DOI 10.1515/gps-2014-0003 — Green Process Synth 2014; 3: 127–132

Réka Gombos* and Ferenc Joó

Selective hydrogenation of cinnamaldehyde and phospholipids in aqueous-organic biphasic systems with ruthenium(II) complex catalysts

Abstract: The new water-soluble complex [RuH(OOc)(*m*tppms)$_3$] (OOc=octanoate, *m*tppms=monosulfonated triphenylphosphine) was synthesized and – together with the known [RuH(OAc)(*m*tppms)$_3$] (OAc=acetate) – applied for aqueous-organic biphasic hydrogenation of cinnamaldehyde as well as for hydrogenation of soybean liposomes under mild conditions. The complexes showed pronounced selectivity (up to 75%) towards the hydrogenation of the C=O function in the α,β-unsaturated aldehyde; the selectivity was influenced by the pH of the aqueous phase and the hydrogen pressure. The C=C double bonds in soybean lecithin were only slowly reduced, however, at 5 bar H_2 pressure the reaction rate was sufficient to achieve substantial conversion (approximately 20% of all double bonds) in the unsaturated fatty acids.

Keywords: biphasic; cinnamaldehyde; hydrogenation; liposomes; ruthenium.

***Corresponding author: Réka Gombos,** Department of Physical Chemistry, University of Debrecen, Debrecen 10, P.O. Box 7, H-4010 Hungary, e-mail: gombos.reka@science.unideb.hu
Ferenc Joó: Department of Physical Chemistry, University of Debrecen, Debrecen 10, P.O. Box 7, H-4010 Hungary; and MTA-DE Homogeneous Catalysis and Reaction Mechanisms Research Group, Debrecen 10, P.O. Box 7, H-4010 Hungary

1 Introduction

Water is a very special and useful solvent for green chemistry [1]. In environment-concerned processes, it can replace organic solvents, thus preventing pollution [2]. In addition, it is abundant, cheap, nonflammable and has a high heat capacity; this makes it attractive from both economic and safety viewpoints. We initiated the study of aqueous organometallic catalysis several years ago [3, 4]. Due to its protic nature and high polarity water cannot be a general solvent for organic transformations, still, there is an increasing number of publications on practical aqueous organic and organometallic syntheses [5]. In several catalytic processes, the catalyst is made water-soluble by using water-soluble ligands to replace their hydrophobic analogs [6, 7]. A case in point is the use of sulfonated triphenylphosphines, e.g., monosulfonated triphenylphosphine (*m*tppms) (diphenylphosphinobenzene-*m*-sulfonate) instead of triphenylphosphine (PPh_3) in complex catalysts such as [RhCl(*m*tppms)$_3$] (the water-soluble analogue of Wilkinson's catalyst) [8] or in [RuH(OAc)(*m*tppms)$_3$] (OAc=acetate) [9].

Apart from use in synthetic chemistry, water is the solvent of life. Water-soluble hydrogenation catalysts have gained important applications in the modification of biomembranes by modulating the fluidity of cell membranes by catalytic hydrogenation of their unsaturated lipid constituents [10]. The palladium(II) complex of Alizarin red, [Pd(QS)$_2$] (QS=1,2-dihydroxyalizarin-3-sulfonate) proved to be a highly active and selective catalyst for the hydrogenation of aqueous lipid dispersions (liposomes) and various cell suspensions [11]. Recent investigations revealed that – in contrast to earlier assumptions – cell membranes are not characterized by a uniform distribution of the various lipids, but contain well distinguishable conglomerates (so-called rafts) of specific lipids around certain proteins [12]. It seemed to us that catalytic hydrogenation could discriminate between the loose and raft-bound lipids, especially in cases where the catalyst itself is bound to the rafts. For this purpose we synthesized an Ru(II)-carboxylato complex, [RuH(OOc)(*m*tppms)$_3$] (OOc=octanoate), with a relatively long aliphatic carbon chain which could help the complex to be incorporated into such rafts, and studied its catalytic behavior, together with that of [RuH(OAc)(*m*tppms)$_3$] in hydrogenation of liposomes. The latter Ru(II)-hydrido complex has been known for a long time, however, its selectivity for C=C vs. C=O hydrogenation has not been studied yet. In order to obtain information on such selectivity of [RuH(OAc)(*m*tppms)$_3$] we carried out biphasic hydrogenation of the unsaturated aldehyde (E)-3-phenyl-2-propenal (cinnamaldehyde). [RuH(OOc)(*m*tppms)$_3$] was not applied as a catalyst for cinnamaldehyde hydrogenation, since due to its lipophilicity, it was expected to move preferentially to the organic phase. The results of these investigations are reported below.

2 Materials and methods

The following were synthesized as described in the literature: *m*tppms [13], {[$RuCl_2$(*m*tppms)$_2$]$_2$} [13] and [RuH(OAc)(*m*tppms)$_3$] [14]. Hydrated ruthenium(III) chloride was purchased from Pressure Chemical Co. (Pittsburgh, PA, USA). Sodium octanoate was obtained by titration of 0.1 M aqueous octanoic acid solution by NaOH until pH 8.94, followed by evaporation to dryness. Soybean lecithin (BiYo-Product Kft, Komárom, Hungary) was purchased from a local pharmacy. Solvents were obtained from Molar Chemicals (Budapest, Hungary) and gases were supplied by Linde Gas Hungary (Budapest, Hungary). All other chemicals were high purity products supplied by Sigma-Aldrich. ^{1}H- and ^{31}P-NMR spectra were recorded on a Bruker Avance 360 MHz spectrometer. IR spectra in KBr discs were recorded on a Perkin Elmer Spectrum One (Perkin Elmer Hungary, Budapest, Hungary) FT-IR spectrometer.

[RuH(OAc)(*m*tppms)$_3$] was obtained by both methods described in the literature [14], i.e., by the direct reaction of hydrated $RuCl_3$, HOAc and KOH in refluxing ethanol and in the reaction of {[$RuCl_2$(*m*tppms)$_2$]$_2$}, *m*tppms, Na acetate and H_2 in refluxing ethanol. The latter synthesis avoids the presence of inorganic impurities. ^{1}H-NMR (H_2O/MeOH 5/1) δ_H: -17.41 ppm (q), $^2J_{PH}$=25 Hz; ^{31}P-NMR (H_2O/MeOH 5/1) δ_P: 47.43 ppm (s), 81.55 ppm (s).

For the synthesis of [RuH(OOc)(*m*tppms)$_3$], 0.5 g (0.5 mmol Ru) {[$RuCl_2$(*m*tppms)$_2$]$_2$}, 0.2 g (0.5 mmol) *m*tppms and 0.166 g (1 mmol) Na octanoate were suspended in 10 ml 96% ethanol and the mixture was refluxed in a H_2 atmosphere for 16 h. Upon cooling, a yellow precipitate was obtained. This was washed with cold ethanol and acetone, dried above P_4O_{10} and stored under argon, protected from light. Yield 583.5 mg, 81%. ^{1}H NMR (H_2O/MeOH 5/1) δ_H: -18.79 ppm (q), $^2J_{PH}$=29 Hz; ^{31}P NMR (H_2O/MeOH 5/1) δ_P: 45. 98 ppm (s), 80.12 ppm (s). IR (KBr, ν/cm^{-1}), ν(Ru-H): 1996; ν(OCO, asym): 1532; ν(OCO, sym): 1435; ν(SO_3,E): 1196; ν(SO_3,A_1):1037.

2.1 Hydrogenation of liposomes

Soybean lecithin (4 mg) was dissolved in 0.4 ml chloroform. The chloroform was evaporated by an argon stream and 6 ml ion-exchanged water or 6 ml phosphate buffer (pH 6.93) was added. The mixture was sonicated for 3×2 min (Branson Sonifier 250, Branson Ultrasonics, Danbury, CT 06810, USA) with cooling between the 2 min intervals. The liposome obtained this way was deoxygenated by several vacuum-argon refill cycles; [RuH(OAc)(*m*tppms)$_3$] or [RuH(OOc)(*m*tppms)$_3$] was added under inert conditions and the reaction mixture was stirred under hydrogen for the desired time. For reactions under H_2 pressure, homemade heavy-wall glass hydrogenation reactors were used. Analysis of the reaction mixtures was done by gas chromatography (HP 5890 Series II GC, SP2330 30×0.25 mm, FID, carrier gas nitrogen, column temperature 190°C, isotherm, temperature of the injector and detector 250°C) after extraction and transesterification of the lipids to methyl esters (HCl/MeOH).

Unsaturated fatty acids in soybean lecithin are found only in the C:18 series (18:1 oleic acid; 18:2 linoleic acid; 18:3 linolenic acid) therefore the unsaturation of the lipid can be calculated as $unsaturation=A_{18:1}+2\times A_{18:2}+3\times A_{18:3}$ (A=peak area). Extent of hydrogenation was characterized by the ratio (percentage) of remaining unsaturation to the unsaturation of the initial sample, $x=100\times$(*unsaturation of hydrogenated lipid*)$\times$(*unsaturation of control*)$^{-1}$. Alternatively, conversion is defined as $conv=100-x$.

2.2 Hydrogenation of cinnamaldehyde

A total of 13 mg (0.01 mmol) [RuH(OAc)(*m*tppms)$_3$] was placed into a glass pressure reactor sealed by a rubber septum, which was subsequently deoxygenated. Deoxygenated ion-exchanged water (3 ml) or 0.2 M aqueous acetate buffer was added under argon, followed by 100 µl (0.8 mmol) cinnamaldehyde. The reaction mixture was vigorously stirred at a temperature of 80°C. After the desired time, the reactor was cooled, 0.5 ml of the reaction mixture was mixed with 1 ml of water and 1 ml toluene, vortexed, centrifuged and the organic phase was filtered through $MgSO_4$. The dry organic phase was analyzed by gas chromatography (Agilent 7890A Gas Chromatograph; Chrompack HP-5 30 m×32 mm×0.25 µm; FID; carrier gas nitrogen, temperature program: 130°C/6 min, 60°C/min to 250°C, 250°C for 5 min).

Turnover frequency (TOF) is defined as $TOF=$(*mol converted cinnamaldehyde*)$\times$(*mol catalyst*)$^{-1}\times h^{-1}$.

3 Results and discussion

3.1 Synthesis of [RuH(OOc)(*m*tppms)$_3$]

This compound was obtained by the method previously employed for the synthesis of RuH(OAc)(*m*tppms)$_3$] [14]. ^{1}H- and ^{31}P-NMR data are agreement with an Ru(II)-monohydride with an octahedral structure, where the three

phosphorus ligands are meridional and the hydride is in the *cis*-position to all three. The solid state IR spectrum shows characteristic vibration frequency for a terminal Ru-hydride at 1996 cm^{-1} and the ν(OCO, asym) and ν(OCO, sym) vibrations are displayed at 1532 cm^{-1} and 1435 cm^{-1}, respectively, yielding a Δν=ν(OCO, asym)–ν(OCO, sym)=97 cm^{-1}. These data are in good agreement with those found earlier for the analogous carboxylato complexes [RuH(OAc)$(PPh_3)_3$] [15] and [RuH(OAc)(*m*tppms)$_3$] [14] with Δν values of 77 cm^{-1} and 93 cm^{-1}, respectively. It is generally accepted [15] that Δν~120 cm^{-1} refers to bidentate coordination of carboxylato ligands, and, indeed, for [RuH(OAc)$(PPh_3)_3$] this was confirmed by single crystal X-ray diffraction structure determination [16]. The NMR characteristics are also consistent with a *trans*-dihydride structure with three meridional phosphines and a monodentate carboxylato ligand, as was suggested in the case of a related formato complex, *trans*-[Ru$(H)_2$(OOCH)(*m*tppms)$_3$] [17]. Nevertheless, based on the IR properties, we prefer the formulation as a monohydride; further studies are underway to decide the exact structure of the compound.

Whereas [RuH(OAc)(*m*tppms)$_3$] dissolves well in water [14], [RuH(OOc)(*m*tppms)$_3$] is less soluble; however at concentrations required for catalysis (e.g., 4 mg$(ml)^{-1}$) it gives clear solutions.

3.2 Hydrogenation of cinnamaldehyde with [RuH(OAc)(*m*tppms)$_3$] catalyst

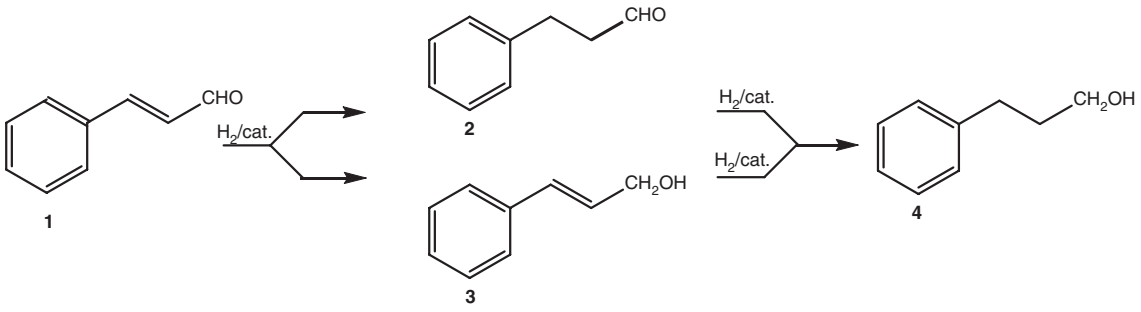
Hydrogenation of α,β-unsaturated carbonyl compounds is an important reaction in fragrance and flavor industries and cinnamaldehyde (**1**) is often used for testing catalysts with regard to their selectivity in hydrogenation of C=C or C=O bonds [18, 19]. Products of the hydrogenation (Scheme 1) can be the saturated aldehyde, 3-phenylpropanal (**2**), the unsaturated alcohol, 3-phenyl-2-propen-1-ol (**3**) and the saturated alcohol, 3-phenylpropan-1-ol (**4**) of which **3** is the most desired compound.

Since cinnamaldehyde is only slightly soluble in water, reactions using an aqueous solution of the catalyst are, in fact, biphasic. According to the literature, aqueous organic biphasic hydrogenation of cinnamaldehyde with Rh(I)-phosphine catalysts usually affords the C=C hydrogenation product **2** [18] while Ru(II)-phosphine catalysts can be 100% selective to the unsaturated alcohol [20, 21] **3**, however, the selectivity strongly depends on the pH of the aqueous phase [21].

We have found that [RuH(OAc)(*m*tppms)$_3$] catalyzed the hydrogenation of cinnamaldehyde under mild conditions (80°C, 4–7 bar H_2) both in water and in aqueous acetate buffer, as solvent, at various pH values. The pressure dependence of the composition of the reaction mixture is shown in Figure 1. At 7 bar H_2 after 4 h, the conversion of **1** was 52.6% which corresponds to a TOF of 10.5 h^{-1}. This TOF is close to the TOF (14 h^{-1}) which was obtained with {[$RuCl_2$(*m*tppms)$_2]_2$}+3 *m*tppms at 1 bar H_2 pressure [21]. It is seen from the Figure, that the major product is the most valuable unsaturated alcohol, **3**; furthermore, its yield increased upon increasing the hydrogen pressure, and reached 48% under 10 bar H_2. Such a beneficial effect of hydrogen pressure on the selectivity of cinnamaldehyde hydrogenation has already been observed with similar Ru(II)-*m*tppms catalysts [22]. It is also important, that **2** and **4** are formed in <10% yield, each, even at 10 bar H_2 pressure.

Knowing the pH-sensitivity of cinnamaldehyde hydrogenations, we carried out reactions in 0.2 M acetate buffer solutions of pH 3.6, 4.6 and 5.6. Acetate buffer seemed a reasonable choice, since the catalyst contains an acetato ligand; unfortunately, it does not allow the reactions to be studied at higher pH values. The results are shown in Figure 2.

The hydrogenations of cinnamaldehyde in acetate buffer were run only for 2 h, so the conversion at pH 5.5 (23.8 %) is only slightly less than half the conversion in water after 4 h (26.4 %) (see also Figure 3 later). In the studied range, the pH has a small but important effect on



Scheme 1 Possible products of cinnamaldehyde hydrogenation.

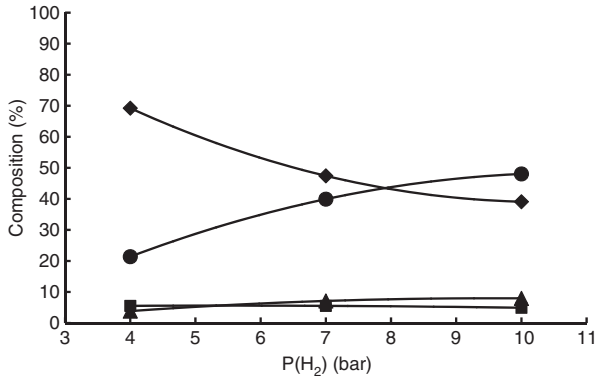


Figure 1 Effect of pressure on the hydrogenation of cinnamaldehyde with [RuH(OAc)(*m*tppms)$_3$] catalyst. ◆ cinnamaldehyde, ■ 3-phenyl-2-propanal, ▲ 3-phenyl-2-propan-1-ol, ● 3-phenyl-2-propen-1-ol. Conditions: 0.01 mmol catalyst, 0.8 mmol cinnamaldehyde, 3 ml water, 80°C, 4 h.

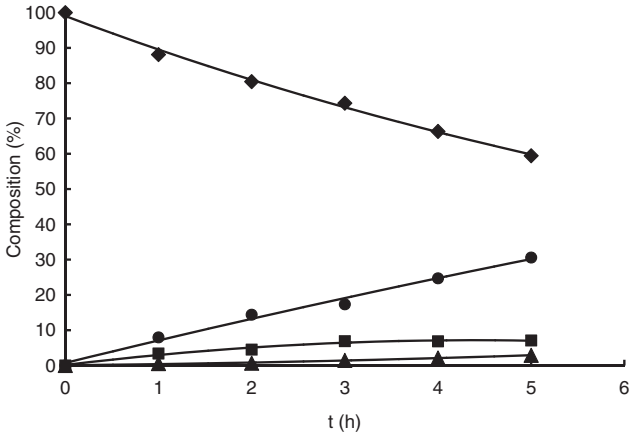


Figure 3 Time-course of the hydrogenation of cinnamaldehyde with [RuH(OAc)(*m*tppms)$_3$] catalyst. ◆ cinnamaldehyde, ■ 3-phenyl-2-propanal, ▲ 3-phenyl-2-propan-1-ol, ● 3-phenyl-2-propen-1-ol. Conditions: 0.01 mmol catalyst, 0.8 mmol cinnamaldehyde, 3 ml phosphate buffer (pH 7.0), 80°C, P(H_2)=7 bar.

the rate (Figure 2) and product distribution: the yield of **3** increased to 14.8% at pH 5.5. The yield of **2** varied from 3.3% (pH 3.6) to 6.2 % (pH 5.5), while that of **4** remained below 2%, so that at pH 5.5 cinnamyl alcohol was dominant (64%) among all hydrogenation products.

The time course of the hydrogenation was investigated with 7 bar H_2 pressure using a 0.2 M phosphate buffer of pH 7.0 as the solvent (Figure 3). The reaction proceeded with a steady rate and high selectivity. After 5 h at 59.4% cinnamaldehyde conversion, the ratio of **3** to (**2**+**3**+**4**) was 75.4%. After 4 h, the conversion was 33.7% (TOF=6.7 h^{-1}), so phosphate buffer slightly decreased the rate of the reaction relative to the case of water or acetate buffer as solvents; such an unfavorable effect of phosphate buffer has already been detected [23] with similar water-soluble catalysts.

In summary, it can be concluded that in aqueous biphasic systems under mild conditions, [RuH(OAc)(mtppms)$_3$] proved to be an active and selective catalyst for the hydrogenation of cinnamaldehyde, a representative α,β-unsaturated carbonyl compound. The major product in all cases was cinnamyl alcohol (**3**), a valuable chemical for flavor and fragrance industries.

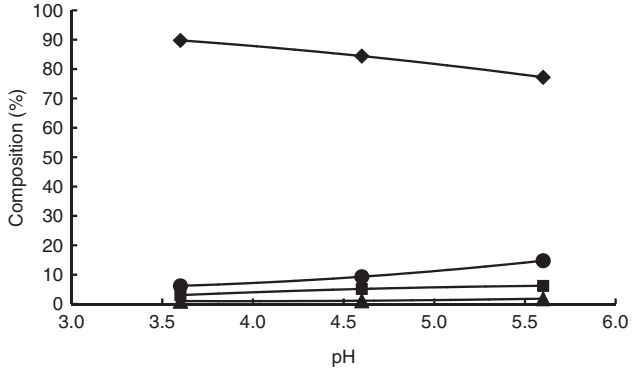


Figure 2 Effect of pH on the hydrogenation of cinnamaldehyde with [RuH(OAc)(*m*tppms)$_3$] catalyst. ◆ cinnamaldehyde, ■ 3-phenyl-2-propanal, ▲ 3-phenyl-2-propan-1-ol, ● 3-phenyl-2-propen-1-ol. Conditions: 0.01 mmol catalyst, 0.8 mmol cinnamaldehyde, 3 ml acetate buffer, 80°C, 2 h, P(H_2)=7 bar.

3.3 Hydrogenation of soybean lecithin with [RuH(OAc)(*m*tppms)$_3$] and [RuH(OOc)(*m*tppms)$_3$] catalysts

Hydrogenation of soybean lecithin liposomes was studied with both catalysts under mild conditions. Depending on their composition, liposomes are stable only around physiological temperatures, therefore we choose 40°C as the maximum reaction temperature. Both ion-exchanged water and phosphate buffer (pH 6.93) were used as solvents. The results are expressed as remaining unsaturation of the lipids as defined in the experimental section and are summarized in Table 1.

With phosphate buffer as the solvent, at 25°C and 1 bar H_2 pressure [RuH(OAc)(*m*tppms)$_3$] proved to be a very inefficient catalyst (entry 1); however, at 40°C, approximately 8% reduction of total unsaturation was observed (entry 2). This slow reduction of the C=C double bonds is in accord with the selectivity of these catalysts towards hydrogenation of the C=O function in cinnamaldehyde.

Table 1 Hydrogenation of soybean liposomes by [RuH(OAc)(*m*tppms)$_3$] and [RuH(OOc)(*m*tppms)$_3$] catalysts.

Entry	Catalyst	Solvent	P(H_2) (bar)	t (h)	T (°C)	Unsaturation (%)
1	[RuH(OAc)(*m*tppms)$_3$]	buffer	1	2	25	99.8
2	[RuH(OAc)(*m*tppms)$_3$]	buffer	1	2	40	91.6
3	[RuH(OOc)(*m*tppms)$_3$]	buffer	1	2	40	98.8
4	[RuH(OOc)(*m*tppms)$_3$]	buffer	1	1	40	99.2
5	[RuH(OOc)(*m*tppms)$_3$]	buffer	1	3	40	98.0
6	[RuH(OOc)(*m*tppms)$_3$]	buffer	5	2	40	89.4
7	[RuH(OAc)(*m*tppms)$_3$]	buffer	5	2	25	96.3
8	[RuH(OAc)(*m*tppms)$_3$]	water	5	2	25	89.2
9	[RuH(OAc)(*m*tppms)$_3$]	water	1	2	40	82.1
10	[RuH(OAc)(*m*tppms)$_3$]	water	5	2	40	78.7

Conditions: 4 mg soybean lecithin dispersed in 6 ml solvent; 6 mg catalyst; pH of 0.2 m phosphate buffer 6.93.

Furthermore, the C=C double bonds of lipids are buried inside the double layer of the vesicles and are not freely available to the catalysts [24]. Nevertheless, it should be added here that modification of the fluidity of biomembranes does not require removal of a high percentage of unsaturation, since the cells may disrupt easily as a consequence of increased rigidity of their boundary membranes [25]. In the light of this requirement, 5–8% saturation of the constituent lipids is already sufficient to trigger physiological processes, such as, for example, *de novo* synthesis of unsaturated fatty acids to counteract the undesirable fluidity change [26]. At 1 bar H_2 pressure, but otherwise identical conditions, [RuH(OOc)(*m*tppms)$_3$] was even less active, although the hydrogenation proceeded steadily in time (entries 3–5). Increasing the H_2 pressure to 5 bar resulted in a significant increase of conversion up to approximately 10% (entry 6). A similar increase of conversion was observed with [RuH(OAc)(*m*tppms)$_3$] at 25°C (entries 1 and 7). Unbuffered, ion-exchanged water was found to be a better solvent for hydrogenation of soybean liposomes. With [RuH(OAc)(*m*tppms)$_3$] catalyst at 40°C, we found 82.1% remaining unsaturation in water (entry 9); this compares favorably to the 91.6% observed for hydrogenation in phosphate buffer (entry 2). The rate-decreasing effect of phosphate buffer was also observed in hydrogenations of cinnamaldehyde (see above). Finally, increase of the H_2 pressure increased the conversion in water, too, and the lowest remaining unsaturation, 78.7% was determined at 5 bar and 40°C (entry 10). In our earlier experiments [26] we did not see any harmful effect of increased hydrostatic pressure on live cells or protoplasts at P(H_2)~10 bar.

In summary, the carboxylato complexes [RuH(OAc)(*m*tppms)$_3$] and [RuH(OOc)(*m*tppms)$_3$] seem to be suitable for hydrogenation of biomembranes under biologically acceptable conditions. Obviously, a great deal of optimization work is still to be done, including the determination of time course of hydrogenations at various H_2 pressures, the effect of other buffers, osmotics and salts present in culture media, survival response of cells to hydrogenation conditions, etc.). Such experiments are in progress in our laboratory and the results will be presented in due time.

Acknowledgments: The authors are grateful for the support of the Hungarian National Research Foundation through grants No. K101372 and NK100857. The research was also supported by the EU and co-financed by the European Social Fund under the project ENVIKUT (TÁMOP-4.2.2.A-11/1/KONV-2012-0043).

Received January 3, 2014; accepted February 25, 2014; previously published online March 25, 2014

References

[1] Anastas PT, Series Ed. In *Handbook of Green Chemistry – Green Solvents*. Li CJ, Ed., Reactions in Water. Wiley-VCH: Weinheim, Vol. 5, 2010.
[2] Kohlpaintner CW, Fischer RW, Cornils B. *Appl. Catal. A.: General* 2001, 221, 219–225.
[3] Joó F, Tóth Z. *J. Mol. Catal.* 1980, 8, 369–383.
[4] Joó F. *Aqueous Organometallic Catalysis*, Kluwer: Dordrecht, 2001.
[5] Cornils B, Herrmann WA. *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH: Weinheim, 2004.
[6] Schaper LA, Hock SJ, Herrmann WA, Kühn FE. *Angew. Chem. Int. Ed.* 2013, 52, 270–289.

[7] Czégéni CE, Papp G, Kathó Á, Joó F. *J. Mol. Catal. A.: Chemical* 2011, 340, 1–8.
[8] Udvardy A, Kathó Á. *React. Kinet. Catal. Lett.* 2008, 95, 81–87.
[9] Joó F, Tóth Z, Beck MT. *Inorg. Chim. Acta* 1977, 25, L61–L62.
[10] Quinn PJ, Joó F, Vígh L. *Prog. Biophys.Mol. Biol.* 1989, 53, 71–103.
[11] Joó F, Balogh N, Horváth LI, Filep G, Horváth I, Vígh L. *Anal. Biochem*. 1991, 194, 34–40.
[12] Vereb G, Szöllősi J, Matkó J, Nagy P, Farkas T, Vígh L, Mátyus L, Waldmann TA, Damjanovich S. *PNAS* 2003, 100, 8053–8058.
[13] Joó F, Kovács J, Kathó Á, Bényei AC, Decuir T, Darensbourg DJ. *Inorg. Synth*. 1998, 32, 1–8.
[14] Tóth Z, Joó F, Beck MT. *Inorg. Chim. Acta* 1980, 42, 153–161.
[15] Robinson SD, Uttley MF. *J. Chem. Soc., Dalton Trans.* 1973, 1912–1920.
[16] Skapski AC, Stephens FA. *J. Chem. Soc., Dalton Trans.* 1974, 390–395.
[17] Papp G, Horváth H, Laurenczy G, Szatmári I, Kathó Á, Joó F. *Dalton Trans*. 2013, 42, 521–529.
[18] Grosselin JM, Mercier C, Allmang G, Grass F. *Organometal.* 1991, 10, 2126–2133.
[19] Hernandez M, Kalck P. *J. Mol. Catal. A.: Chem.* 1997, 116, 131–146.
[20] Joó F. *Acc. Chem. Res.* 2002, 35, 738–745.
[21] Joó F, Kovács J, Bényei AC, Kathó Á. *Angew. Chem. Int. Ed.* 1998, 37, 969–970.
[22] Papp G, Elek J, Nádasdi L, Laurenczy G, Joó F. *Adv. Synth. Catal*. 2003, 345, 172–174.
[23] Scolaro C, Hartinger CG, Allardyce CS, Keppler BK, Dyson PJ. *J. Inorg. Biochem.* 2008, 102, 1743–1748.
[24] Vígh L, Horváth I, Joó F, Thompson GA Jr. *Biochim. Biophys. A.* 1987, 921, 167–174.
[25] Duda E, Benkő S, Horváth I, Galiba E, Páli T, Joó F, Vígh L. In *Advances in Psychoneuroimmunology*, Bérczi I, Szelényi J, Eds., Plenum Press: New York, 1994, pp. 181–190.
[26] Vígh L, Joó F, Cséplő Á. *Eur. J. Biochem*. 1985, 146, 241–244.

Réka Gombos (1985) is a bioengineer who started working at the Department of Physical Chemistry, University of Debrecen in 2008. Her research area is the synthesis of transition metal complexes and the chemical modification of biomembranes by catalytic hydrogenation with the synthesized complexes.

Ferenc Joó (1949) is a pioneer of aqueous organometallic chemistry, which he has been interested in since the early 1970s. This also includes investigations on modification of biomembranes by catalytic hydrogenation. Presently, he is involved in homogeneous catalytic hydrogenation of carbon dioxide and storage and recovery of H_2. He started working at the Department of Physical Chemistry, University of Debrecen in 1972 and still is there, now as a Professor and member of the Hungarian Academy of Sciences.