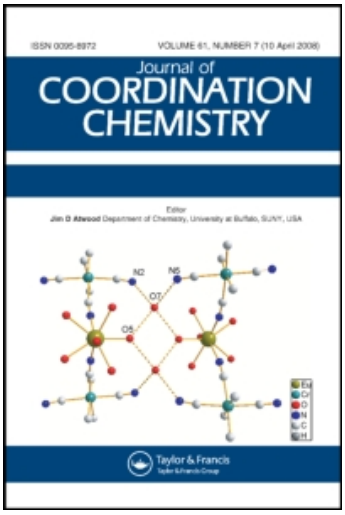


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Influence of water-soluble sulfonated phosphine ligands on ruthenium catalyzed generation of hydrogen from formic acid

Weijia Gan[a]; Céline Fellay[a]; Paul J. Dyson[a]; Gábor Laurenczy[a]
[a] Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

First published on: 14 June 2010

To cite this Article Gan, Weijia , Fellay, Céline , Dyson, Paul J. and Laurenczy, Gábor(2010) 'Influence of water-soluble sulfonated phosphine ligands on ruthenium catalyzed generation of hydrogen from formic acid', Journal of Coordination Chemistry, 63: 14, 2685 — 2694, First published on: 14 June 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.492470
URL: http://dx.doi.org/10.1080/00958972.2010.492470

Journal of Coordination Chemistry
Vol. 63, Nos. 14–16, 20 July–20 August 2010, 2685–2694

Taylor & Francis
Taylor & Francis Group

Influence of water-soluble sulfonated phosphine ligands on ruthenium catalyzed generation of hydrogen from formic acid†

WEIJIA GAN, CÉLINE FELLAY, PAUL J. DYSON and GÁBOR LAURENCZY*

Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

(*Received 30 January 2010; in final form 23 March 2010*)

Hydrogen can be generated from formic acid in aqueous phase homogeneous catalytic reactions using ruthenium catalysts with water-soluble phosphine ligands. A comparison of tri-, di-, and mono-sulfonato triphenylphosphine, disulfonato diphenyl-alkyl-phosphines (Ph_2PR; R=Me, *n*-Bu, Cyp), and monosulfonato phenyl-dialkyl-phosphines ($PhPR_2$; R=Me, Cyp) is described. Using two equivalents of water-soluble phosphine per ruthenium ion, significant turnover frequencies are observed for the decomposition of formic acid. The influence of basicity, water solubility (related to the structures and behavior in aqueous solution), electronic properties, and steric effects of the phosphines on the rate of the hydrogen generation are investigated.

Keywords: Hydrogen storage; Formic acid decomposition; Homogeneous catalysis; Water-soluble sulfonato phosphines; Ruthenium

1. Introduction

Hydrogen is attracting increasing attention as an important alternative energy carrier, for both environmental and economic reasons, and efficient energy conversion can be achieved when combined with fuel cells [1]. However, the actual use of hydrogen for mobile applications is still limited mainly due to the storage and delivery problems. Formic acid (HCOOH), which contains 53 g hydrogen per liter (or 4.4 w%), and its conjugate base, the formate salt ($HCOO^-$), are well-known hydrogen sources and potential hydrogen-storage materials [2]. Dehydrogenation of formic acid (equation (1)) generates hydrogen under catalytic conditions, while carbon monoxide, which causes catalyst poisoning, can be produced by thermally driven dehydration at elevated temperatures (equation (2)).

$$HCOOH \rightarrow H_2 + CO_2 \quad (1)$$

$$HCOOH \rightarrow H_2O + CO \quad (2)$$

*Corresponding author. Email: gabor.laurenczy@epfl.ch
†Dedicated to Professor Rudi van Eldik on the occasion of his 65th birthday in recognition of his seminal contributions to the field of coordination chemistry.

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.492470

Formic acid decomposition into H_2 and CO_2 has been extensively studied under heterogeneous [3–6] and homogeneous [7–10] conditions during the past 40 years. Recently, considerable progress has been made in this area; new catalytic systems have been developed, based on the ruthenium salts with the water-soluble *m*-trisulfonato triphenylphosphine (*m*TPPTS) ligand [11–14], which selectively decompose HCOOH into carbon monoxide free hydrogen and carbon dioxide in a very wide pressure range. Beller *et al*. [15–18] have also found that a number of ruthenium complexes with arene and phosphine ligands catalyze the selective decomposition of HCOOH into H_2 and CO_2. These results on homogeneous catalytic formic acid decomposition reactions are considered as a breakthrough in hydrogen storage and delivery, making this system suitable for practical applications [19, 20]. Wills *et al*. [21] suggested that the reaction mechanism of the decomposition of formic acid in a $HCOOH/Et_3N$ azeotrope using a Rh/TsDPEN tethered catalyst is closely related to that of the mechanism in operation in the asymmetric transfer hydrogenation of ketones. Indeed, Fukuzumi *et al*. [22] have shown that formic acid can be decomposed selectively in aqueous solution using $[Rh(Cp^*)(bpy)(H_2O)]^{2+}$.

Homogeneous catalytic reactions in water, applying transition metal complexes as catalysts, have been growing in importance over the last few decades. Compared with organic solvents, water, which is nontoxic, nonflammable, has a high-heat capacity and is inexpensive, has garnered much attention as a green solvent [23, 24]. Reactions carried out in water also provide the opportunity to finely tune the pH of the reaction media, which can lead to changes in reactivity and selectivity. The most common approach to constrain a catalyst in an aqueous phase has been to design ligands containing hydrophilic substituents. The hydrophilic ligand must also provide the necessary steric and electronic properties to endow the catalyst with the desired stability, activity, and selectivity [25]. The most common class of hydrophilic phosphine ligands is those with anionic or hydrophilic substituents appended to the organic ''core'', such as sulfonate [26–28], carboxyl [29, 30], hydroxyl [31–33], or nitrogen containing [34] substituents. The anionic substituents remain charged over a broad pH range, allowing them to be used to solubilize organometallic species in a variety of aqueous-phase catalytic processes. The first and till now the most common way to make a ligand water-soluble is to use a sulfonate group $-SO_3^-$ [25]. Sulfonate is an attractive water-soluble moiety because it can easily be attached to ligands and is stable under a wide range of reaction conditions. The $-SO_3^-$ groups are most commonly introduced to aryl substituents on phosphines by electrophilic sulfonation using SO_3/H_2SO_4. Ahrland *et al*. [35] first reported the sulfonation of triphenylphosphine to give the monosulfonato triphenylphosphine *m*TPPMS . The trisulfonato derivative *m*TPPTS, first prepared by Kuntz [26, 36] and used in Rh-/Ru-based aqueous hydrogenation [37, 38], has become a standard ligand in aqueous phase organometallic chemistry and is used in industrial catalytic processes [39, 40]. Other sulfonato alkyl- and arylphosphines, with different steric and electronic properties, have been synthesized and used to affect the activity of catalysts derived from these ligands [41–43].

The aim of this work, described herein, was to study the application of water-soluble sulfonato aryl- and alkyl-/arylphosphine ligands in aqueous-phase ruthenium(II)-catalyzed hydrogen generation from formic acid. Consequently, the influence of water solubility, related to the structures and behavior in aqueous solution, and electronic and steric effects of the phosphines on the reaction rate was ascertained.

2. Experimental

2.1. *Materials*

TPPTS was prepared according to the literature procedure [44] with a modified purification process [45, 46], and contained <1% of TPPDS and phosphine oxides. Me-diphenylphosphine disulfonate (Me-DPPDS), Bu-DPPDS, Cyp-DPPDS, DiMe-MPPMS, DiCyp-MPPMS were synthesized according to reported procedures [42, 47] by Dr. László T. Mika (Eötvös University, Budapest, Hungary). All other reagents were obtained from commercial sources and used without purification: ruthenium(III) chloride hydrate (99%, Platinum Metals Online, Australia), formic acid (98–100%, Merck KGaA), sodium formate salt (99%, Acros Organics), TPPDS (>95%, Sigma–Aldrich), deuterium oxide (99.9 at. %D, Aldrich).

2.2. *NMR measurements*

^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on a Bruker Avance DRX 400 NMR spectrometer. TSPSA and phosphoric acid (external standards) were used as reference for the ^{1}H- and ^{31}P-NMR measurements, respectively. The spectra were fitted with WINNMR and NMRICMA/MATLAB programs (non-linear least squares fit to determine the spectral parameters).

2.3. *Kinetic studies*

Kinetic measurements were performed in 10 mm external diameter medium pressure sapphire NMR tubes [48, 49]. In a typical formic acid decomposition reaction, $RuCl_3 \cdot 2H_2O$ (0.056 mmol, 14.7 mg) was dissolved in a formic acid:sodium formate (9 : 1, 10 mol L^{-1}) aqueous solution (1 mL H_2O), containing two equivalents of the appropriate water-soluble phosphine (0.112 mmol). The catalytically active species were formed by heating the sapphire tube at 90°C in an electric heating jacket, with the decomposition reaction monitored via pressure increase. After the tube was cooled to room temperature and depressurized, the recycling experiments were performed by the addition of formic acid (10 mmol, 0.38 mL). For **L3**–**L7**, the first cycle was operated under nitrogen, and the subsequent recycling experiments were performed after depressurization in air.

3. Results and discussions

Decomposition of a 10 mol L^{-1} formic acid/sodium formate (9 : 1) solution, catalyzed by $RuCl_3$ ($c = 22.5$ mmol L^{-1}) and two equivalents of *m*TPPTS (**L1**) at 90°C, was achieved in approximately 30 min, reaching about 95% conversion [12, 13]. Under the same conditions, di(*m*-sulfonato)triphenyl phosphine (*m*TPPDS, **L2**) and other related water-soluble (*m*-sulfonatophenyl)-dialkyl phosphines and di(*m*-sulfonatophenyl)-alkyl phosphines (**L3**–**L7**) in combination with ruthenium trichloride were investigated.

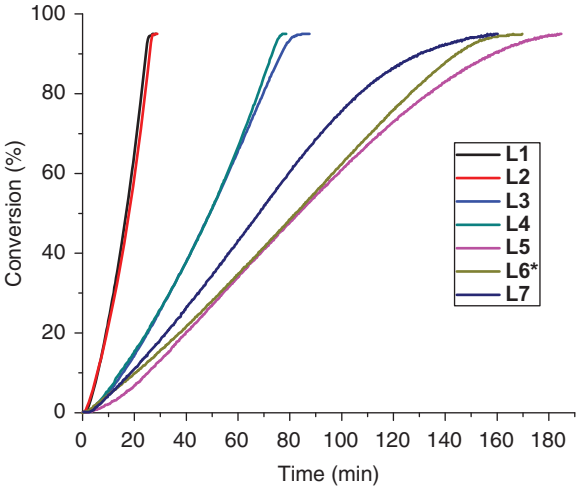


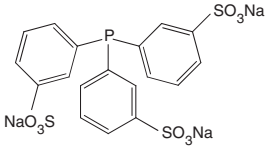
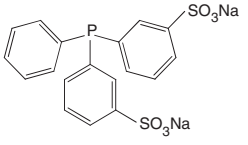
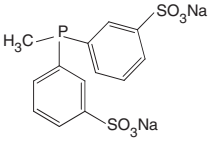
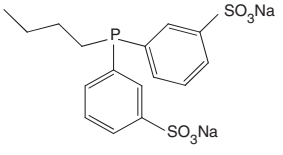
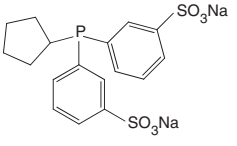
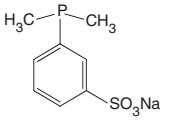
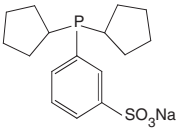
Figure 1. Kinetic curves for the decomposition of formic acid using different phosphine ligands coordinated to ruthenium. 1.0 mL H_2O, 56.3 mmol L^{-1} ruthenium trichloride, 10 mol L^{-1} HCOOH:HCOONa (9 : 1), two equivalents of phosphine; 90°C, addition of 0.38 mL HCOOH for recycling, the kinetic curves for the fifth cycle (after activation period) of each ligand are displayed (*for **L6**, the second cycle is displayed because of catalyst decomposition following the third cycle).

The formic acid decomposition reactions were monitored by the pressure increase, resulting from the formation of H_2 and CO_2, measured in medium pressure sapphire NMR tubes connected to an electronic pressure gauge. The catalysts were prepared *in situ* from $RuCl_3$ and two equivalents of the appropriate water-soluble phosphines in aqueous solution, and activated, since the kinetics of first catalytic cycle is substantially slower than the subsequent ones [12]. As shown previously, two equivalents of phosphine gave a very robust catalyst [13]. One equivalent of *m*TPPTS (**L1**) was not sufficient to stabilize the catalytically active species and activity was progressively lost during the recycling. The system with three equivalents of *m*TPPTS resulted in stable species, but the rate of formic acid decomposition was lower than that observed with two equivalents.

When two equivalents of the water-soluble phosphines were used per ruthenium ion, the significant turnover frequencies (TOF) for hydrogen generation are observed with **L1**–**L7** (figure 1). The ruthenium/*m*TPPDS (**L2**) system had a similar catalytic activity to Ru/*m*TPPTS, while all the other ligands led to slower reactions. With methyl-di(*m*-sulfonato-phenyl)phosphine (**L3**) or butyl-di(*m*-sulfonato-phenyl)phosphine (**L4**), formic acid decomposition was achieved in about 80 min. Moreover, 2.5–3 h were needed when using the catalytic systems containing cyclopentyl-di(*m*-sulfonato-phenyl)phosphine (**L5**), dimethyl-(*m*-sulfonato-phenyl)phosphine (**L6**), or dicyclopentyl-(*m*-sulfonato-phenyl)phosphine (**L7**). No traces of CO could be detected by FT-IR spectroscopy (detection limit *ca* 3 ppm) in the samples of gases generated with these catalytic systems.

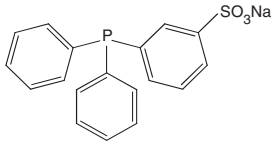
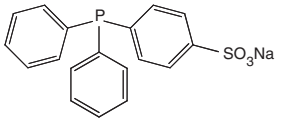
Change in the ^{31}P-NMR chemical shifts of the free water-soluble phosphines (table 1) indicate that the removal of a sulfonato group from the *meta* position slightly increases the basicity of the phosphine, as expected, and it is further increased by replacing the phenyl ring with a butyl or methyl substituent. Consequently, the replacement of two

Table 1. ^{31}P-NMR (162 MHz) chemical shift (δ) of water-soluble phosphine in D_2O and Tolman cone angle.

Water-soluble phosphine	δ (ppm)	Tolman cone angle Θ (°) [53, 62]
 *m*TPPTS (**L1**)	−5.9	166
 *m*TPPDS (**L2**)	−6.3	157
 Me-DPPDS (**L3**)	−25.0	–
 Bu-DPPDS (**L4**)	−15.3	–
 Cyp-DPPDS (**L5**)	−3.4	–
 DiMe-MPPMS (**L6**)	−43.1	–
 DiCyp-MPPMS (**L7**)	+2.9	–

(*Continued*)

Table 1. Continued.

Water-soluble phosphine	δ (ppm)	Tolman cone angle Θ (°) [53, 62]
 *m*TPPMS (**L8**)	−6.7	152
 *p*TPPMS (**L9**)	−6.9	138

phenyl groups with two methyl substituents results in the most basic phosphine studied herein. In contrast, replacement of a phenyl group with a cyclopentyl substituent decreases the basicity of the phosphine, thus the least basic phosphine studied herein is the one with dicyclopentyl rings [42].

The differences in catalytic activity can be influenced by steric effects, diverse solubilities in aqueous systems probably leading to different structures in water, and electronic effects. The water solubility is summarizing and simplifying several ligand properties, although we have not investigated this in detail in this study. Solubility is strongly related to the ligand structure in aqueous solution as shown in case of the *m*TPPMS, having hydrophilic and hydrophobic moities, where self association, self aggregation, micelle formation have been observed [50–52]. The solubility of the *m*TPPMS-Na salt is much lower than the *m*TPPTS-Na_3 ($28\,g\,L^{-1}$ *versus* $1100\,g\,L^{-1}$) [53]. For *m*TPPTS, such aggregations are not identified. In the solid state, these hydrophilic–hydrophobic interactions and structures are well defined for *m*TPPMS [53]. It is also known that *m*TPPMS can act as a surfactant [54–56]. In the case of very fast H_2 and CO_2 gas formation, using this ligand as catalyst precursor, we have observed some foam formation. Although a large number of hydrophilic phosphines have been investigated, the Tolman cone angle has been reported for only a small subset of these ligands. The cone angle of *m*TPPTS (**L1**) ligand has been proposed in a wide range, from 145° to 178° [57–60]. The cone angle of *m*TPPDS (**L2**) has not been determined under identical conditions, but a calculated value of 157° has been suggested [61]. However, it has been indicated that the position of the sulfonate groups influences the cone angle of the phosphine to a greater extent than their number [62]. Ligands **L3**, **L4**, and **L6** with *n*-alkyl substituents all have smaller cone angles than the other phosphine ligands used in the study. During the recycling of catalysts following depressurization and addition of formic acid, the system with **L1**–**L5** maintain maximum activity for more than 20 cycles, whereas an obvious ruthenium metal aggregation was observed from the third cycle of ruthenium/**L6** system. This could be attributed to the fact that **L6** is the most basic ligand of this series and to the smallest cone angle. In the catalytic

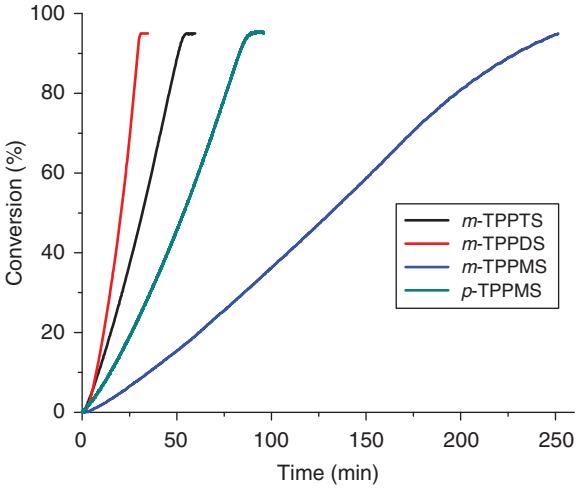


Figure 2. Influence of the different triarylphosphines *m*TPPTS (**L1**), *m*TPPDS (**L1**), *m*TPPMS (**L8**), and *p*TPPMS (**L9**) on the reaction rate. 22 mmol L^{-1} $RuCl_3$, two equivalents of phosphine, 4 mol L^{-1} HCOOH:HCOONa (9 : 1), 2.5 mL H_2O:D_2O (1 : 1), 90°C, addition of 0.38 mL HCOOH for recycling, kinetic curves displayed after the activation period.

system containing **L7**, which is the least basic and most hydrophobic ligand of the series, the activity was progressively lost from the sixth cycle.

As mentioned above, the sulfonate moieties are responsible for ensuring the water solubility of the phosphines. Under the catalytic conditions investigated, *m*TPPMS (**L8**) afforded complexes that were poorly soluble in the reaction medium (we could not increase the catalyst concentration for this ligand to study its effect on the hydrogen generation without having precipitation), whereas *m*TPPDS (**L2**) and *m*TPPTS (**L1**) gave soluble complexes, allowing us to study the effect of the catalyst concentration on the reaction rate. The position of the sulfonate group also influences the solubility and the activity. For example, at high catalyst concentrations, complexes containing *m*TPPMS were not completely soluble, while with *p*TPPMS (**L9**), precipitation occurred only towards the end of the reaction. As expected, the solubility of these phosphines depends primarily on the ratio of non-hydrogen atoms to water-soluble groups [25].

Using $RuCl_3$ and *m*TPPMS (**L8**) catalytic precursors, the activity became low and deactivation occurred during recycling (figure 2). Under the same reaction conditions (i.e., lower HCOOH concentration), the highest catalytic activity was observed with *m*TPPDS (**L2**), which can be explained as a compromise between solubility, related to the structure and behavior in the aqueous solution of the catalytically active species, steric hindrance and basicity. The sulfonate groups have only minor electronic influence [59, 61], which is clear from the comparison of the chemical shifts of the related mono-, bis- and tris-sulfonato phosphines. It has been shown that the cone angle of the phosphine ligand increases with the number of sulfonate groups in *meta* position (PPh_3 146°, *m*TPPMS 151.9°, *m*TPPDS 157°, *m*TPPTS 160°) [53]. However, Joó *et al.* [62] have indicated that the position of the sulfonate groups influences the cone angle of the phosphine to a greater extent than their number; *para* sulfonato phosphines having similar cone angles to PPh_3 (*p*TPPMS 138°, *p*TPPTS 139°). The good catalytic activity

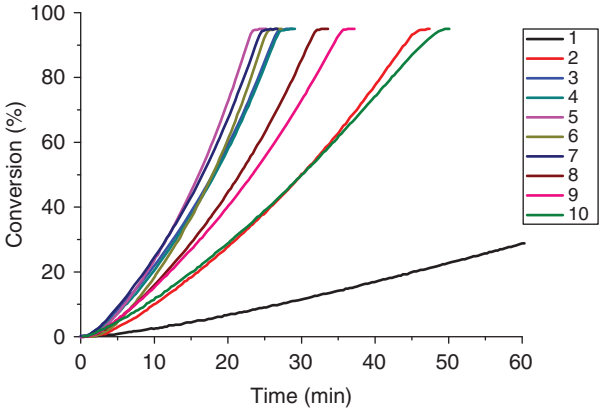


Figure 3. Effect of ruthenium chloride concentration on the reaction rate in the presence of *m*TPPDS (**L2**).1.0 mL H_2O, 10 mol L^{-1} HCOOH:HCOONa (9 : 1), two equivalents of *m*TPPDS, 90°C, addition of 0.38 mL HCOOH for recycling, kinetic curves of the fifth cycle (after activation period) of each catalyst are displayed.

Table 2. Effect of ruthenium concentration on the rate of hydrogen production.[a]

Entry	$RuCl_3$ concentration (mmol)	Reaction time (min)[b]	TOF (h^{-1})[b]
1	14	160	268
2	28	45	476
3	56	27	397
4	84	27	397
5	98	23	266
6	112	25	214
7	168	25	214
8	224	32	84
9	280	35	61
10	336	50	36

[a]Kinetic measurements were performed in 1.0 mL H_2O, containing 10 mol L^{-1} HCOOH/HCOONa (9 : 1) and two equivalents of *m*TPPDS (**L2**); the reactions were carried out at 90°C and the catalysts were recycled by addition of 0.38 mL HCOOH.
[b]Data were obtained and calculated for to the fifth cycle (after activation period) of the catalyst.

observed for *m*TPPTS and *m*TPPDS relative to *m*TPPMS is probably due to their significantly higher hydrophilic properties expressed via the solubility and related to the structures in aqueous solution of the catalytically active species.

$RuCl_3$, combined with two equivalents of *m*TPPDS (**L2**), is a very efficient pre-catalyst for formic acid decomposition (figure 3). At the catalyst concentration of 98 mmol L^{-1}, the shortest reaction time is observed in the hydrogen generation process (table 2). The decrease of the reaction rate at higher catalyst concentrations is likely to be due to the formation of chloro-bridged dimers, which have been previously shown to be less active in related catalytic processes compared to monometallic species in the case of rhodium catalysts [63], although active dimeric catalysts are known [64]. Indeed, dimeric Ru-*m*TPPMS and Ru-*m*TPPTS complexes with chloride bridges are known [65–67]. The effect of pH and concentration on the formation and equilibrium distribution of the water soluble monomeric and dimeric ruthenium-*m*TPPMS hydrides and chlorides has also been described [68].

4. Conclusions

We have shown that the water-soluble sulfonato aryl- and aryl-/alkylphosphine ligands can be applied successfully in aqueous-phase ruthenium(II)-catalyzed formic acid decomposition into hydrogen and carbon dioxide. The hydrogen obtained with these catalytic systems is free from CO and is therefore suitable for use in all types of fuel cells. The water solubility (related to the structures and behavior in aqueous solution), electronic and steric effects of the phosphines on the reaction rate was studied. The very good activity observed with *m*TPPTS and *m*TPPDS is probably due to a compromise between steric effects and their basicities, but notably the high stability and high solubility of these ligands.

Acknowledgments

The authors are grateful to the Swiss National Science Foundation and the EPFL for financial support. We also thank Dr László T. Mika (Eötvös University, Budapest, Hungary) for generously donating the phosphines.

References

[1] L. Schlapbach, A. Züttel. *Nature*, **414**, 353 (2001).
[2] R. Williams, R.S. Crandall, A. Bloom. *Appl. Phys. Lett*., **33**, 381 (1978).
[3] D.H.S. Ying, R.J. Madix. *Inorg. Chem*., **17**, 1103 (1978).
[4] C. Xu, D.W. Goodman. *J. Phys. Chem*., **100**, 245 (1996).
[5] M.R. Columbia, A.M. Crabtree, P.A. Thiel. *J. Am. Chem. Soc*., **114**, 1231 (1992).
[6] S.D. Senanayake, D.R. Mullins. *J. Phys. Chem. C*, **112**, 9744 (2008).
[7] D. Foster, G.R. Beck. *J. Chem. Soc., Chem. Commun*., 1072 (1971).
[8] R.M. Laine, R.G. Rinker, P.C. Ford. *J. Am. Chem. Soc*., **99**, 252 (1977).
[9] T. Yoshida, T. Okano, S. Otsuka. *J. Am. Chem. Soc*., **102**, 5966 (1980).
[10] F. Gloaguen, J.D. Lawrence, T.B. Rauchfuss. *J. Am. Chem. Soc*., **123**, 9476 (2001).
[11] G. Laurenczy, C. Fellay, P. Dyson, Hydrogen production from formic acid. *PCT Int. Appl*. 36 (2008). CODEN: PIXXD2 WO 2008047312 A1 20080424 CAN 148:498734 AN 2008:502691.
[12] C. Fellay, P.J. Dyson, G. Laurenczy. *Angew. Chem. Int. Ed*., **47**, 3966 (2008).
[13] C. Fellay, N. Yan, P.J. Dyson, G. Laurenczy. *Chem. Eur. J*., **15**, 3752 (2009).
[14] W. Gan, P.J. Dyson, G. Laurenczy. *React. Kinet. Catal. Lett*., **98**, 205 (2009).
[15] B. Loges, A. Boddien, H. Junge, M. Beller. *Angew. Chem. Int. Ed*., **47**, 3962 (2008).
[16] A. Boddien, B. Loges, H. Junge, M. Beller. *ChemSusChem*, **1**, 751 (2008).
[17] H. Junge, A. Boddien, F. Capitta, B. Loges, J.R. Noyes, S. Gladiali, M. Beller. *Tetrahedron Lett*., **50**, 1603 (2009).
[18] B. Loges, A. Boddien, H. Junge, J.R. Noyes, W. Baumann, M. Beller. *Chem. Commun*., 4185 (2009).
[19] F. Joó. *ChemSusChem*, **1**, 805 (2008).
[20] S. Enthaler. *ChemSusChem*, **1**, 801 (2008).
[21] D.J. Morris, G.J. Clarkson, M. Wills. *Organometallics*, **28**, 4133 (2009).
[22] S. Fukuzumi, T. Kobayashi, T. Suenobu. *ChemSusChem*, **1**, 827 (2008).
[23] C.J. Li. *Chem. Rev*., **93**, 2023 (1993).
[24] C.J. Li. *Chem. Rev*., **105**, 3095 (2005).
[25] K.H. Shaughnessy. *Chem. Rev*., **109**, 643 (2009).
[26] E. Kuntz. Patents FP 2314910, 1975; GP 2627354, 1976; US 4248802 (1981).
[27] F. Joó, J. Kovács, A. Kathó, A.C. Benyei, T. Decuir, D.J. Darensbourg. *Inorg. Synth*., **32**, 1 (1998).
[28] B. Mohr, D.M. Lynn, R.H. Grubbs. *Organometallics*, **15**, 4317 (1996).
[29] T. Jarolim, J. Podlahova. *J. Inorg. Nucl. Chem*., **38**, 125 (1976).
[30] O. Herd, A. Hessler, M. Hingst, M. Tepper, O. Stelzer. *J. Organomet. Chem*., **522**, 69 (1996).

[31] J. Chatt, G.J. Leigh, R.M. Slade. *J. Chem. Soc., Dalton Trans*., 2021 (1973).
[32] K. Issleib, H.M. Mobius. *Chem. Ber. Recl*., **94**, 102 (1961).
[33] A. Buhling, P.C.J. Kamer, P.W.N.M. Vanleeuwen. *J. Mol. Catal. A*, **98**, 69 (1995).
[34] I. Tóth, B.E. Hanson, M.E. Davis. *Organometallics*, **9**, 675 (1990).
[35] S. Ahrland, J. Chatt, N.R. Davies, A.A. Williams. *J. Chem. Soc*., 276 (1958).
[36] E.G. Kuntz. *Chem. Tech*., **17**, 570 (1987).
[37] F. Joó, M.T. Beck. *React. Kinet. Catal. Lett*., **2**, 257 (1975).
[38] F. Joó, Z. Tóth, M.T. Beck. *Inorganica Chim. Acta*, **25**, L61 (1977).
[39] B. Cornils. *J. Mol. Catal. A*, **143**, 1 (1999).
[40] P.J. Dyson, D.J. Ellis, G. Laurenczy. *Adv. Synth. Catal*., **345**, 211 (2003).
[41] Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Toth, B. Heil. *Organometallics*, **8**, 542 (1989).
[42] L.T. Mika, L. Orha, N. Farkas, I.T. Horváth. *Organometallics*, **28**, 1593 (2009).
[43] H. Jänsch, S. Kannenberg, G. Boche. *Eur. J. Org. Chem*., 2923 (2001).
[44] S. Hida, P.J. Roman, A.A. Bowden, J.D. Atwood. *J. Coord. Chem*., **43**, 345 (1998).
[45] T. Bartik, B. Bartik, B.E. Hanson, T. Glass, W. Bebout. *Inorg. Chem*., **31**, 2667 (1992).
[46] W.A. Herrmann, C.W. Kohlpainter. *Inorg. Synth*., **32**, 8 (1998).
[47] L.T. Mika, A butadién metoxikarbonilezésének mechanizmusvizsgálata in situ spektroszkópiával és vízoldható foszfinligandumok szintézise, PhD thesis, Eötvös University, Hungary (2010) (Unpublished results, in Hungarian).
[48] G. Laurenczy, F. Joo, L. Nadasdi. *Inorg. Chem*., **39**, 5083 (2000).
[49] A. Cusanelli, U. Frey, D.T. Richens, A.E. Merbach. *J. Am. Chem. Soc*., **118**, 5265 (1996).
[50] F. Joó, É. Papp, Á. Kathó. *Topics in Catal*., **5**, 113 (1998).
[51] G. Oehme, I. Grassert, N. Flach. In *Aqueous Organometallic Chemistry and Catalysis*, NATO ASI Series 3: High Technology, I.T. Horváth, F. Joó (Eds), Vol. 5, pp. 245, Kluwer, Dordrecht (1995).
[52] G. Wright, J. Bjerrum. *Acta Chem. Scand*., **16**, 1262 (1962).
[53] M.R. Barton, Y. Zhang, J.D. Atwood. *J. Coord. Chem*., **55**, 969 (2002).
[54] P.J. Baricelli, D. Baricelli, E. Lujano, L.G. Melean, M. Borusiak, F. López-Linares, L.J. Bastidas, M. Rosales. *J. Mol. Catal. A: Chem*., **271**, 180 (2007).
[55] F. Joó. *Acc. Chem. Res*., **35**, 738 (2002).
[56] L. Magna, Y. Chauvin, G.P. Niccolai, J.-M. Basset. *Organometallics*, **22**, 4418 (2003).
[57] C.A. Tolman. *Chem. Rev*., **77**, 313 (1977).
[58] D.J. Darensbourg, C.J. Bischoff, J.H. Reibenspies. *Inorg. Chem*., **30**, 1144 (1991).
[59] D.J. Darensbourg, C.J. Bischoff. *Inorg. Chem*., **32**, 47 (1993).
[60] H. Gulyás, A.C. Benyéi, J. Bakos. *Inorg. Chim. Acta*, **357**, 3094 (2004).
[61] Q. Peng, Y. Yang, C. Wang, X. Liao, Y. Yuan. *Catal. Lett*., **88**, 219 (2003).
[62] G. Papp, J. Kovács, A.C. Bényei, G. Laurenczy, L. Nádasdi, F. Joó. *Can. J. Chem*., **79**, 635 (2001).
[63] S.B. Duckett, C.L. Newell, R. Eisenberg. *J. Am. Chem. Soc*., **116**, 10548 (1994).
[64] K. Severin. *Chem. Eur. J*., **8**, 1514 (2002).
[65] M. Hernandez, P. Kalck. *J. Mol. Catal. A: Chem*., **116**, 117 (1997).
[66] M. Hernandez, P. Kalck. *J. Mol. Catal. A: Chem*., **116**, 131 (1997).
[67] R.A. Sanchez-Delgado, M. Medina, F. López-Linares, A. Fuentes. *J. Mol. Catal. A: Chem*., **116**, 167 (1997).
[68] F. Joó, J. Kovács, A.Cs. Bényei, Á. Kathó. *Catal. Today*, **42**, 441 (1998).