ <i>meso</i>	1:2	40	1	640	4000(13)	4
8 <sup>[a]</sup>	A/ <i>meso</i>	1:2	80	4556	5579	11000 (3)	11
9 <sup>[c]</sup>	A/ <i>meso</i>	1:2	60	1791	6654	50000(12)	5
10 <sup>[d]</sup>	<b>1</b>	1:1	60	1459	1459	11000(5)	11
11 <sup>[e]</sup>	<b>2</b>	1:1	60	2201	2688	11000(5)	11
12 <sup>[f]</sup>	<b>3</b>	1:1	60	2406	2045	11000(5)	11
13 <sup>[d]</sup>	<b>1</b>	1:2	60	1868	1868	11000(5)	11
14 <sup>[e]</sup>	<b>2</b>	1:2	60	2687	2687	11000(5)	11
15 <sup>[f]</sup>	<b>3</b>	1:2	60	2866	2866	11000(5)	11
16 <sup>[g]</sup>	<b>1</b>	1:2	60	51	-	154(3)	1
17 <sup>[h]</sup>	<b>2</b>	1:2	60	102	-	409(6.5)	1
18 <sup>[i]</sup>	<b>3</b>	1:2	60	153	-	529(5.5)	1
19 <sup>[j]</sup>	A/ <i>meso</i>	1:2	60	665	2354	11000 (5)	11

Reaction conditions: <sup>[a]</sup> [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (**A**) 12.0 μmol; L (*meso*-P4 or *rac*-P4 ligands, 1-4 equiv. to Ru); FA/DMOA (11:10) 5.0 mL (density at 25 °C = 0.894 mg mL<sup>-1</sup>, FA 24.0 mmol), PC 1.0 mL. Gas evolution measured by manual gas buret. <sup>[b]</sup> [Ru(cod)(methylallyl)]<sub>2</sub> (**B**) 24.0 μmol. <sup>[c]</sup> [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (**A**) 1.20 μmol. <sup>[d]</sup> [Ru(*meso*-P4)Cl<sub>2</sub>](**1**) 24.0 μmol. <sup>[e]</sup> [RuCl(H)(*meso*-P4)](**2**) 24.0 μmol. <sup>[f]</sup> [Ru(H)<sub>2</sub>(*meso*-P4)](**3**) 24.0 μmol. <sup>[g]</sup> As for <sup>[d]</sup>, no base, PC 4.0 mL. <sup>[h]</sup> As for <sup>[e]</sup>, no base, PC 4.0 mL. <sup>[i]</sup> As for <sup>[f]</sup>, no base, PC 4.0 mL. <sup>[j]</sup> As for <sup>[a]</sup>, Hg added. <sup>[k]</sup> Defined as mmol<sub>H<sub>2</sub> produced</sub> / mmol<sub>catalyst</sub> × h<sup>-1</sup>, calculated at conversions observed after 10 min. <sup>[l]</sup> Sum of TONs (defined as mmol<sub>H<sub>2</sub> produced</sub> / mmol<sub>catalyst</sub>) calculated after each batch experiment and recycling (n runs). Run time (h) in parenthesis.

For each system, recycling experiments were carried out to evaluate catalyst stability by adding neat FA to the reaction mixture resulting from the previous run (see Experimental Section). FA/DMOA DH in the presence of **A**/meso-P4 (0.1 %mol, Ru:P4 = 1:1) at 60 °C resulted in complete and selective conversion to H<sub>2</sub> + CO<sub>2</sub> after 70 min (no CO detected by off-line FTIR gas analysis),<sup>8l</sup> with TON = 1000 and initial TOFs (10 min, run 2) of 1817 h<sup>-1</sup> (Table 1, entry 1). Catalyst recycling proved to be efficient for up to 11 consecutive runs and notably, complete FA consumption was invariably observed after each cycle with almost identical reaction profiles and TOFs, reaching overall TON = 11000 after 7h total reaction time (entry 1). The catalytic system performance was improved by increasing the Ru/meso-P4 ratio to 1:2.<sup>8d</sup> An overall TON = 11000, corresponding to complete conversion for 11 consecutive runs, was obtained after 5h of total reaction time, with a constant TOF<sub>10min</sub> = 2354 h<sup>-1</sup> for runs 2-11 (entry 2). Further increase of the Ru/meso-P4 ratio to 1:4 gave no significant change in the catalytic activity (entry 3).

In sharp contrast to the Fe analogue reported earlier by us,<sup>10g</sup> the Ru/meso-P4 system showed significantly better performance than Ru/rac-P4. Using the *in situ* system **A**/rac-P4 (0.1 %mol, Ru:P4=1:2) at 60 °C, full FA conversion was again obtained for 8 consecutive runs but initial TOF<sub>10min</sub> for runs 2-8 decreased from 2354 to 1740 h<sup>-1</sup> under otherwise identical conditions (entries 2 vs 4).

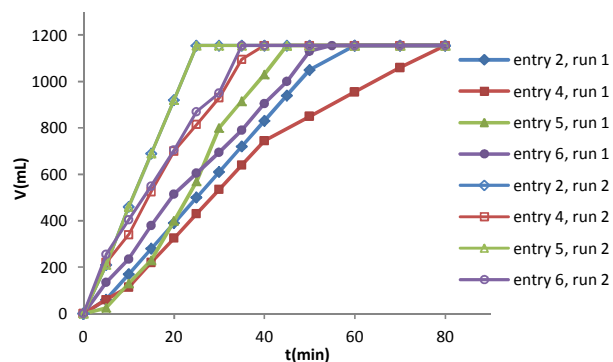
An interesting feature of the catalytic tests with **A**/P4 is the markedly different behaviour of the first runs from the following ones, apparent from an inspection of the reaction profiles (Figure 1).



**Figure 1.** Reaction profiles for FA DH using in situ catalytic system **A**/P4 (entries 1-4 in Table 1; full symbols: run 1; empty symbols: run 2). Reaction conditions: [RuCl(benzene)<sub>2</sub>]<sub>2</sub>(**A**) 12.0 μmol; ligand 12.0 - 48.0 μmol; FA/DMOA (11:10) 5.0 mL; catalyst = 0.1% mol, 60 °C.

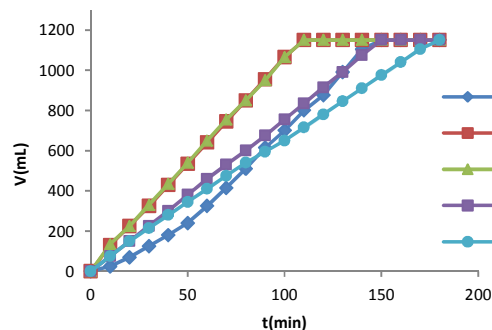
The different induction times are likely related to the formation of the active catalytic species, and can be expected to depend on the choice of metal precursor, type and amount of ligand under the same conditions. Once the active catalytic species is formed, no additional induction period is required, as deduced by the almost superimposable reaction profiles and identical TOF values for runs 2-n upon recycling (Table S1, ESI). A slight dependence on the Ru/P4 ratio was also observed, and the 1:2 ratio was found to be optimal to reach the highest initial TOFs (Table 1). A second catalytic system

was then obtained *in situ* by the combination of meso-P4 and rac-P4 with the chloride-free Ru precursor [Ru(cod)(methylallyl)<sub>2</sub>] (**B**), used by Leitner<sup>14</sup> and Cantat<sup>15</sup> for CO<sub>2</sub> hydrogenation and FA disproportionation to MeOH, respectively. Under the same conditions (catalyst 0.1 %mol, 60 °C, Ru/P4 = 1:2), the catalytic system **B**/meso-P4 showed comparable activity to **A**/meso-P4 in the recycling experiments from run 2 to 11 (entries 5 vs. 2), but the induction period observed for the first run was shorter with TOF<sub>10min</sub> = 870 h<sup>-1</sup> (entry 5). Also in the case of **B**/P4, rac-P4 showed to give a slightly less efficient catalytic system, with overall TON = 8000 after 8 consecutive runs and initial TOF<sub>10min</sub> for the second run decreasing from 2354 to 2073 h<sup>-1</sup> (entries 5 vs. 6). Thus, we focused the rest of our studies on catalytic protocols involving meso-P4 only. A comparison of reaction profiles for **A**/P4 vs. **B**/P4 (first and second runs) is shown in Figure 2.



**Figure 2.** Reaction profiles for FA DH using in situ catalytic system **A**/P4 and **B**/P4 (entries 2, 4-6 in Table 1; full symbols: run 1; empty symbols: run 2). Reaction conditions: [RuCl(benzene)<sub>2</sub>]<sub>2</sub>(**A**) 12.0 μmol or [Ru(cod)(methylallyl)<sub>2</sub>] (**B**) 24.0 μmol; ligand 12.0 - 48.0 μmol; FA/DMOA (11:10) 5.0 mL; catalyst = 0.1% mol, 60 °C.

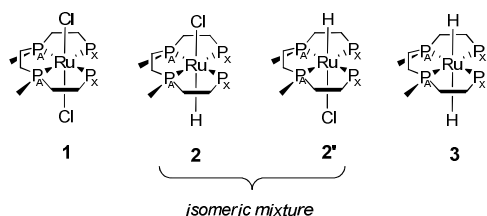
The effects of temperature and catalyst loading were then evaluated. Reducing the reaction temperature to 40 °C (entry 7) using the **A**/meso-P4 system (0.1% mol) resulted in ca. 98% conversion with significant decrease TOF<sub>10min</sub> = 640 h<sup>-1</sup> obtained for run 2. On the other hand, increasing the temperature to 80 °C gave higher TOF<sub>10min</sub> (run 2) = 5579 h<sup>-1</sup> (entry 8). The catalytic system was recycled for 11 consecutive cycles without loss of activity, reaching complete FA conversion for every run (TON = 11000, 11 runs).



**Figure 3.** Reaction profiles of catalytic runs using in situ catalytic system **A**/meso-P4 in the recycling experiment. Reaction conditions: [RuCl(benzene)<sub>2</sub>]<sub>2</sub>(**A**) 1.2 μmol; meso-P4 4.8 μmol, FA/DMOA (11:10), 5.0 mL; FA:catalyst = 10000; 60 °C. For recycling

experiments, neat FA (1.22 mL aliquots) was added to the reaction vessel kept at 60 °C after the end of each run.

It was possible to lower the catalyst loading to 0.01% mol (entry 9), still achieving full FA conversion reaching  $\text{TOF}_{10\text{min}}$  (run 2) =  $6654 \text{ h}^{-1}$ , and to carry out five consecutive runs giving an overall TON = 50000. Disappointingly, a drop in activity from the second to the fifth cycle was observed (Figure 3). Then, well-defined Ru complexes<sup>13</sup> *trans*-[RuCl<sub>2</sub>(meso-P4)] (**1**), *trans*-[RuCl(H)(meso-P4)] (**2**) (isomeric mixture, see Chart 3) and *trans*-[Ru(H)<sub>2</sub>(meso-P4)] (**3**) were tested for comparison. A series of batch FA DH experiments were performed under the conditions summarised in Table 1. A catalytic activity comparable to that obtained with the *in situ* formed system **A**/meso-P4 was observed with **1**, but with a shorter induction period resulting in a higher  $\text{TOF}_{10\text{min}}$  =  $1459 \text{ h}^{-1}$  (entry 10). Complete conversions were reached for 11 consecutive runs over 5h reaction time, with an overall TON of 11000. Interestingly, the  $\text{TOF}_{10\text{min}}$  values were the same for the first and second runs and onwards, at variance with the **A**/meso-P4 *in situ* system.



**Chart 3.** Ruthenium complexes *trans*-[RuCl<sub>2</sub>(meso-P4)] (**1**), *trans*-[Ru(H)Cl(meso-P4)] (isomeric mixture, **2** and **2'**) and *trans*-[Ru(H)<sub>2</sub>(meso-P4)] (**3**) with NMR labeling (P<sub>A</sub>, P<sub>X</sub>) on P atoms.

Under the same conditions complex **2** gave a higher  $\text{TOF}$  =  $2201 \text{ h}^{-1}$  for both first and second runs (entry 11), reaching complete conversions for 11 consecutive runs, with an overall TON of 11000. In the case of **3**, a slightly higher  $\text{TOF}$  =  $2406 \text{ h}^{-1}$  was obtained, again with the same values for all runs (entry 12).

Literature data show that the catalyst stability can be often improved by addition of free phosphine.<sup>10c</sup> The experiments described above (entries 10-12) were thus repeated in the presence of an additional equivalent of meso-P4, to get a formal Ru:L = 1:2 ratio. In the case of complex **1**, a higher  $\text{TOF}_{10\text{min}}$  =  $1868 \text{ h}^{-1}$  was obtained for the both first and second runs (entry 13). The same behavior was observed for **2** and **3**, with  $\text{TOF}_{10\text{min}}$  of 2687 and  $2866 \text{ h}^{-1}$ , respectively (entries 14, 15).

We were interested to evaluate the possible activity of our complexes for FA DH in absence of base, which has been rarely described in the case of Ru complexes. The tests carried out under the conditions applied for runs 13-15 were thus repeated without DMOA using the same amount of FA (12.0 mmol). A moderate activity was observed also under these conditions (entries 16-18), albeit reaching only a maximum TON = 529 with **3**.

Finally, we could rule out the possibility of catalysis by colloidal Ru aggregates by repeating the standard test using **A**/meso-P4

in the presence of Hg(0), which gave comparable results to the standard run (entry 19 vs. 2).

### Continuous feed FA DH and gas mixture direct utilisation.

On the basis of the results described above, showing that our catalytic protocols allowed for catalyst recycling without significant loss of activity, we decided to establish the potential to work under continuous FA feed and measure the overall amount of H<sub>2</sub>/CO<sub>2</sub> gas mixture that could be obtained under such conditions. In a proof-of-concept, unoptimised system the thermostated reactor was connected to a flowmeter to monitor the amount of gas mixture produced over the time using a dedicated program running on a personal computer (details in Experimental Section and ESI, including photos of the apparatus). In a typical test, using [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (**A**, 0.012 mmol), meso-P4 (2 equiv.), DMOA (4.0 mL) and PC (1.0 mL) and heating to 60 °C, after a pre-activation first run, a constant rate of 35 μL/min FA feed was used. Under these conditions, a constant gas evolution was observed over a period of ca. 48 h resulting in a TON = 220848 corresponding to ca. 129.4 L of H<sub>2</sub> (Figure S3 in ESI). System engineering and catalyst deactivation studies under batch and continuous feed conditions are in progress.

Finally, as off-line FT-IR analysis of the gas mixture produced during all catalytic runs revealed absence of CO (detection limit 0.02% by FTIR),<sup>81</sup> we were interested to check whether the as-obtained gas stream could be directly used to feed a standard H<sub>2</sub>/O<sub>2</sub> PEM fuel cell to produce electricity. The continuous feed hydrogen generation setup described above was thus combined with a H<sub>2</sub>/O<sub>2</sub> PEM demonstration kit fuel cell. The gas mixture flow obtained (see Experimental Section) was directly conveyed into the fuel cell measuring the electrical power generated. Under these conditions, the maximum electrical power, after an initial 300 mW maximum peak, stabilised to 280 mW (measured at 700 mV) to remain constant for the set time of the proof-of-concept experiment (10 h). The power generated was sufficient to operate a small demonstration fan (500 mW) connected to the fuel cell, for the whole duration of the experiment.

### Mechanistic Studies

To shed light on the mechanism of catalytic FA DH by meso-P4/Ru most active systems, we carried out selected NMR experiments under different conditions. To start, we investigated the stoichiometric reaction of meso-P4 and **A** in PC at 60 °C, which resulted in the quantitative formation of complex **1** as the sole product ( $\delta_{\text{P}}$ : 97.3 (P<sub>A</sub>), 39.4 (P<sub>X</sub>),  $^2J_{\text{trans}}$  = 290 Hz, see Chart 3 for P atom labeling).

Established that **1** is the actual catalyst precursor when the *in situ* catalytic system meso-P4/**A** is employed, we investigated the reaction of **1** with FA. Complex **1** appeared to be rather unreactive towards FA (ca. 7.4 equiv.) at room temperature in d<sub>8</sub>-THF in the absence of base, in agreement with initial catalytic tests (*vide supra*). Thus, DMOA was added to the reaction mixture (ca. 6.75 equiv. to **1**; FA/DMOA = 11:10). The reaction of DMOA and FA was evident from the <sup>1</sup>H NMR



spectrum, as the signal of the acidic proton (11.18 ppm) disappeared, while the peak observed for the formic proton shifted from 7.92 ppm to 8.05 ppm. Under these conditions,  $^1\text{H}$  NMR showed also a new singlet at 4.55 ppm which was attributed to molecular  $\text{H}_2$ , indicating that FA DH occurred to some extent even at room temperature. Upon gentle heating (40 °C, 30 min), FA DH proceeded further and  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR analysis revealed the formation of the hydrido chloride complexes **2** ( $\delta_{\text{P}}$ : 92.1 ( $\text{P}_A$ ), 54.1 ( $\text{P}_X$ ),  $^2J_{\text{trans}} = 248$  Hz) and **2'** ( $\delta_{\text{P}}$ : 115.4 ( $\text{P}_A$ ), 56.4 ( $\text{P}_X$ ),  $^2J_{\text{trans}} = \text{ca. } 246$  Hz),<sup>13</sup> with complex **1** still being the most abundant P-containing species in solution.

In a separate experiment, in contrast to **1**, complex **2** reacted with FA (ca. 6.8 equiv.) affording  $\text{H}_2$  without the need of an added base under otherwise analogous conditions, as indicated by  $^1\text{H}$  NMR analysis. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra measured during the reaction monitoring, only the peaks of **2** and **2'** were observed, suggesting that the hydrido chloride complex is the resting state of the reaction under these conditions. Accordingly, the only  $^1\text{H}$  NMR resonances observed in the hydride region were the two pentets assigned to the hydride atoms of **2** ( $\delta$ : -20.9,  $^2J_{\text{HP}} = 20$  Hz) and **2'** ( $\delta$ : -17.89,  $^2J_{\text{HP}} = 18$  Hz).<sup>13</sup>

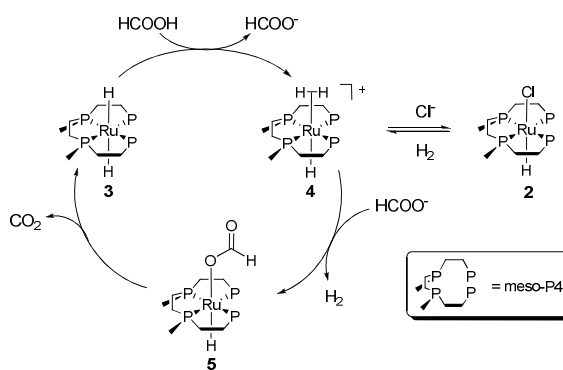
Next, we explored the reactivity of **3** with FA. A solution of **3** in  $d_8$ -THF was placed in a Wilmad quick pressure valve NMR tube under  $\text{N}_2$ . Addition of FA (ca. 6.8 equiv.) resulted in the conversion of **3** into a new complex **5** with characteristic  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances centred at 97.8 and 58.0 ppm and a hydride signal which, in the presence of unreacted FA, appeared as a broad, unresolved peak at -22.91 ppm. These signals were attributed to *trans*-[Ru(H)( $\eta^1$ -O<sub>2</sub>CH)(*meso*-P4)] (**5**) and confirmed by independent synthesis of such complex, which was obtained by reacting **3** with  $^{13}\text{CO}_2$  in  $d_8$ -THF ( $\delta_{\text{P}}$ : 97.8 ( $\text{P}_A$ ), 58.0 ( $\text{P}_X$ ),  $^2J_{\text{trans}} = 267$  Hz;  $\delta_{\text{C}}$ : 166.52 ppm,  $^1J_{\text{CH}} = 188$  Hz, Ru-O $\underline{\text{C}}(\text{O})\text{H}$ ;  $\delta_{\text{H}}$ : -22.11, pentet,  $^2J_1 = ^2J_2 = 20.30$  Hz,  $^2J_3 = ^2J_4 = 20.36$  Hz, Ru-H). Furthermore, a small amount of the known complex  $^{13}\text{C}$  *trans*-[Ru(H)( $\eta^2$ -H<sub>2</sub>)(*meso*-P4)] (**4**) was detected in solution shortly after the addition of FA to the solution of **3** in  $d_8$ -THF. Complex **4** was identified due to its characteristic  $^1\text{H}$  NMR resonances at -4.99 (brs) and -12.33 ppm (pentet),<sup>13</sup> whereas the  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances of **4** could not be detected due to the very low concentration under such conditions. The  $^1\text{H}$  NMR signal at 4.54 ppm indicated formation of  $\text{H}_2$ . In less than 1h at room temperature, all FA was completely consumed, and during the whole reaction time the only P-containing species detected by  $^{31}\text{P}\{^1\text{H}\}$  NMR was **5**, which can be regarded as the resting state of the reaction under turnover conditions in the absence of chloride anions. Once FA was completely consumed, the hydride signal of **5** was observed as a well-resolved pentet at -22.16 ppm.

These observations suggest that the first step in the catalytic cycle consists in the protonation of **3** by FA affording transient **4**, which undergoes facile ligand substitution to give **5** and  $\text{H}_2$ .  $\text{CO}_2$  elimination from **5** to regenerate **3** closing the catalytic cycle is evidently the rate limiting step in the reaction. In order to induce  $\text{CO}_2$  elimination from **5**, the NMR tube was heated to 60 °C for 1.5h, with the quick pressure valve kept open under a  $\text{N}_2$  atmosphere to allow the evolved  $\text{CO}_2$  to escape from the

tube. Surprisingly, even after 1.5h only a minor amount of **5** was converted back to **3**, indicating a significant kinetic barrier for  $\text{CO}_2$  elimination from **5** in  $d_8$ -THF alone. Evidently, the decarboxylation step is significantly faster under turnover conditions, suggesting that the elimination of  $\text{CO}_2$  may be promoted by the acid itself. To confirm this hypothesis, complex **5** was synthesised in NMR scale upon reacting **3** with  $^{13}\text{CO}_2$ , and the excess  $^{13}\text{CO}_2$  was subsequently replaced with  $\text{N}_2$  through several freeze-pump-thaw cycles. Addition of  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (ca. 1.3 equiv.) to the resulting solution containing **5** rapidly gave **4** as the sole P-containing product, indicating that  $\text{CO}_2$  elimination had occurred rapidly in the presence of acid giving **3** which was easily protonated to give **4** ( $\delta_{\text{P}}$ : 108.6 ( $\text{P}_A$ ), 64.8 ( $\text{P}_X$ ),  $^2J_{\text{trans}} = 193$  Hz), as previously reported.<sup>13</sup> Notably, **4** is known to undergo facile dihydrogen ligand exchange in the presence of  $\text{Cl}^-$  ions to afford **2**, which in turn could explain why complexes **3** and **4** could not be observed in the FA DH experiments starting from either **1** or **2**. In fact, comparable catalytic activities were observed under the same reaction conditions using either  $[\text{RuCl}_2(\text{benzene})_2]_2$  or  $[\text{Ru}(\text{COD})(\text{methylallyl})_2]$  as metal precursors, albeit needing different induction periods, suggesting that Ru/P4-catalysed FA DH is likely to proceed via the same key catalytic intermediates, independently of the catalyst precursor used. The hydrido chloride complex should not be involved directly in the mechanism, but rather act as reservoirs. On the other hand, hydride ligands are well known to have a high *trans* effect and are therefore expected to induce high reactivity at the *trans* position, thus *trans*-dihydrido species such as **3** can be expected to be highly active.<sup>16</sup>

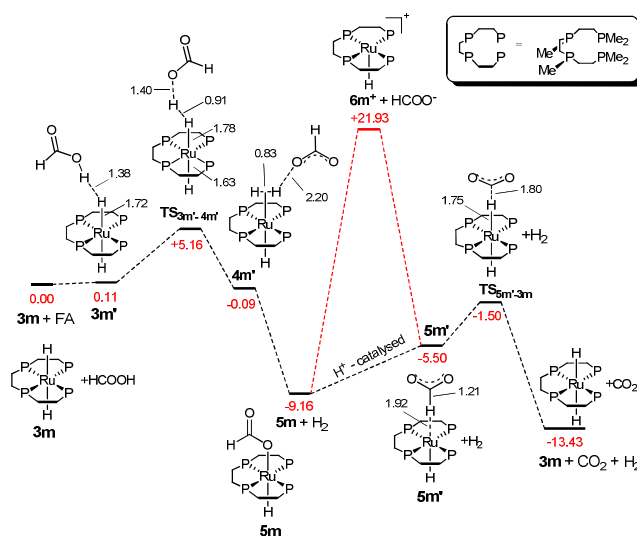
On the basis of these experiments and considerations, we propose the catalytic mechanism illustrated in Scheme 1. Under catalytic conditions, complex **3** is protonated by  $\text{HCOOH}$  affording the hydrido dihydrogen complex **4**. The labile  $\eta^2$ - $\text{H}_2$  ligand in **4** can be easily displaced by a formate anion, affording **5** and releasing  $\text{H}_2$ .  $\text{CO}_2$  elimination from **5**, which is the rate-limiting step of the FA DH reaction, gives back **3** closing the catalytic cycle.

The proposed mechanism was further supported by DFT calculations at the b3lyp/6-311++(d,p)G level of theory,<sup>17</sup> using the Stuttgart–Dresden pseudopotential<sup>18</sup> for the Ru center and the PCM continuum solvation model<sup>19</sup> (see ESI for details).



Scheme 1. Proposed simplified mechanism for FA DH catalysed by **3**.

In the model systems, the phenyl substituents on phosphorus were replaced by methyl groups in order to decrease significantly the computational cost. Steric effects could therefore be underestimated. The axial sites of octahedral *trans* complexes of the meso-P4 ligand are inequivalent due to the arrangement of the substituents on P; as a result, one axial site is "surrounded" by four substituents whereas the other axial site has only two groups near it, resulting in a significantly different steric hindrance on the two sides of the P4 plane. In the following discussion we will thus focus on the catalytic reaction occurring on the less hindered site, which is expected to be significantly more accessible in the *real* system. The overall reaction pathway is described in Scheme 2.



**Scheme 2.** Energy profile for the dehydrogenation of FA starting from **3m**. Free energies are given in kcal/mol, selected bond distances are in Å.

The protonation of the dihydride **3m** by FA proceeds, as expected, with a negligible barrier ( $\Delta G^\ddagger = +5.16$  kcal/mol) and is essentially thermoneutral ( $\Delta G = -0.09$  kcal/mol). Internal reaction coordinate (IRC) calculations confirmed that the found transition state ( $TS_{3m'-4m'}$ ) connects intermediate **3m'** and **4m'**. The optimised structure of **4m'** shows significant van der Waals interactions between one O of the formate anion and one H of the dihydrogen ligand ( $d_{O-H} = 220.083$  pm  $\ll$  272 pm; 272 pm = sum of the van der Waals radii). From **4m'**, favourable ligand exchange results in the formation of the hydrido formate complex **5m** and  $H_2$  ( $\Delta G = -9.07$  kcal/mol). Overall, the reaction of **3m**+FA to afford **5m**+ $H_2$  is exoergic by -9.16 kcal/mol.

Formate complex **5m** is coordinatively saturated and thus  $\beta$ -H elimination from **5m** to afford **3m**+ $CO_2$  is unlikely, since it would require dissociation of one of the phosphine arms.<sup>10d</sup> On the other hand, isomerisation of O-bound formate complex **5m** into its H-bound isomer (**5m'**) appears to be feasible ( $\Delta G = +3.67$  kcal/mol) and subsequent  $CO_2$  elimination via  $TS_{5m'-3m}$  is predicted to occur with a negligible barrier ( $\Delta G^\ddagger = 4.00$  kcal/mol), giving back **3m**. Our attempts to locate a transition

state for a strictly intramolecular isomerisation<sup>20</sup> failed, while a purely dissociative pathway<sup>21</sup> appears to be energy demanding ( $\Delta G_{diss} = +31.09$  kcal/mol), which is in agreement with the experimental observation that complex **5** is significantly stable towards  $CO_2$  elimination in the absence of acid (*vide supra*). However, the experimental evidence described above clearly demonstrated the catalytic effect of  $H^+$  in promoting the elimination of  $CO_2$  from **5** with concurrent regeneration of **3**.

## Experimental Section

### General methods and materials

$[RuCl_2(benzene)]_2$ <sup>22</sup> and complexes **1-3**<sup>13</sup> were prepared according to literature procedures. 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 300 spectrometer.  $[Ru(COD)(methylallyl)]_2$  and propylene carbonate (PC) were purchased from commercial suppliers and used without further purification. Ligand 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos-1, P4) was supplied by Pressure Chemicals Inc., Pittsburgh, PA. Deuterated solvents for NMR measurements were purchased from commercial suppliers and stored onto activated 4A molecular sieves under  $N_2$  before use.

**Synthesis of *trans*-[Ru(H)( $\eta^1$ -O<sub>2</sub>CH)(meso-P4)] (**5**):** *Method a*): 4.5 mg (5.8  $\mu$ mol) of *trans*-[Ru(H)<sub>2</sub>(meso-P4)] (**3**) were placed in a Wilmad quick pressure valve NMR tube under  $N_2$  and dissolved in 200  $\mu$ L of  $d_8$ -THF. The NMR tube was placed in liquid nitrogen to freeze the  $d_8$ -THF solution of **3**, evacuated, warmed up to room temperature, and re-filled with  $^{13}CO_2$ .  $^1H$ ,  $^{31}P\{^1H\}$  and  $^{13}C\{^1H\}$  NMR spectra showed the exclusive formation of *trans*-[Ru(H)( $\eta^1$ -O<sub>2</sub><sup>13</sup>CH)(meso-P4)] (**5**). *Method b*): 3.0 mg (3.9  $\mu$ mol) of *trans*-[Ru(H)<sub>2</sub>(meso-P4)] (**3**) were placed in a Wilmad quick pressure valve NMR tube under  $N_2$  and dissolved in 200  $\mu$ L of  $d_8$ -THF. HCOOH (1.0  $\mu$ L, 26.5  $\mu$ mol; ca. 6.8 equiv.) was added to the tube.  $^{31}P\{^1H\}$  NMR analysis after 1h revealed quantitative formation of **5** as the sole P-containing product. NMR data ( $d_8$ -THF, 25 °C):  $\delta_P$ : 97.8 (P<sub>X</sub>), 58.0 (P<sub>A</sub>),  $^2J_{trans} = 267.2$  Hz;  $\delta_C$ : 166.52 ppm,  $^1J_{CH} = 187.90$  Hz, Ru-O $\underline{C}$ (O)H);  $\delta_H$ : -22.11, pentet,  $^2J_1 = ^2J_2 = 20.30$  Hz,  $^2J_3 = ^2J_4 = 20.36$  Hz, Ru-H).

**Typical procedure for the FA DH tests:** In a typical experiment, a solution of catalyst (typically 0.024 mmol) in propylene carbonate (1.0 mL) was placed under a nitrogen atmosphere in a magnetically stirred glass reaction vessel thermostated by external liquid circulation and connected to a reflux condenser and gas-buret (5.0 mL scale). After heating to 40-60 °C, the adduct HCOOH/OctNMe<sub>2</sub> 11:10 (5.0 mL) was added and the experiment started. The gas evolution was monitored throughout the experiment by reading the values reached on the burets. The gas mixtures were analyzed off-line by FTIR spectroscopy using a 10 cm gas cell (KBr windows) to check for



CO formation (detection limit 0.02%).<sup>8i,10g</sup> Each test was repeated at least twice for reproducibility.

**Typical procedure for recycling experiments:** In each recycling test, as soon as the gas volume evolution reached the theoretical value expected for complete FA conversion, the apparatus was flushed with nitrogen to remove any traces of hydrogen and carbon dioxide. The reaction mixture containing the catalyst and the amine, kept at working reaction temperature chosen for the previous run, was used as such for the following runs by addition of neat HCOOH (0.900 mL, 24.0 mmol) through a syringe, repeating the procedure for the desired number of consecutive runs.

**Typical procedure for continuous feed FA DH tests:** In a typical test, the glass thermostated reactor was charged with [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (A, 0.012 mmol), meso-P4 (2 equiv.), DMOA (4.0 mL) and PC (1.0 mL) and heated to 60 °C. Neat FA was then added (24.0 mmol). After 100% conversion was reached (first run completed), a second aliquot (24.0 mmol) of FA was added. After 40% conversion was reached, a peristaltic pump (Gilson) was connected to a flask containing FA (>99%, Aldrich) and set to add a continuous feed of 35 μL/min to the reaction vessel (setting time zero of the experiment). The resulting gas flow was conveyed by tubing to a Bronkhorst LOW-ΔP-FLOW mass flowmeter model F-101D-AGD-22-V with maximum flow rate of 1NL min<sup>-1</sup> connected to a personal computer for monitoring using the FlowDDE2 V4.65 program. A scheme and photos of the setup are available in ESI.

**Typical procedure for electrical power generation.** The as-obtained gas flow from a continuous feed FA DH test (set time 10 h, see above for other conditions) was diverted from the flowmeter into a small demonstration H<sub>2</sub>/O<sub>2</sub> PEM fuel cell (www.h-tec.com/en/education/shop/demonstration/fuel-cell-kit/) connected to a personal computer recording the power generated during the experiment by Chroma DC Load Program Test Report program. Additionally, the electric power was used to run a small electric fan throughout the duration of the experiment.

## Conclusions

In conclusion, Ru(II) complexes bearing the meso-isomer of the linear tetrachosphine ligand 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetrachosphadecane (tetrachos-1, P4) proved to be effective catalysts for selective formic acid dehydrogenation with good yields and TONs in the presence of added amine, both under batch and continuous feed experimental conditions. Mechanistic studies based on NMR experiments and DFT calculations highlighted the role of *trans*-[Ru(H)<sub>2</sub>(meso-P4)] as key intermediate in the catalytic cycle, suggesting that HCOOH activation occurs only on one H atom of the octahedral complex, thanks to the *trans*-effect of the second hydrido ligand. These findings contribute to the growing number of mechanistic details on transition metal catalysed hydrogen-rich small molecules activation, and in turn help chemists to

tailor the synthesis of more effective catalysts and protocols for hydrogen production from liquid hydrogen organic carriers (LOHCs).

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