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Hydrogen Production by Selective Dehydrogenation of HCOOH Catalyzed by Ru-Biaryl Sulfonated Phosphines in Aqueous Solution

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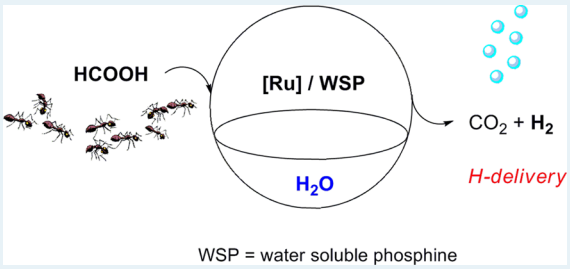
Supporting Information

ABSTRACT: The selective dehydrogenation of aqueous solutions of HCOOH/HCOONa to H_2 and CO_2 gas mixtures has been investigated using $RuCl_3 \cdot 3H_2O$ as a homogeneous catalyst precursor in the presence of different monoaryl-biaryl or alkyl-biaryl phosphines and aryl diphosphines bearing sulfonated groups. All catalytic systems were used in water without any additives and proved to be active at 90 °C, giving high conversions and good TOF values. As an alternative Ru(II) metal precursor, the known dimer $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ was also tested as in situ catalyst with selected phosphines as well as an isolated Ru(II)-catalyst with one of them. By using high-pressure NMR (HPNMR) techniques, indications on the nature of the active species involved in the catalytic cycles were obtained.



KEYWORDS: *aqueous-phase catalysis, formic acid, hydrogen generation, ruthenium, sulfonated phosphines*

INTRODUCTION

In the quest for efficient hydrogen sources[1] from cheap and safe materials, for on-demand use in devices such as fuel cells, producing only water as byproducts,[2] the activation of abundant hydrogen-rich organic compounds has been proposed as a possible solution.[3] In this context, formic acid (HCOOH), which contains 4.4 wt % of hydrogen, as well as its conjugate base, formate anion, are receiving considerable attention as promising materials for H-storage and delivery.[4] The selective decomposition of HCOOH through dehydrogenation yields only H_2 and CO_2 gas mixtures. Furthermore, the CO_2 derived from this reaction can be recycled by hydrogenation to give HCOOH, resulting in a reversible hydrogen storage−release system with potentially zero carbon emission.[5] Both dehydrogenation of HCOOH and hydrogenation of CO_2 need appropriate catalysts to provide selective reactions under mild conditions, including both homogeneous and heterogeneous catalysis.[3d,6]

The first study on the homogeneous dehydrogenation of formic acid (FA) dates back to 1967, when Coffey reported a highly active iridium phosphine complex for this reaction, with TOF (turnover frequency) of 1187 h^{-1} albeit at elevated temperatures.[7] Afterward, many research groups contributed to this field of research and several iron,[8] ruthenium,[9] rhodium,[10] and iridium[11] complexes were described in the literature as FA dehydrogenation homogeneous catalysts. Important results were recently obtained by Beller and co-workers who investigated the ruthenium-catalyzed dehydrogenation of HCOOH under mild conditions in the presence of different amines and HCOOH/amine ratios.[12] An optimized catalytic system was obtained by combining the $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ precursor with diphosphines such as 1,2-bis-(diphenylphosphino)methane (dppm) and 1,2-bis-(diphenylphosphino)ethane (dppe).[13] Remarkable results were presented by the same research group concerning the use of iron(II) tetrafluorborate together with tris[(2-diphenylphosphino)ethyl]phosphine $[P(CH_2CH_2PPh_2)_3$, $PP_3]$ in propylene carbonate, which afforded TOFs (turnover frequencies) up to 9425 h^{-1} and TONs (turnover numbers) higher than 92 000 at 80 °C without the need of an added base.[14] Good catalytic performances in HCOOH dehydrogenation were also reported by some of us with the octahedral complexes $[Ru(\kappa^4\text{-}NP_3)Cl_2]$ and $[Ru(\kappa^3\text{-triphos})(MeCN)_3](PF_6)_2$ ($NP_3 = N(CH_2CH_2PPh_2)_3$, triphos = $MeC(CH_2PPh_2)_3$) in the presence of *n*-octylamine at 80 °C together with a detailed computational study which clarified some mechanistic details of these systems.[15] All the aforementioned catalysts operate in organic solvents.

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Chart 1. Sulfonated Aryl-Biaryl and Alkyl-Biaryl Monophosphines

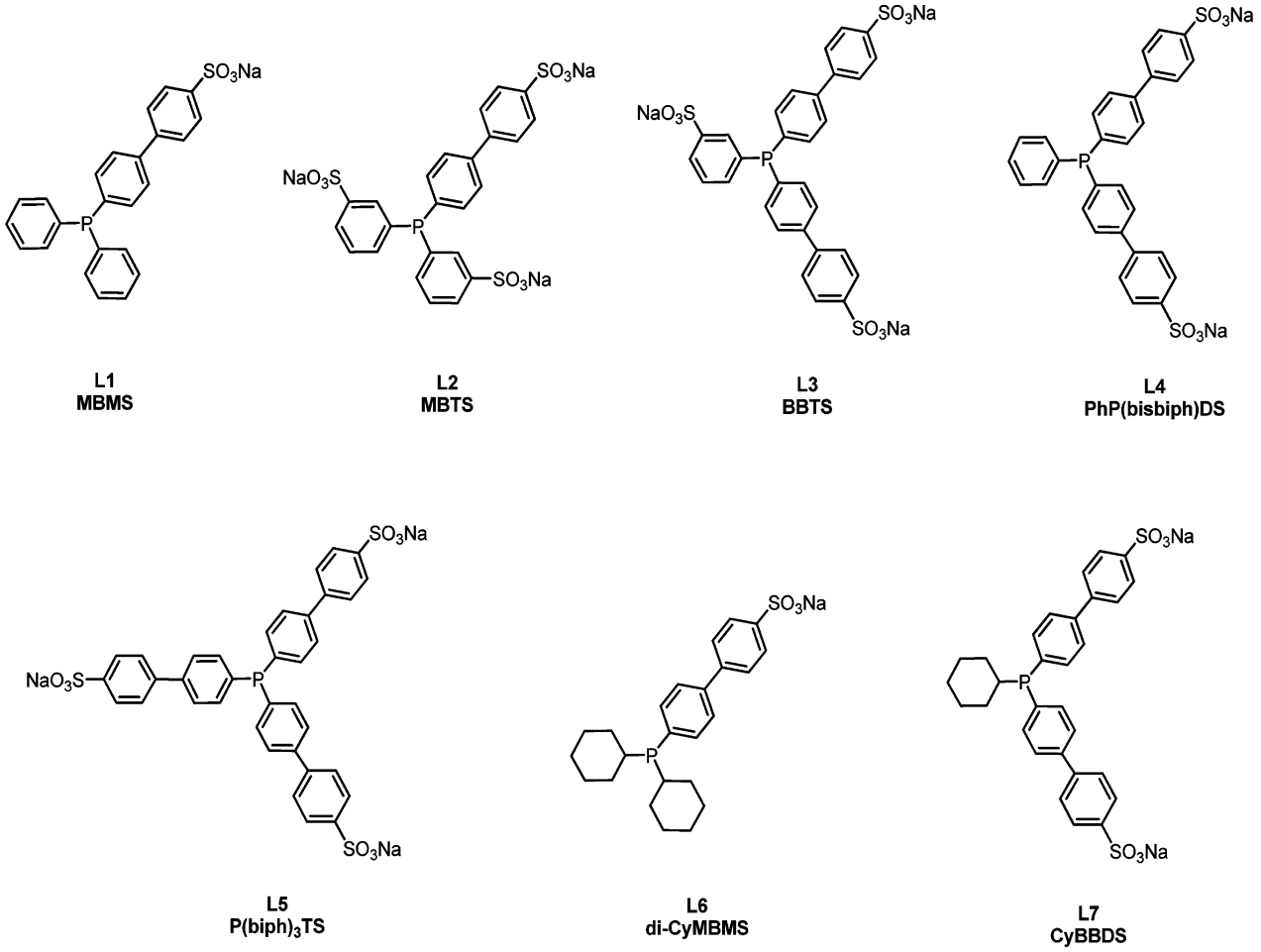

Table 1. Water Solubility, $^{31}P\{^1H\}$ NMR Chemical Shifts of Sulfonated Monophosphines and $^1J_{P-Se}$ Coupling Constants of the Corresponding Selenide Derivatives, Giving a Basicity Scale of the Parent Compound[22]

phosphine	$S(H_2O)_{25\ °C}$	$^{31}P\{^1H\}$ (δ, ppm)[a]	$^1J_{P-Se}$ [Hz][b]	ref
L1 (MBMS)	280 g/L	−5.9	739	20b
L2 (MBTS)	1.0 kg/L	−5.5	752	20a
L3 (BBTS)	1.0 kg/L	−6.4	746	20a
L4 (Ph(P(bisbiph)DS)	850 g/L	−7.7	739	20b
L5 ($P(biph)_3TS$)	1.0 kg/L	−6.9	739	20a
L6 (di-CyMBMS)	50 g/L	0.4	707	20b
L7 (CyBBDS)	520 g/L	−6.5	734	20b
***m*-TPPTS**	1.1 kg/L	−5.1	754	19a, b
***m*-TPPMS**	12 g/L	−3.9	745	19c

[a]Chemical shift values in D_2O. [b]Coupling constant values obtained in absolute EtOH.

A different approach in this field was followed by Laurenczy et al., who performed the selective FA dehydrogenation in aqueous phase by using hydrophilic ruthenium-based catalysts, generated in situ from $[Ru(H_2O)_6](tos)_2$ (tos = toluene-4-sulfonate) or commercial hydrated $RuCl_3$ in the presence of the water-soluble ligand *meta*-trisulfonated triphenylphosphine (*m*-TPPTS).[16] The resulting Ru(II) species catalyzed the dehydrogenation reaction already at 25 °C, reaching a TOF of 460 h^{-1} at 120 °C. Notably, this system was shown to be active in a wide temperature range between 25 and 170 °C, giving in all cases conversions of 90−95%. Furthermore, the hydrogen produced was of high purity, and no CO formation was observed by FTIR (detection limit 2 ppm) even at high temperatures, making this catalytic system suitable for fuel cell applications. The influence of different hydrophilic ligands on the FA dehydrogenation in the presence of $RuCl_3 \cdot 3H_2O$ has also been investigated in detail. These studies showed that ligand basicity, its hydrophilic properties, and its steric effects were the main parameters which influenced the catalytic activity.[17]

The most common method to convey active catalysts in water is to design ligands containing hydrophilic substituents, and the anionic sulfonate group ($-SO_3^-$) is one of the most attractive because of its stability in a wide range of reaction conditions.[18]

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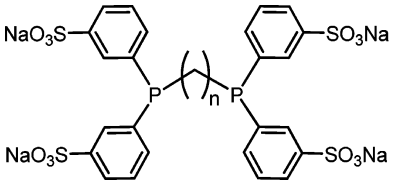
Hereby, we present results on catalytic FA dehydrogenation using a small library of monodentate alkyl-biaryl, aryl-biaryl sulfonated phosphines, and selected tetrasulfonated diphosphines with Ru(III) and Ru(II) metal precursors. Mechanistic studies using high-pressure (HP) NMR techniques gave indications on the role of stable Ru-hydrido species which are formed during catalysis.

RESULTS AND DISCUSSION

Among sulfonated ligands,[19] the phosphines shown in Chart 1 were synthesized by some of us[20] and previously used in the Pd-catalyzed cleavage of allylcarbonate (Tsuji–Trost reaction) and in the aqueous biphasic Rh-catalyzed hydroformylation of terminal alkenes. All these ligands contain at least one biaryl group and differ in the number and position of $-SO_3^-$ substituents. Besides the influence on the water solubility and basicity properties (Table 1), these structural differences can have a significant impact on their coordination behavior and, therefore, on the catalytic activity of the corresponding complexes. On the other hand, the water-soluble diphosphines 1,2-bis[bis(*m*-sodiosulfonatophenyl)phosphino]ethane (DPPETS, **L10**), 1,2-bis[bis(*m*-sodiosulfonatophenyl)-phosphino]propane (DPPPTS, **L9**), and 1,2-bis[bis(*m*-sodiosulfonatophenyl)phosphino]butane (DPPBTS, **L8**) (see Chart 2) were reported as useful ligands to synthesize several Rh, Pt, and Pd coordination compounds which were able to catalyze different reactions in aqueous phase.[21]

Chart 2. Sulfonated Aryl Diphosphines



n= 4, **L8 (DPPBTS)**
n= 3, **L9 (DPPPTS)**
n= 2, **L10 (DPPETS)**

In this study, the above-mentioned sulfonated phosphines were applied as stabilizing ligands in the aqueous-phase dehydrogenation of formic acid, by using either the commercially available $RuCl_3 \cdot 3H_2O$ or the $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ dimer as catalyst precursors. The latter was also used as synthon to obtain an isolated Ru(II)-arene phosphine complex, which was also tested as catalyst. Several tests were performed under different reaction conditions and the recycling of the catalysts was also investigated. For the first time, the bidentate phosphines **L10**, **L9**, and **L8** were used with Ru(III) or Ru(II) precursors for catalytic FA dehydrogenation reactions.

Formic Acid Dehydrogenation Tests with $RuCl_3 \cdot 3H_2O$/Monophosphines. On the basis of the results obtained with Ru/*m*-TPPTS systems (Ru = $[Ru(H_2O)_6](tos)_2$ (tos = toluene-4-sulfonate) or $RuCl_3 \cdot 3H_2O$),[16] we decided to test the water-soluble mono- and diphosphines listed in Charts 1 and 2 under comparable catalytic conditions.

The dehydrogenation of a standard concentration formic acid/sodium formate solution (4 M, 9:1) was carried out in water without any other additive. The presence of a small amount of formate is useful for the activation of the catalytic species, and the 9:1 ratio was chosen as it was shown previously to be a good compromise between conversion and reaction rate.[5b]

The selective dehydrogenation of HCOOH into H_2 and CO_2 was run under atmospheric pressure in thermostated gas reactors and monitored by gas volume evolution collected in gas burets. Using 9.0 mmol of FA, complete conversion is expected to develop 0.440 L of gas mixture, as calculated from the following equation:

$$V_{298K} = x \text{ mol} \cdot 24.48 \text{ L mol}^{-1} + x \text{ mol} \cdot 24.36 \text{ L mol}^{-1} \quad \text{(eq 1)}$$

where x = mol FA, 24.48 L mol^{-1} = estimated molar volume of H_2 at 298 K, 24.36 L mol^{-1} = estimated molar volume of CO_2 at 298 K.

Table 2. Formic Acid Dehydrogenation Catalyzed by Ru/Aryl-Biaryl Monophosphine Systems (First Catalytic Cycle)[a]

entry	ligand	Ru/L	vol (mL) after 5 min[d]	TOF (h^{-1}) after 5 min[f]	max vol (mL) [t(min)][d]	max conv %[g]	final TON[h]	final TOF (h^{-1})[f]
1[b]	**L1**	1/2	270	1188	385 [10]	87.5	141	846
2[c]	**L1**	1/2	80	348	395 [80]	89.9	144	108
3[b]	**L1**	1/4	390	1716	400 [10]	91	146	876
4[b]	**L2**	1/2	380	1668	380 [5]	86.4	139	1668
5[c]	**L2**	1/2	45	192	365 [50]	83	133	160
6[b]	**L2**	1/4	385	1692	420 [15]	95.5	154	616
7[b]	**L3**	1/2	380	1668	385 [10]	87.5	141	846
8[c]	**L3**	1/2	75	324	380 [60]	86.4	139	139
9[b]	**L3**	1/4	385	1692	390 [10]	88.7	143	858
10[b]	**L4**	1/2	360	1584	410 [20]	93.3	150	450
11[c]	**L4**	1/2	80	348	395 [80]	89.9	144	108
12[b]	**L4**	1/4	405[e]	1776	405 [5]	92.1	148	1776
13[b]	**L5**	1/2	405[e]	1776	415 [13]	94.4	152	700
14[c]	**L5**	1/2	60	264	330 [30]	75.1	121	242
15[b]	**L5**	1/4	405[e]	1776	410 [30]	93.3	150	300
16[b]	***m*-TPPMS**	1/2	250	1092	380 [90]	86.4	139	93
17[b]	***m*-TPPTS**	1/2	375	1644	385 [15]	87.6	141	563
18[b]	**no ligand**	–	15	60	90 [330]	20.5	33	6

[a]Reaction conditions: $RuCl_3 \cdot 3H_2O$, 0.056 mmol; HCOOH, 9 mmol; HCOONa, 1 mmol; H_2O, 2.5 mL; 750 rpm. [b]At 90 °C. [c]At 60 °C [d]The values are averaged from three to six measurements with a reproducibility of ±10%. [e]Volume reached after 3 min. [f]Calculated as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$) × h^{-1}. [g]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ HCOOH}$) × 100. [h]Calculated as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$).

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The precatalysts were formed in situ by using the commercially available $RuCl_3 \cdot 3H_2O$ (22.5 mM solution in water) as catalyst precursor together with at least two equivalents of the appropriate phosphine ligand, using literature reaction conditions,[16] namely, 90 °C with ratios Ru/HCOOH = 1:161 and Ru/ligand = 1:2. In selected cases, the Ru/ligand ratio was increased to 1:4 to verify the effect of a higher ligand concentration on the overall stability and long-term activity of the catalytic systems, for example, upon recycles. Catalytic runs were carried out in the presence of the sulfonated monophosphines (see Chart 1) and selected results are reported in Table 2. In the case of **L1**−**L5**, conversions in the range of 86−93% were obtained within few minutes for the first catalytic cycle (Table 2, entries 1, 4, 7, 10, and 13). As expected by comparison with the known $RuCl_3$/*m*-TPPTS system, a 100% conversion was never reached as the formate salt is not dehydrogenated under these conditions.[16]

In the presence of two equivalents of **L2**, 86.4% conversion was achieved in 5 min, giving the highest TOF = 1668 h^{-1} under these conditions. For all the other monophosphines tested, with the exception of **L1** (Table 2, entry 1), initial TOF values higher than 1500 h^{-1} were calculated after 5 min. The highest conversion (ca. 92.1%) for the first catalytic cycle was observed in the presence of **L5**, which produced 405 mL of gas after only 3 min (initial TOF = 2960 h^{-1}). Gas evolution stopped after 13 min, reaching 94.4% conversion corresponding to a final TOF of 700 h^{-1}.

As for *m*-TPPMS,[17] in the case of **L1**, foam formation was observed upon gas evolution mainly during the first cycle. Interestingly, this behavior was not exhibited by the other monophosphines tested, probably due to a lower surfactant effect and higher water solubility.

In order to compare the activities of our systems with benchmark ligands, some catalytic tests were carried out also with *m*-TPPMS and *m*-TPPTS using our experimental setup (Table 2, entries 16 and 17). During the first cycle, *m*-TPPMS and its biaryl analogue **L1**, reached comparable conversions after 5 min of reaction. Interestingly, the final TOF of the Ru/**L1** system was significantly higher than for Ru/*m*-TPPMS (846 h^{-1} vs 93 h^{-1}, respectively). A similar situation was observed for Ru/*m*-TPPTS and Ru/**L2** systems, with comparable conversions after 5 min but a higher TOF for the latter (Table 2, entries 4 and 17).

The results obtained are in agreement with a higher ligand basicity (see Table 1) than *m*-TPPTS. Recent examples demonstrating that higher basicity and hence a stronger σ-donation of ligands can promote HCOOH dehydrogenation were shown by some of us[23] using methylammonium-substituted aryl phosphines.

In order to check the activities and stabilities of the catalytic systems for repeated runs, recycling experiments were also performed, by adding neat HCOOH (9 mmol) to the reaction mixtures kept at 90 °C at the end of each run, determined by observation that gas evolution had finished. With the exception of **L1** that catalyzed HCOOH dehydrogenation for only three consecutive cycles giving decreasing conversions (63%, TOF = 56 h^{-1} and 68%, TOF = 55 h^{-1} for second and third cycles, respectively), the other four ligands tested, resulted to be active for several cycles. Selected results obtained with **L2** are summarized in Table 3. Eleven consecutive runs were carried out without loss of catalytic activity, obtaining an overall TON of 1506. A slightly slower rate was displayed during the second and third cycles, to reach comparable conversions and TOFs from the fourth cycle on, with average conversions of 86.3%. A similar behavior was observed with **L3**, **L4** and **L5** (see Figures S1, S2, S3 in Supporting Information (SI)), in accordance with literature data obtained with the methylammonium-substituted aryl phosphines.[23]

Table 3. Recycling Tests for HCOOH Dehydrogenation by Using Ru(III)/L2 (1:2) System at 90 °C[a]

cycle	max vol (mL)[*t*(min)][b]	conv %[c]	TON[d]	TOF (h^{-1})[e]
I	380 [5]	86.4	139	1668
II	340 [90]	77.4	124	83
III	360 [60]	81.9	132	132
IV	360 [30]	81.9	132	264
V	380 [15]	86.4	139	556
VI	385 [15]	87.6	141	564
VII	390 [20]	88.7	143	429
VIII	365 [30]	83.0	133	266
IX	380 [15]	86.4	139	556
X	385 [15]	87.6	141	564
XI	390 [15]	88.7	143	572

[a]Reaction conditions: $RuCl_3 \cdot 3H_2O$, 0.056 mmol; **L2**, 0.112 mmol; HCOOH, 9 mmol; HCOONa, 1 mmol; H_2O, 2.5 mL; 750 rpm. For each recycle, 9 mmol of neat HCOOH were added by microsyringe. [b]The values are averaged from three to six measurements with a reproducibility of ±10%. [c]Defined as (mmol $_{\text{produced gas}}$/mmol $_{\text{initial HCOOH}}$) × 100. [d]Calculated as (mmol $_{\text{produced gas}}$/mmol $_{\text{initial Ru}}$). [e]Calculated as (mmol $_{\text{produced gas}}$/mmol $_{\text{initial Ru}}$) × h^{-1}. The number of recycles was determined by time constraint rather than the effective loss in activity of the catalyst.

For all the catalytic tests, at the end of each cycle, aliquots of the gas mixtures were collected in a 10 cm gas cell (KBr disks) and analyzed by FTIR spectroscopy using Wills' method (see the Experimental Section and Figures S6−S9 in SI).[9c] In all cases, the spectra showed only the peaks corresponding to CO_2 with no traces of CO (detection limit of 0.02%), in line with results obtained by some of us with benchmark sulfonated ligands.[16]

Considering the promising results obtained at 90 °C, we decided to explore the effect of temperature on HCOOH dehydrogenation using the most active systems by repeating selected tests at a lower temperature. As reported in Table 2, in all runs performed at 60 °C (entries 2, 5, 8, 11, and 14), fairly similar conversions and TON values were obtained at the end of the first cycle, as expected with a decrease in TOFs (160 h^{-1} vs 1668 h^{-1} in the case of **L2**).

Another important issue to be considered is the possible phosphine degradation during the catalytic runs and upon recycling. This was assessed by taking aliquots of the reaction mixtures after the end of the catalytic runs and carrying out $^{31}P\{^1H\}$ NMR analyses. It was shown that ligand oxidation occurred under these conditions in most cases, as witnessed by the presence of signals in the range 30−40 ppm.[24] Although it is generally accepted that introducing an excess of phosphine at the beginning of the experiments can have a detrimental effect on the rate of dehydrogenation, we decided to verify whether a known excess of ligand could act as a reservoir to stabilize the metal precursor.

Selected experiments were repeated using a Ru/ligand ratio of 1:4 at 90 °C. As shown in Table 2 (entries 3 and 9), conversions and TOFs were comparable to those obtained with a 1:2 ratio in the case of **L1** and **L3**. On the other hand, in the case of **L2**, an improvement of ca. 10% in terms of conversion

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was observed at the end of the first cycle (95.5% vs 86.4%, Table 2, entries 4 and 6), although the reaction rate was significantly slower. No improvements were observed for recycling experiments and, for all the three aryl phosphines considered, not more than four cycles were obtained under these conditions (see Table S1 in SI).

A different behavior was observed with the highly active **L4** and **L5**. With a Ru/ligand = 1:4 ratio, both catalytic systems showed the same initial TOF = 1776 h^{-1} after 5 min, the highest produced (Table 2, entries 12 and 15). Upon recycling (Figure 1), the Ru/**L5** system was active for four cycles maintaining high and constant initial TOFs (5 min) and high conversions (>90%).

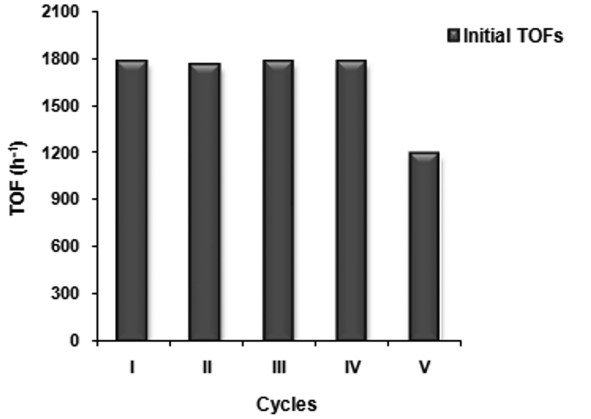

Figure 1. Initial TOFs calculated for conversions after 5 min upon recycling of catalytic system Ru/**L5** (1:4) at 90 °C.

Some biaryl phosphines bearing cycloalkyl instead of aryl groups on P, namely, **L6** and **L7** (Chart 1), were also tested in catalysis under the usual conditions (Table 4). Using a Ru/phosphine = 1:2 ratio, low conversions were observed during the first cycle (61.4% after 5 h for **L6** and 54.6% after 4 h with **L7**, respectively). Although these ligands are more basic than their aryl analogues (Table 1), lower water solubilities and different steric effects could play a detrimental role for these systems. Despite the lower activity in HCOOH dehydrogenation compared to aryl biaryl analogues, the FTIR analysis of the gas mixtures again showed only the signals corresponding to CO_2 (Figure S9 in SI).

Formic Acid Dehydrogenation Catalyzed by $RuCl_3 \cdot 3H_2O$ and Sulfonated Diphosphines. The decomposition of formic acid into H_2 and CO_2 was also investigated using $RuCl_3 \cdot 3H_2O$ in the presence of tetrasulfonated diphosphines $(NaSO_3C_6H_4)_2P(CH_2)_nP(C_6H_4SO_3Na)_2$ (n = 2−4) with different lengths of the carbon atoms chain in the backbone (Chart 2). These ligands have found applications in water phase or biphasic catalysis due to their chelating properties,[21] but to the best of our knowledge they have never been tested for FA dehydrogenation. Selected results are summarized in Table 5.

In the case of **L8** at 90 °C, conversions of ca. 92% were obtained in the first cycle both using a 1:1 or 1:2 ratio Ru/ligand, albeit at different rates (TOF = 226 h^{-1} and 115 h^{-1}, respectively), as shown in Figure 2. The recycling tests gave comparable results both with one and two equivalents of **L8**, providing a final TON after six cycles of 770 and 841, respectively (see Table S2 in SI). A different behavior was observed in the case of **L9** and **L10** ligands, bearing backbones with shorter alkyl chains. At Ru/L = 1:1 ratio, lower conversions (less than 80%) and turnover frequencies were achieved during the first cycle (Figure 2). Under these conditions, both systems remained active for only three cycles, giving a final TON of 388 for **L9** and 342 for **L10**, respectively. Interestingly, using Ru/L = 1:2 ratios, both catalytic systems gave ca. 89% conversions at comparable rates during the first cycle but continued to be active for several recycles. In particular, with **L9** (see Figure S4 in SI) more than seven consecutive cycles were run, resulting in conversions higher than 80% and a final TON of 943. For **L10**, more than six catalytic cycles were possible with constant conversions and TOFs and a final TON of 804.

On the basis of these experiments, it can be concluded that the use of Ru/diphosphines in 1:2 ratios gives high conversions and TONs but lower TOFs than the corresponding Ru/aryl-biarylphosphine analogues, so a compromise between pre-catalyst stability and high reaction rates must be considered in the presence of this series of ligands.

Finally, in order to exclude the formation of soluble ruthenium colloidal particles, mercury poisoning test reactions were performed in the presence of **L2** and **L8**. As illustrated in Table 6, when some drops of Hg(0) were added to catalytic tests using Ru/**L2** = 1:2 and Ru/**L8** =1:1 at 90 °C, comparable conversions and rates as observed without the addition of mercury were obtained, suggesting the absence of active metal particles in solution.

Formic Acid Dehydrogenation Using $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ as Ru(II) Precursor. In a second series of experiments, the catalytic performances were investigated using a preformed Ru(II) complex, namely $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$, instead of $RuCl_3 \cdot 3H_2O$. This Ru(II) η^6-arene dimer has been previously tested by Beller and co-workers as catalytic precursor for hydrogen generation from neat $HCOOH/NEt_3$ (5:2) adducts, obtaining good results at 40 °C in the presence of PPh_3 (TON = 452 after 3 h) and dppe (dppe =1,2-bis(diphenylphosphino)ethane) as stabilizing ligands (TON = 1376 after 3 h).[12b] Further studies showed that the catalytic activity can be improved using a $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$/ligand = 1:6 ratio in the presence of the adduct $HCOOH/NMe_2(n\text{-}C_6H_{11})$ (5:4).[25]

Table 4. HCOOH Dehydrogenation with Ru/Alkyl-Biarylphosphines at 90 °C (First Catalytic Cycle)[a]

phosphine	Ru/L	max vol (mL) [t(min)][b]	conv %[c]	TON[d]	TOF (h^{-1})[e]
L6	1/2	320 [300]	72.8	117	23
L6	1/4	150 [250]	34.1	55	13
L7	1/2	225 [240]	54.6	82	20
L7	1/4	275 [240]	62.5	100	25

[a]Reaction conditions: $RuCl_3 \cdot 3H_2O$, 0.056 mmol; HCOOH, 9 mmol; HCOONa, 1 mmol; H_2O, 2.5 mL; 90 °C; 750 rpm. [b]The values are averaged from three to six measurements with a reproducibility of ±10%. [c]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ HCOOH}$) × 100. [d]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$). [e]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$) × h^{-1}.

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Table 5. HCOOH Dehydrogenation with Ru/Diphosphines at 90 °C (First Catalytic Cycle) Using Ru/L = 1:1 and 1:2[a]

phosphine	Ru/L	max vol (mL) [t(min)][b]	conv %[c]	TON[d]	TOF (h^{-1})[e]
L8 (DPPBTS)	1/1	413 [40]	93.9	151	226
L8 (DPPBTS)	1/2	395 [75]	89.9	144	115
L9 (DPPPTS)	1/1	335 [85]	76.2	122	86
L9 (DPPPTS)	1/2	400 [45]	91.0	146	195
L10 (DPPETS)	1/1	345 [105]	78.5	126	72
L10 (DPPETS)	1/2	390 [40]	88.7	143	214

[a]Reaction conditions: $RuCl_3 \cdot 3H_2O$, 0.056 mmol; HCOOH, 9 mmol; HCOONa, 1 mmol; H_2O, 2.5 mL; 90 °C; 750 rpm. [b]The values are averaged from three to six measurements with a reproducibility of ±10%. [c]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ HCOOH}$) × 100. [d]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$). [e]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$) × h^{-1}.

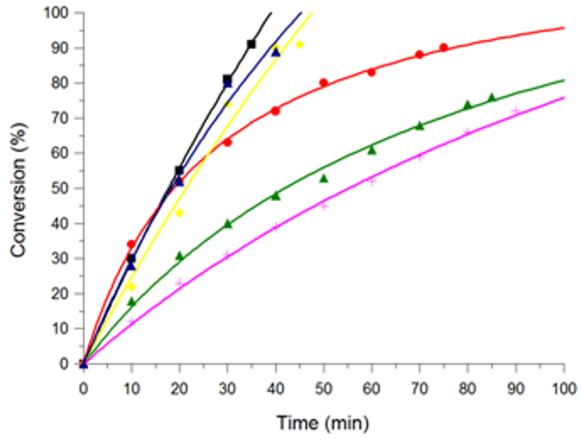

Figure 2. HCOOH dehydrogenation reaction profiles (conversion % vs time) for the first cycle runs using Ru/diphosphines at different Ru/L ratios, at 90 °C. Legenda: Ru/**L8** = 1:1 (black squares), Ru/**L8** = 1:2 (red circles), Ru/**L9** = 1:1 (green triangles), Ru/**L9** = 1:2 (yellow circles), Ru/L**10** = 1:1 (pink crosses), Ru/**L10** = 1:2 (blue triangles). The trend line is shown as a guide and should not be intended as a mathematical fitting of the data.

Table 6. Comparison of Selected Catalytic Tests and Recycling with and without Hg(0)[a]

	max vol mL [t(min)][d]		max vol mL [t(min)][d]	
cycle	[Ru]/**L2**[b]	[Ru]/**L2**/Hg[b]	[Ru]/**L8**[c]	[Ru]/**L8**/Hg[c]
I	380 [5]	390 [5]	400 [35]	395 [35]
II	340 [90]	345 [90]	360 [45]	390 [45]
III	360 [60]	325 [120]	340 [60]	385 [60]
IV	360 [30]	380 [30]	360 [60]	380 [60]
V	380 [15]	390 [15]	375 [60]	385 [60]

[a]Reaction conditions: $RuCl_3 \cdot 3H_2O$, 0.056 mmol; HCOOH, 9 mmol; HCOONa, 1 mmol; H_2O, 2.5 mL; 750 rpm; 90 °C. [b]Ru/**L2** = 1:2. [c]Ru/**L8** = 1:1. [d]The values are averaged from three to six measurements with a reproducibility of ±10%.

Thus, in order to compare the effect of the choice of this metal precursor in water-phase FA dehydrogenation, selected sulfonated ligands were tested together with $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ at 90 °C using a Ru/ligand = 1:2 ratio (monophosphines) and 1:1 ratio (diphosphines), keeping the other reaction parameters constant. Among the monophosphine ligands, catalytic tests were performed with **L1**, **L2**, **L4**, and **L5**. As reported in Table 7, although ligands **L1**, **L4** and **L5** gave similar conversions at the same rate in the first cycle (entries 1, 3, and 4), **L2** showed also with this metal precursor the highest final TOF value (429 h^{-1}), giving a 88.7% HCOOH conversion in 20 min.

By comparing these results with those obtained with $RuCl_3 \cdot 3H_2O$ under the same reaction conditions (for comparison, see Table 2), it is observed that during the first cycle all systems gave almost the same conversions and TONs, but lower final TOFs were obtained with the Ru(II) precursor. During recycling experiments, all Ru(II)/monophosphine systems showed a constant activity from the first cycle (Figure 3), suggesting, as expected, that the active species are formed efficiently from the beginning, without the need for initial metal reduction from Ru(III) to Ru(II). The two systems containing **L2** and **L4** ligands were more active, with more than seven cycles obtained (TON > 1000 after seven cycles).

Among bidentate ligands, **L8** and **L10** were selected and used in 1:1 ratio with $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ at 90 °C, obtaining similar data both in the first cycle (Table 8, entries 5 and 6) and in the recycles. Although with **L8** comparable conversions and TONs were obtained with both Ru(III) and Ru(II) precursors, a remarkable difference was observed for the **L10** ligand. Using $RuCl_3$, two equivalents per ruthenium atom of this diphosphine were needed to have a satisfactory activity, whereas with $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ good results were achieved, both in the first cycle and during recycles, with one equivalent of the ligand per ruthenium atom (Table 8, entry 6), with slightly better final conversions and TONs than those observed with **L8**. This observation is in agreement with data reported by Beller on FA/amine dehydrogenation using the $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$/diphosphine systems where the presence of longer carbon chains in the bidentate ligand led to a decrease in the catalytic activity.[12b] The FTIR spectra of gas mixtures run at the end of each experiment showed again the presence of peaks as a result of CO_2 only.

$[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ was also tested in association with *m*-TPPTS and *m*-TPPMS, as to the best of our knowledge, this combination has not yet been described. Both systems showed comparable results of conversion in the first catalytic cycle (Table 7, entries 7 and 8), although the latter ligand was less active in recycles (see Figure S5 in SI). Finally, a blank test was performed with $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ in the absence of phosphines (entry 9). In this run, ca. 90% conversion was obtained in the first cycle, but the reaction was very slow (6 h, TOF = 24 h^{-1}). Furthermore, a black precipitate was formed at the end of the first cycle, and the catalytic activity dropped severely already in the first recycle (6.8% conversion after 60 min). Although a detailed study of the mechanism active in the presence of this phosphine-free complex was beyond the purpose of the present study, it cannot be excluded that different Ru-arene active species are formed during the catalytic runs under these conditions, perhaps involving polymetallic assemblies such as Ru-arene hydrido clusters (vide infra),[26] or (in the case of arene decoordination at higher temperatures)

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Table 7. Results of Catalytic HCOOH Dehydrogenation (First Cycle) in the Presence of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ at 90 °C[a]

entry	ligand	vol (mL) after 5 min[d]	TOF (h^{-1}) after 5 min[e]	max vol (mL) [t(min)]	conv %[f]	TON[g]	TOF (h^{-1})[e]	TON tot. [no. cycles][g]
1[b]	**L1**	288	1264	415 [60]	94.4	152	152	761 [5]
2[b]	**L2**	320	1404	390 [20]	88.7	143	429	1020 [7]
3[b]	**L4**	140	612	400 [60]	91.0	146	146	1027 [7]
4[b]	**L5**	380	1668	395 [30]	89.9	144	288	578 [4]
5[c]	**L8**	125	552	405 [60]	92.1	148	148	712 [5]
6[c]	**L10**	47	206	412 [67]	93.7	151	135	738 [5]
7[b]	**m-TPPTS**	160	696	395 [60]	89.9	144	144	730 [5]
8[b]	**m-TPPMS**	380	1668	400 [30]	91.0	146	292	428 [3]
9[b]	**no ligand**	50	216	395 [360]	89.9	144	24	155 [2]

[a]Conditions: [Ru]/HCOOH = 1:161; 90 °C. [b][Ru], 0.028 mmol; monophosphine, 0.112 mmol. [c][Ru], 0.028 mmol; diphosphine, 0.056 mmol. [d]The values are averaged from three to six measurements with a reproducibility of ±10%. [e]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$) × h^{-1}. [f]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ HCOOH}$) × 100. [g]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$). The number of recycles was determined by time constraint rather than the effective loss in activity of the catalytic system.

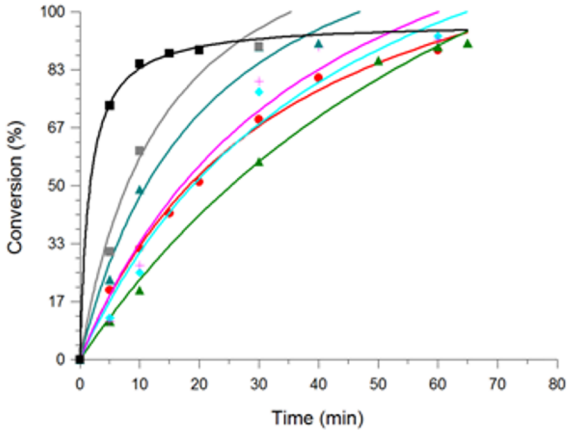

Figure 3. Reaction profiles for HCOOH dehydrogenation recycling experiments (conversion % vs time) using $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$/**L2** = 1:4 molar ratio at 90 °C. Cycle I (black squares), II (red circles), III (green triangles), IV (light blue diamonds), V (pink crosses), VI (dark blue triangles), VII (gray squares). The trend line is shown as a guide and should not be intended as a mathematical fitting of the data.

Table 8. Results of Catalytic HCOOH Dehydrogenation and Recycles in the Presence of $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (2) at 90 °C[a]

cycle	max vol (mL) [t(min)][b]	conv %[c]	TON[c]	TOF (h^{-1})[d]
I	190 [70]	86.2	139	119
II	185 [50]	83.9	135	162
III	195 [30]	88.5	143	286
IV	200 [30]	90.8	146	292
V	205 [20]	93.1	150	450
VI	200 [20]	90.8	146	438
VII	195 [20]	88.5	143	429

[a]Reaction conditions: $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$, 0.028 mmol; HCOOH, 4.51 mmol; HCOONa, 0.50 mmol; H_2O, 2 mL; 750 rpm. For each recycle, 4.51 mmol of neat HCOOH were added by microsyringe. Expected volume for 100% conversion, 0.220 mL. [b]The values are averaged from three to six measurements with a reproducibility of ±10%. [c]Defined as (mmol $_{produced\ gas}$/mmol $_{initial\ HCOOH}$) × 100. [c]Calculated as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$). [d]Calculated as (mmol $_{produced\ gas}$/mmol $_{initial\ Ru}$) × h^{-1}.

formato-bridged dimeric species as described by other authors.[9,27]

Complex $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (**2**) was independently synthesized (vide infra) and tested as an isolated Ru(II)-catalyst for FA dehydrogenation. The results summarized in Table 8 showed that **2** was active for several cycles giving an average 89% conversion and a final TON of 1002 after seven cycles. This value is very similar to that obtained with $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$/**L2** in situ system under the same reaction conditions (total TON = 1020 after seven cycles, see Table S3 in SI); however, preformed complex **2** gave higher TOFs during recycling.

Synthesis of $[RuCl_2(MBMS)_2]_2$ (1) and $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (2). The syntheses of defined Ru complexes to be used as precatalysts instead of in situ formation were attempted following various methods.

On the basis of the procedures reported in literature for *m*-TPPMS,[19c,28] $[RuCl_2(PPh_3)_3]$ and **L1** (2.4 equiv) were reacted in THF under reflux conditions. After 4 h, a brown precipitate was filtered off, dissolved in CD_3OD, and analyzed by $^{31}P\{^1H\}$ NMR showing a broad singlet at 53.8 ppm in ca. 50% NMR purity, the rest being free phosphine oxide, at a chemical shift value compatible with a species such as $[RuCl_2(MBMS)_2]_2$ (**1**).[28] The complex was found to be poorly stable in solution, giving undefined decomposition products when left in D_2O for 30 min, as observed by $^{31}P\{^1H\}$ NMR, and therefore, it was not considered further for catalytic tests.

The reaction of phosphine MBTS (**L2**) with $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (**L2**: Ru = 2) gave complex $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (**2**) in 83% purity as a microcrystalline powder, which was sufficiently stable both as a solid and in water solution and was used as an isolated catalyst (see Table 8).

Complex **2** was also converted selectively to the corresponding monohydride $[Ru(\eta^6\text{-}C_6H_6)H(MBTS)_2]Cl$ (**3**) by two independent reactions. In one case, it was dissolved in D_2O and pressurized with 40 bar H_2. After 3 h at 60 °C, the $^{31}P\{^1H\}$ and ^1H NMR spectra showed a singlet at 53.5 ppm and a triplet at −9.41 ppm ($^2J_{HP}$ = 36 Hz), respectively. Furthermore, in the positive range of chemical shifts of ^1H NMR spectrum, a singlet at 5.62 ppm suggested that benzene was still coordinated to the metal.[29] The same ^{31}P and ^1H NMR signals were also obtained by reacting **2** (25 mg, 0.016 mmol) with an excess of HCOONa (11 mg, 0.16 mmol) in degassed D_2O (0.8 mL). After stirring for 2 h at 60 °C, the reaction mixture was analyzed by $^{31}P\{^1H\}$ NMR and ^1H NMR, showing again the signals corresponding to **3** as shown in Figure 4.

Mechanistic Studies by High-Pressure HPNMR Techniques. In order to identify the main species formed in situ and the possible intermediates involved in the catalytic cycle, NMR studies were carried out using HPNMR techniques.

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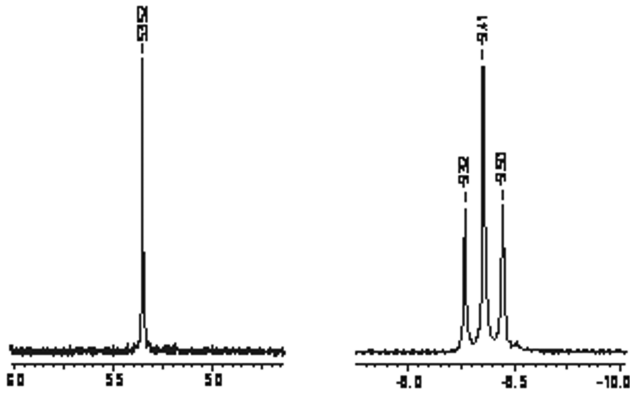

Figure 4. $^{31}P\{^{1}H\}$ NMR (161.97 MHz, left) and ^{1}H NMR (400.13 MHz, negative range, right) spectra of the monohydride $[RuH(\eta^6\text{-}C_6H_6)(MBTS)_2]^+$ (**3**).

These mechanistic studies have been reported in detail for Ru/*m*-TPPTS systems, and a reaction mechanism involving two competing cycles has been proposed.[16b] By considering the structural analogy with *m*-TPPTS and the higher purity of ligand, phosphine **L2** was chosen for these experiments with both Ru(III) and Ru(II) precursors.

At first, a HPNMR experiment was carried out as follows. An aqueous solution containing $RuCl_3{\cdot}3H_2O$ and **L2** (1:2 ratio) was prepared under nitrogen atmosphere and transferred into a 10 mL medium-pressure sapphire NMR tube. At room temperature, the first $^{31}P\{^{1}H\}$ NMR spectrum showed the peaks corresponding to the free ligand (−6.9 ppm), phosphine oxide (33.5 ppm), and a new species characterized by a singlet at 55.0 ppm. In analogy with data obtained under identical conditions with *m*-TPPTS (54.0 ppm),[30] we attribute this signal to the formation of complex *trans*-$[Ru(MBTS)_2(H_2O)_4]^{2+}$ (**4**). In the TPPTS-based system, complexes $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$[31] and $RuCl_2(TPPTS)_3$[32] were detected in solution at chemical shift values close to 57.0 ppm, albeit these species were obtained in slightly different reaction conditions.

Subsequently, the NMR tube was pressurized with 100 bar of H_2 and heated to 70 °C. The $^{31}P\{^{1}H\}$ NMR pattern changed, showing two broad singlets at 57.8 (ca. 23%) and 52.4 ppm (ca. 77%), as shown in Figure 5a. In the corresponding ^{1}H NMR spectrum, two triplets at −10.48 ppm ($^{2}J_{HP}$= 36 Hz, ca. 77%) and −10.88 ppm ($^{2}J_{HP}$= 36 Hz, ca. 23%) were observed, turning into two singlets by ^{31}P decoupling (Figure 5b,c). Again, it is possible to compare these values with literature data.[33] It was reported that *cis*- and *trans*-$[RuH(TPPTS)_2(H_2O)_3]^+$ gave two $^{31}P\{^{1}H\}$ NMR peaks at 51 (*cis*) and 55 ppm (*trans*) with corresponding triplets in the ^{1}H NMR spectrum at −9.7 (*cis*) and −9.6 ppm (*trans*), both with a $^{2}J_{HP}$ = 38 Hz. Therefore, we attribute the signals observed to the complexes *cis*- and *trans*-$[RuH(MBTS)_2(H_2O)_3]^+$(**5**). In particular, the most abundant isomer (δ_P 52.4; δ_H −10.48) resulted to be stable in solution for several hours both under hydrogen pressure and upon pressure release.

Subsequently, $H^{13}COONa$ (3 equiv respect to Ru) was added to the NMR tube containing **5**. In ^{31}P and ^{1}H NMR spectra, the signal due to **5** was still present as the major species, accompanied by a series of minor signals in the range δ_P 73.4−70.1 ppm. The corresponding $^{13}C\{^{1}H\}$ NMR spectrum contained small signals at ca. 201 and 172 ppm. The small broad peaks in the range δ_P 56.0−57.6 and the two doublets at δ_C 172.96 (J_{HC} = 208 Hz) and 172.80 (J_{HC} = 205 Hz) can likely be attributed, in analogy with the TPPTS system,[16b] to the formation of *cis*- and *trans*-$[Ru(MBTS)_2(\eta^1\text{-}O\text{-}O_2CH)(H_2O)_3]^+$ (**6**) by ligand exchange from complex **4** still present in solution. By further heating to 70 °C, signals due to complex **5** were still visible in the $^{31}P\{^{1}H\}$ NMR spectrum, suggesting high stability of such species. The proposed geometries of the main species based on NMR data are shown in Chart 3.

An HPNMR experiment under quasi-catalytic conditions in the presence of Ru(III)/**L2** was then carried out. To an aqueous solution containing $RuCl_3{\cdot}3H_2O$/**L2** (1:2) and $H^{13}COONa$ (1 equiv), $H^{13}COOH$ (10 equiv) was added, and the reaction was monitored by variable-temperature HPNMR. After heating to 80 °C, complex **5**, already observed in the previous experiment, was formed in a minor amount during the reaction. The main species detected in solution were characterized by a broad peak at 43.4 ppm in $^{31}P\{^{1}H\}$ NMR, a signal at −13.87 ppm in ^{1}H NMR, and a series of signals in the range 198.07−203.06 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum. A

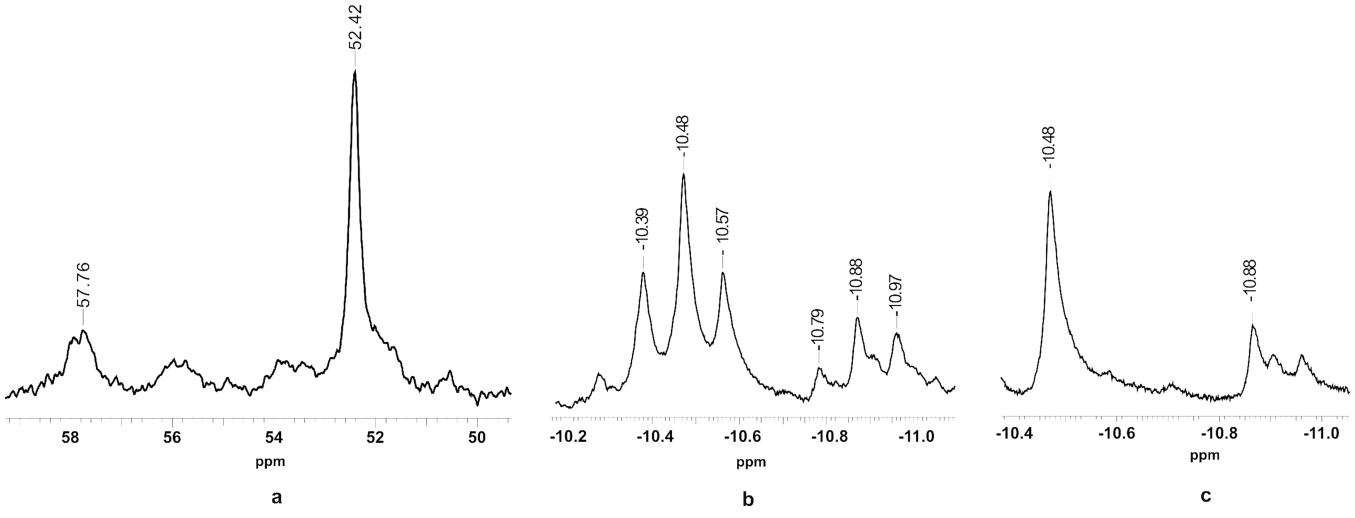

Figure 5. (a) Room temperature $^{31}P\{^{1}H\}$ HPNMR (161.97 MHz), (b) ^{1}H HPNMR water suppression (400.13 MHz), and (c) $^{1}H\{^{31}P\}$ HPNMR water suppression (400.13 MHz) spectra of *cis*- and *trans*-$[RuH(MBTS)_2(H_2O)_3]^+$ (**5**).

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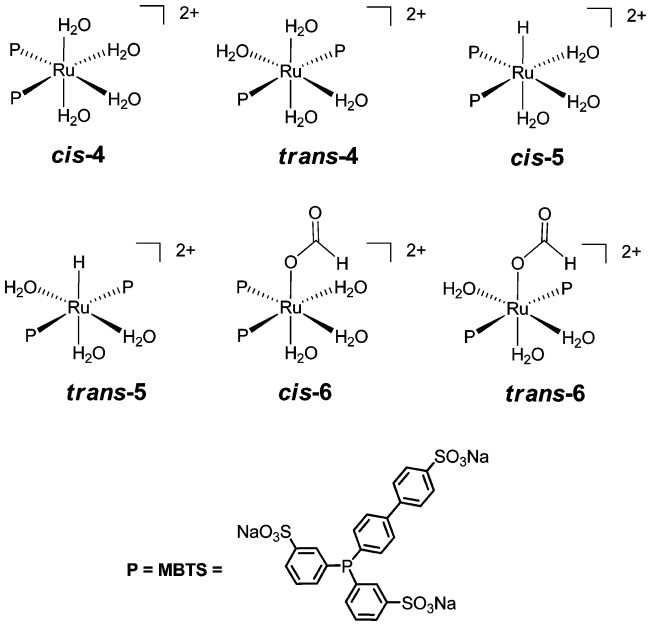
Chart 3. Proposed Geometries for Complexes 4−6



set of similar experiments using TPPTS was reported by some of us[16b] and showed the formation of complexes with comparable chemical shift values, which were tentatively attributed to $[RuH(CO_2)(TPPTS)_2(H_2O)_2]^+$. In that system, it was proposed that such a species is in equilibrium with the more stable complex $[RuH(HCO_3)(TPPTS)_2(H_2O)_2]$, whose concentration increases after 40% conversion of initial HCOOH and reaches a maximum at the end of the catalytic run (basic pH). Although we do not have enough evidence for a conclusive attribution for the NMR pattern observed under these conditions, and we cannot in principle exclude the formation of traces of Ru-carbonyl species described by other authors,[9,27] our proposal agrees with data reported for the closely structurally related Ru/TPPTS system.

HPNMR experiments were also run in the presence of **L2** and $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ as metal precursor. In a first experiment, $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ and **L2** (1:4) were dissolved in water, and the solution was placed in an NMR sapphire tube. At room temperature, the $^{31}P\{^1H\}$ NMR showed the formation of complex $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (**2**, in 1:5 ratio with remaining free ligand), as confirmed by the presence of a singlet at 22.3 ppm and comparison with the value observed from the independent synthesis reported above. The tube was then pressurized with H_2 gas (100 bar) at room temperature, and a new species was formed as evidenced by a broad signal at 52.7 ppm in $^{31}P\{^1H\}$ NMR. The corresponding ^1H NMR spectrum displayed an intense broad signal at −8.56 ppm, a value expected upon formation of ruthenium hydrido-clusters $[Ru_4H_4(\eta^6\text{-}C_6H_6)_4]^{2+}$ and $[Ru_4H_6(\eta^6\text{-}C_6H_6)_4]^{2+}$ as described earlier by Süss-Fink,[26] together with a less intense triplet at −10.22 ppm ($^2J_{HP}$ = 36 Hz). Upon increasing the temperature to 70 °C, the former signal disappeared with a corresponding increase of the latter, reaching a 1:8 ratio with **2**. In the corresponding $^{31}P\{^1H\}$ NMR spectrum, the signal at 52.7 ppm was the major species observed. On the basis of NMR data for *m*-TPPTS analogue,[34] and confirmed by independent synthesis (vide infra), these signals were attributed to the monohydride cationic complex $[RuH(\eta^6\text{-}C_6H_6)(MBTS)_2]^+$ (**3**). The presence of Ru-coordinated η^6-benzene was confirmed by a singlet at 4.94 ppm in the ^1H NMR spectrum. After depressurization and addition of $H^{13}COONa$ (3 equiv with respect to Ru), the $^{31}P\{^1H\}$ NMR pattern showed the disappearance of the signal due to **2** and the presence of **3** as main species in solution. Another small signal at 43.2 ppm was also present. Interestingly, the same signal was observed as the only species present in the $^{31}P\{^1H\}$ NMR spectra obtained by analyzing aliquots of the solutions taken after recycling tests listed in Table 8. The corresponding ^1H NMR spectrum showed a triplet at −15.12 ppm ($^2J_{HP}$ = 20.01 Hz) and no signals due to Ru-coordinated benzene. This suggests that under catalytic conditions and recycling, the arene ligand is released, giving Ru-hydrido species similar to those observed in the case of systems using Ru(III) precursors.

CONCLUSIONS

In this study, a series of sulfonated biaryl monophosphines and aryl diphosphines were used as efficient stabilizers for aqueous-phase formic acid dehydrogenation to H_2 + CO_2 gas mixtures. Monodentate aryl-biaryl phosphines gave comparable overall TONs to *m*-TPPMS and *m*-TPPTS under the same experimental conditions. The choice of Ru/L ratios (1:2 vs 1:4) did not affect significantly the catalytic performances. For most ligands, after a first fast initial run (highest TOF), a second run gave a decrease of reaction rate, related to the reduction from Ru(III) to Ru(II) active species which once formed gave again fast reactions (from third cycle). Good recycling capacities of these catalytic systems were also assessed (up to 11 consecutive recharges for **L2**). The aryl diphosphines tested showed high stability of the catalytic system, reflected in slightly slower initial reaction rates. Cycloalkyl groups on phosphorus gave less stable systems which in turn resulted in worse catalytic performance. Both Ru(III) salt and Ru(II) arene complex were used as metal precursors and proved to be efficient in the catalytic reaction studied. Mechanistic studies by HPNMR experiments, although complicated by the presence of many species formed under the conditions tested, highlighted the formation of stable water-soluble Ru-hydrido species mirroring previous studies carried out with aryl sulfonated phosphine analogues.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under an inert atmosphere of dry nitrogen by standard Schlenk techniques unless otherwise noted. Doubly distilled water was used after deoxygenation through a stream of nitrogen for several hours. $RuCl_3{\cdot}3H_2O$ (Pressure Chemicals 99.5%,), formic acid (Sigma-Aldrich, 98−100%) and sodium formate (Sigma-Aldrich, 99%) were bought from commercial suppliers and used without further purification. $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ was prepared as reported in the literature.[35] Sulfonated monophosphines[20a,b] and diphosphines were synthesized according to literature procedures.[21] HPNMR experiments were performed in 10 mm medium-pressure sapphire tubes, and NMR spectra were run on a Bruker Avance DRX 400 MHz spectrometer. H_2 (99.95%) and CO_2 (99.9%) were acquired from Carbagas-CH; enriched $H^{13}COOH$ and $H^{13}COONa$, (99% in ^{13}C) were obtained from Cambridge Isotope Laboratories. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance II 300 spectrometer (operating at 300.13, 75.47, and 121.50 MHz, respectively) and on a Bruker Avance II 400 spectrometer (operating at 400.13,

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100.61, and 161.98 MHz, respectively) at room temperature. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). Electrospray mass spectrometry (ESI-MS) analysis was measured on a LCQ Orbitrap mass spectrometer (ThermoFisher, San Jose, CA, U.S.A.) equipped with a conventional ESI source by direct injection of the sample solution and are reported in the form m/z (intensity relative to base = 100). Infrared spectra of gas mixtures were measured on a PerkinElmer FT-IR Spectrum BX II instrument using a 10 cm gas phase cell equipped with KBr windows.

Formic Acid Catalytic Dehydrogenation Tests. All catalytic tests were performed under an inert atmosphere of nitrogen in a 25 mL glass jacketed reactor heated by external liquid circulation. The three-necked round bottomed flask was connected to a reflux condenser, which was in turn connected to a setup of two manuals burets to measure the amount of gas generated during the catalytic reaction. In a typical experiment, the flask reactor was charged under a nitrogen atmosphere with either $RuCl_3{\cdot}3H_2O$ (14.7 mg, 0.056 mmol) or $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (14.0 mg, 0.028 mmol), the water-soluble phosphine (0.112 or 0.224 mmol, depending on the Ru/ligand ratio) and sodium formate (68 mg, 1 mmol). Degassed H_2O (2.5 mL) was then added by syringe, and the resulting solution was heated to the desired temperature and kept stirring at ca. 750 rpm. Pure HCOOH (0.34 mL, 9.00 mmol) was then added, and the course of dehydrogenation reaction was monitored via gas evolution. Aliquots of gas mixtures were collected for FTIR analyses in a 10 cm gas phase cell (KBr windows). For recycling experiments, when no more gas generation was observed, the apparatus was flushed with nitrogen to remove any traces of H_2 and CO_2, then neat HCOOH (0.34 mL, 9.00 mmol) was added by syringe, and a new run was started. In the case of catalytic tests performed with $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (**2**), the procedures described above were followed by maintaining the same Ru/HCOOH ratio (in details: **2**, 50 mg, 0.028 mmol; HCOOH, 0.17 mL, 4.51 mmol; HCOONa, 34.1 mg, 0.50 mmol). The values of % conversion summarized in tables were calculated from gas volume evolution as the average of three or four measurements with a reproducibility of ±10%.

HPNMR Mechanistic Experiments. *Method A.* A typical experiment to explore the reactivity of Ru/L under hydrogen pressure and further reaction with sodium formate is hereby described. In a Schlenk tube, $RuCl_3{\cdot}3H_2O$ (38.7 mg, 0.148 mmol) or $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (37.0 mg, 0.074 mmol) and the water-soluble phosphine **L2** (190.8 mg, 0.296 mmol) were dissolved in degassed water (2 mL) under a nitrogen atmosphere. The resulting red solution was transferred to a 10 mm medium-pressure sapphire NMR tube and pressurized with 100 bar of H_2. HPNMR experiments were run at several temperatures by heating the sample directly in the NMR probe. Before the addition of $H^{13}COONa$ (30.6 mg, 0.444 mmol), the solution was cooled to room temperature and depressurized, then $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ spectra were taken at different temperatures.

Method B. A typical experiment to test the behavior of Ru/L systems under quasi-catalytic conditions of FA dehydrogenation is hereby described. In a Schlenk tube, $RuCl_3{\cdot}3H_2O$ (67.9 mg, 0.26 mmol), **L2** (335.1 mg, 0.52 mmol), and $H^{13}COONa$ (20 mg, 0.29 mmol) were dissolved in H_2O (2 mL). The obtained solution was transferred to a 10 mm sapphire NMR tube, and $H^{13}COOH$ (0.1 mL, 2.6 mmol) was added by syringe. The reaction was monitored by NMR taking $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ spectra at different temperatures.

Synthesis of $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]Cl$ (2). The method described by Tokunaga et al.[36] for $[Ru(\eta^6\text{-}C_6H_6)Cl(TPPTS)_2]Cl$ was adapted for this synthesis. In a three-necked flask with reflux condenser, under an inert atmosphere of nitrogen, $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (30 mg, 0.06 mmol) and MBTS (**L2**, 154.7 mg, 0.24 mmol) were dissolved in degassed H_2O (12 mL). When the temperature reached 90 °C, both solids were completely dissolved, and the reaction solution was stirred at this temperature for 1 h. The solvent was then removed under reduced pressure, yielding 120 mg of a crystalline brown powder (83% pure on the basis of $^{31}P\{^1H\}$ NMR). $^{31}P\{^1H\}$ NMR (161.97 MHz, D_2O, 20 °C): δ (ppm) 23.2 (s). ^1H NMR (400.13 MHz, D_2O, 20 °C): δ 8.31−7.43 (m, 32 H, Ar-*H*); 5.86 (s, 6H, C_6H_6). $^{13}C\{^1H\}$ NMR (75.47 MHz, D_2O, 20 °C): δ 143.33 (Ar-*C*), 143.04 (Ar-*C*), 142.02 (Ar-*C*), 141.88 (Ar-*C*), 136.74 (Ar-*C*), 136.34 (Ar-*C*), 134.45 (Ar-*C*), 131.52 (Ar-*C*), 130.63 (Ar-*C*), 128.48 (Ar-*C*), 128.16 (Ar-*C*), 127.56 (Ar-*C*), 127.18 (Ar-*C*), 126.07 (Ar-*C*), 96.88 (η^6-C_6H_6). MS (nESI$^+$): m/z 1502.67 (100) $[Ru(\eta^6\text{-}C_6H_6)Cl(MBTS)_2]^+$.

■ ASSOCIATED CONTENT

Supporting Information

General methods and materials; additional tables and reaction profiles for FA dehydrogenation reactions; and FT-IR spectra of gas mixtures analyses. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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