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Aqueous–Organic Biphasic Hydrogenation of *trans*-Cinnamaldehyde Catalyzed by Rhodium and Ruthenium Phosphane-Free Porphyrin Complexes

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The synthesis and spectroscopic characterization of new rhodium and ruthenium complexes with a porphyrin, possessing carboxylic groups in the arms of the porphyrin ring, is described. The complexes are completely soluble in water in the presence of a base (KOH or triethylamine). These phosphane-free and air-stable complexes were evaluated as catalysts in the aqueous hydrogenation of *trans*-cinnamaldehyde. Catalysis was more efficient with the ammonium salts of the complexes rather than the corresponding potassium carboxylate salts, preferably in water/toluene rather than in neat water. The effect of catalyst concentration, reaction temperature, hydrogen pressure and methanol addition on the catalytic activity of the complexes in the presence of triethylamine in an aqueous–organic biphasic system was investigated. The catalysts were presumably homogeneous, and could be recycled and reused without any significant difference in activity and selectivity. This is the first time that porphyrin–metal complexes have been used as catalysts for hydrogenation of α,β-unsaturated aldehydes.

Introduction

Homogeneous catalysis with organometallic compounds has been established as an essential tool for synthetic organic chemists with immense academic and industrial interest.[1] It is important to mention that during the first decade of the 21st century three Nobel Prizes have been dedicated to this field of chemistry: Knowles, Noyori and Sharpless for asymmetric catalysis (2001); Chauvin, Grubbs and Schrock for metathesis (2005); and Heck, Negishi and Suzuki for palladium-catalyzed coupling reactions (2010). The mild reaction conditions and high selectivity are some of the advantages of homogeneous catalysis over heterogeneous catalysis. However, wider use is hampered by difficulties in catalyst recovery and recycling, and one possible technology to address this problem is homogeneous, multiphase catalysis.[2] The use of environmentally benign solvents, such as water, in homogeneous catalysis has been an important area of research for green chemistry because water is inexpensive, non-toxic, non-flammable and environmentally sustainable.[3] Biphasic catalysis with water-soluble complexes has attracted great attention since it was successfully applied on an industrial scale (Ruhrchemie/Rhône–Poulenc process for hydroformylation of propene).[4]

Hydrogenation of α,β-unsaturated aldehydes, such as cinnamaldehyde, is a challenge of high importance because the hydrogenation products are important compounds in the synthesis of fine chemicals, pharmaceuticals and fragrances. The aldehyde exhibits two reactive sites for hydrogenation (C=C and C=O), of which the C=C bond is thermodynamically and kinetically favoured. Selective hydrogenation of the C=C bond in cinnamaldehyde leads to hydrocinnamaldehyde, which has a wide range of uses, for example, as a food additive in the flavouring industry[5] and as an intermediate in the preparation of pharmaceuticals used in the treatment of human immunodeficiency virus (HIV),[6] while hydrogenation of the C=O bond produces cinnamyl alcohol used in the manufacture of perfumes.[7] In addition to some excellent results in transfer hydrogenation of aldehydes and ketones in aqueous media, which is a topic that has recently been reviewed by Xiao and Wu,[8] the most common catalysts in homogeneous aqueous biphasic H_2 hydrogenation of unsaturated aldehydes are complexes modified with hydrophilic phosphanes, principally sulfonated phosphanes, such as tris-*meta*-sulfonatophenylphosphane (TPPTS), and *meta*-sulfonatophenyldiphenylphosphane (*m*TPPMS).[9,10] Because phosphorus ligands are toxic and often air sensitive, catalysis under phosphane-free conditions is a challenge of high importance. However, phosphane-free catalysts for homogeneous aqueous hydrogenation of α,β-un-

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saturated aldehydes are limited to $[Rh_4(CH_3CN)_4Cl_4(O_2CnPr)_4]$[11] and metal–protein complexes[12] for H_2 hydrogenation, and $RhCl_3$/methyltrioctylammonium chloride,[13] $[RuCl_2(\eta^6\text{-}p\text{-cymene})L]$ (L = 1-butyl-3-methylimidazol-2-ylidene)[14] and an iridium complex with 4,4′-dihydroxy-2,2′-bipyridine[15] for transfer hydrogenation. In addition, Xiao and co-workers have developed an iridium complex with *N*-(*p*-trifluoromethyltoluenesulfonyl)ethylenediamine ($[Ir(CF_3TsEN)]$) as a phosphane-free versatile catalyst for the hydrogenation of α,β-unsaturated aldehydes in aqueous media, which led to excellent chemoselectivity for the hydrogenation of the C=O bond in both H_2[16] and transfer hydrogenation,[17] and should be regarded as one of the most efficient and environmentally benign catalytic systems for aldehyde reduction to date.

The regioselective hydrogenation of unsaturated aldehydes in aqueous media is strongly dependent on the nature of the active catalyst and the reaction conditions. Classical catalysts are based principally on Rh,[10a–10b,10h,10k–10l,11–13] which are suitable for C=C bond saturation, and Ru,[10a,10c–10g,10i–10j,10l,14] which favour C=O bond hydrogenation. The selectivity is pH dependent. Extensive experimental investigations,[9,10e,10f,10i] as well as theoretical studies,[18] by Joó et al. in acidic or basic aqueous media proved that the selectivity was related to the presence of different hydride complexes at different pH values of the water layer. The hydrogen pressure also has a dramatic effect on selectivity.[10j] Other parameters that affect the selectivity are catalyst concentration, reaction temperature and the addition of a suitable co-solvent. Engineering aspects of aqueous biphasic hydrogenation of α,β-unsaturated aldehydes have also been investigated by theoretical and experimental analyses of mass-transport rates at the gas/liquid and the liquid/liquid interface.[19]

Porphyrins are constructed from four pyrrole units linked by carbon atoms in a planar arrangement with an 18π aromatic character, and have received much attention over a wide range of chemistry and biological processes, including functional dyes, photodynamic therapy, artificial photosynthesis, catalysis, light-emitting materials, non-linear optical materials, metal ligands, and supramolecules.[20] Metalloporphyrins have also been used as hydrogenation catalysts, mainly of olefins, ketones and enamides.[21] In recent years, we have contributed towards the synthesis of new metalloporhyrin derivatives mainly as biomimetic complexes.[22] As a part of our ongoing research in transition-metal homogeneous catalysis under phosphane-free conditions,[23] recently, we reported, for the first time, the use of porphyrins as ligands in the Suzuki reaction in aqueous media in air.[24] Herein, we report the synthesis of new rhodium and ruthenium complexes with a porphyrin and their evaluation for the aqueous biphasic H_2 hydrogenation of *trans*-cinnamaldehyde. To the best of our knowledge, this work represents the first study of the application of porphyrins as ligands for the hydrogenation of cinnamaldehyde, and also one of the very few investigations concerning phosphane-free ligands in the aqueous biphasic hydrogenation of α,β-unsaturated aldehydes.

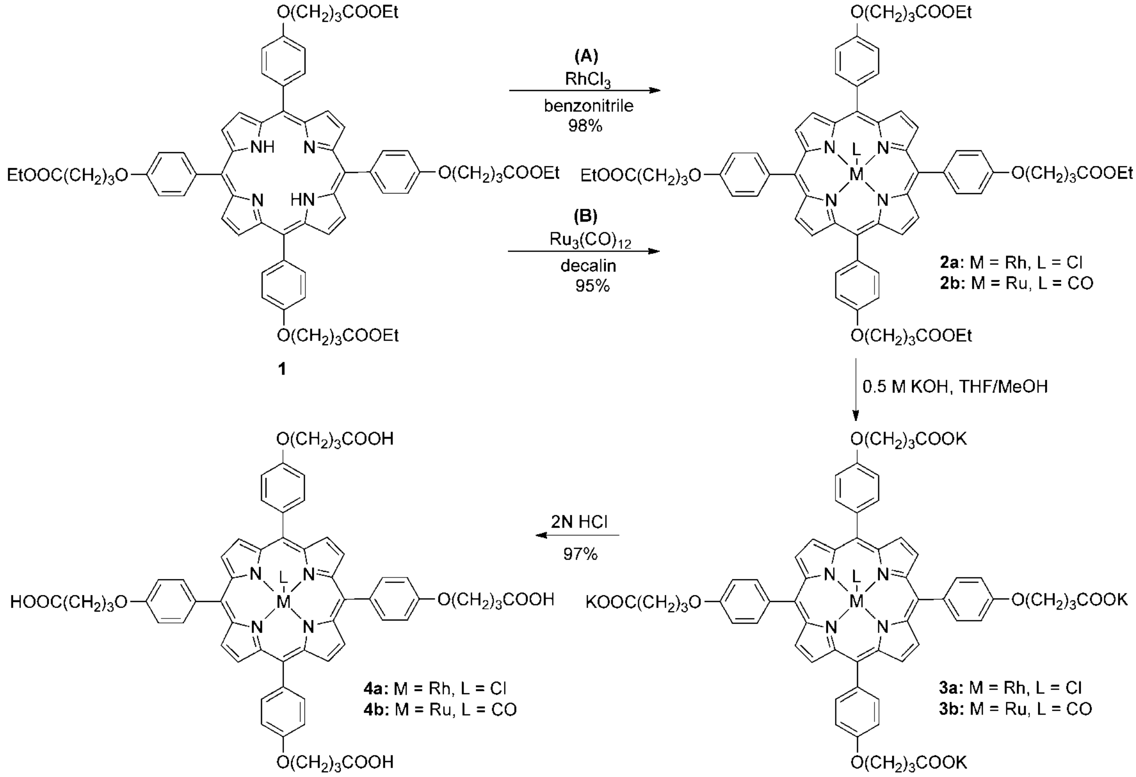
An important problem in homogeneous catalysis is the distinction of true homogeneous catalysis from soluble or other metal-particle catalysis, and this problem has been reviewed in details by Finke and Widegren.[25] Although the activity and/or selectivity of soluble or other metal-particle catalysts is expected to be different from that of true homogeneous catalysts, there is no single definitive experiment for this distinction. Hg^0 is known to poison heterogeneous catalysis and has little or no effect on homogeneous catalysts.[26] On the other hand, Crabtree and Anton discovered that dibenzo[*a*,*e*]cyclooctatetraene (DCT) seemed to bind strongly to metal complexes, but not to metal surfaces, and thus, poisoned some homogeneous catalysts, but not heterogeneous ones.[27] These two tests seem to complement each other, however, there are several limitations, such as failure to produce results for some metal systems. Herein, the above-mentioned tests were used to provide information for the nature of our porphyrin systems (homogeneous vs. heterogeneous).

Results and Discussion

Synthesis and Characterization of Porphyrin Complexes

The preparation of rhodium and ruthenium complexes with a porphyrin, possessing carboxylic groups in the arms of the porphyrin ring, was achieved by the synthetic sequence shown in Scheme 1. Porphyrin **1** was prepared as described previously by our group through the alkylation of 4-hydroxybenzaldehyde with ethyl 4-bromobutyrate and subsequent reaction of the resulting aldehyde with pyrrole.[24] After optimization of the metallating reagent and the reaction conditions, insertion of rhodium was achieved by addition of $RhCl_3$ to **1** in benzonitrile at reflux (path A), and insertion of ruthenium by addition of $[Ru_3(CO)_{12}]$ to **1** in decalin at reflux (path B), leading to the corresponding metal complexes **2a** and **2b** in high yields. The complexes were characterized by spectroscopic techniques. The visible absorption spectrum of porphyrin **1** had a Soret band at 422 nm and four Q bands (519, 555, 589 and 651 nm).[24] In the rhodium complex **2a**, the Soret band was found at 427 nm and the Q bands were reduced to two (537 and 574 nm). In a similar way, the Soret band in ruthenium complex **2b** appeared at 415 nm and the two Q bands were recorded at 531 and 566 nm. These features are characteristic of metal insertion into a porphyrin system. Moreover, the absence of negative chemical shifts in the ^1H NMR spectra of **2a** and **2b**, in contrast to the free base **1**,[24] is also indicative that the porphyrin has fully been metallated. The chemical shift for the carbonyl group Ru–C=O in the ^{13}C NMR spectrum of **2b** is observed at δ = 181.9 ppm, which is in agreement with other ruthenium carbonyl porphyrins.[28] In addition, the measured accurate masses for compounds **2a** and **2b** fit exactly to the proposed formulas $C_{68}H_{68}ClN_4O_{12}Rh$ and $C_{69}H_{68}N_4O_{13}Ru$, respectively.

To avoid possible de-metallation in complexes **2a** and **2b** by hydrolysis of the ester moieties under strongly acidic conditions,[29] these complexes were subjected to saponifica-



Scheme 1. Synthesis of Rh and Ru complexes with a porphyrin possessing carboxylic groups in the arms.

tion with a large excess of an aqueous solution of KOH in THF/MeOH, yielding the corresponding potassium carboxylate salts **3a** and **3b**, respectively. Synthesis and characterization of the corresponding complexes, possessing free carboxylic groups in the arms of the porphyrin ring, was an important challenge, and thus, complexes **4a** and **4b** were synthesized in high yields by the dropwise addition of a 2 N aqueous solution of HCl into an aqueous solution of the corresponding potassium salt until the pH reached 3 and a precipitate was formed. Under these conditions, the complexes were stable and de-metallation did not take place. Complexes **4a** and **4b** were not soluble in water, and thus, purification was achieved by filtration of the reaction mixture and extensive washing with water. The UV/Vis spectra of **4a** and **4b** are similar to those of **2a** and **2b**. The ^{1}H NMR chemical shift for the carboxylic proton in **4a** and **4b** appeared as a broad singlet at about $\delta = 12$ ppm, and the chemical shift for the carbonyl group Ru–C=O in the ^{13}C NMR spectrum of **4b** was observed at $\delta = 180.2$ ppm in agreement with other ruthenium carbonyl porphyrins.[28] In the FTIR spectrum of the ruthenium complex **4b**, the bands corresponding to C=O stretching vibration were observed at 1926 and 1695 cm^{-1} for Ru–C=O and carboxylic C=O, respectively.[30] The measured accurate masses for **4a** and **4b** fit exactly to the proposed formulas $[M - Cl]^+$ $C_{60}H_{52}N_4O_{12}Rh$ and $[M - CO]^+$ $C_{60}H_{52}N_4O_{12}Ru$, respectively. In the solid state, both complexes are air stable for at least six months. As explained above, potassium carboxylate salts **3a** and **3b** were prepared by the addition of a large excess of KOH to **2a** and **2b**, respectively, and this excess KOH could not be completely removed by centrifugation. Therefore, for the use of these complexes as catalysts, syntheses were achieved by the addition of an aqueous solution of KOH to complexes **4a** or **4b**, possessing four free carboxylic groups in a molar ratio of 4:1.

Aqueous Biphasic Hydrogenation of Cinnamaldehyde

General

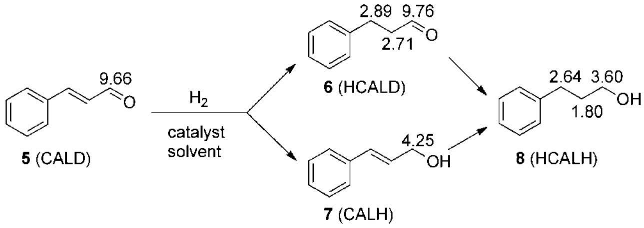
Rhodium and ruthenium porphyrin complexes were evaluated as catalysts in the aqueous hydrogenation of *trans*-cinnamaldehyde (**5**), chosen as a model compound of α,β-unsaturated aldehydes (Scheme 2). Hydrogenations were carried out for 24 h with a **5**/catalyst ratio of 100:1. In the first step, we compared the catalytic activity and selectivity of the potassium carboxylate salts **3a** and **3b** with the corresponding complexes **4a** and **4b**, respectively, which were completely soluble in water in the presence of triethylamine due to the formation of the corresponding ammonium salts (Table 1). These catalytic systems were prepared by mixing metal complex **4a** or **4b** and triethylamine in water in a molar ratio of 1:150. Neat water or a mixture of water/toluene (1:1 v/v) was used as the solvent. Under identical conditions (1.0 mM of the metal complex in water, 60 °C, 30 bar, 24 h), the catalytic activity and selectivity of rhodium complex **3a** for hydrocinnamaldehyde (**6**) is higher in the biphasic system of water/toluene than in neat water as the solvent (Table 1, entry 2 vs. 1). This biphasic system also increases the selectivity of catalyst **4a**/Et$_3$N (Table 1,

Table 1. Hydrogenation of *trans*-cinnamaldehyde catalyzed by potassium or ammonium carboxylate salts of porphyrin complexes with water or water/toluene as the solvent.[a]

Entry	Catalyst	Solvent	T [°C]	P [bar][b]	Conversion [%][c]	Selectivity **6**/**7**/**8** [%][c]
Rh catalysis						
1	**3a**	H_2O	60	30	53	72:12:16
2	**3a**	$H_2O/PhCH_3$[d]	60	30	92	78:6:16
3	**4a**[e]	H_2O	60	30	100	49:14:37
4	**4a**[e]	$H_2O/PhCH_3$[d]	60	30	95	82:–:18
Ru catalysis						
5	**3b**	H_2O	60	100	64	48:24:28
6	**3b**	$H_2O/PhCH_3$[d]	60	100	63	42:30:28
7	**4b**[e]	H_2O	60	100	100	–:–:100
8	**4b**[e]	$H_2O/PhCH_3$[d]	60	100	100	–:32:68

[a] [M] = 1.0 mM in H_2O; cinnamaldehyde/metal complex = 100:1; 24 h. [b] Initial H_2 pressure at room temp. [c] Determined by ^1H NMR spectroscopy. [d] $H_2O/PhCH_3$ (v/v) = 1:1. [e] The water-soluble catalyst was prepared by mixing the metal complex and Et_3N in water in a ratio of 1:150.

entry 4 vs. 3), leading to the best results (95% conversion, 82% selectivity for **6**). Optimization of the catalytic system and the solvent was also performed for ruthenium catalysis under identical conditions (1.0 mM of the metal complex in water, 60 °C, 100 bar, 24 h). The activity of **3b** in neat water or in water/toluene was the same (64 or 63% conversion of **5**), however, the selectivity for cinnamyl alcohol (**7**) was slightly higher in the biphasic system (Table 1, entry 6 vs. 5). The best results were obtained with **4b**/Et_3N, which led to quantitative hydrogenation of **5** (Table 1, entries 7 and 8). Neat water as a solvent led to quantitative hydrogenation of both C=C and C=O bonds and the formation of hydrocinnamyl alcohol (**8**), whereas in the biphasic system the selectivity for **7** was found to be 32% with no formation of **6**.



Scheme 2. Hydrogenation of *trans*-cinnamaldehyde and some characteristic ^1H NMR chemical shifts.

All of the above-mentioned results clearly indicate that hydrogenation of **5** is more efficient with complexes **4a** and **4b** in the presence of triethylamine in the biphasic system of water/toluene, and thus, further investigations were performed by using these catalytic systems. As shown below, the effect of catalyst concentration, reaction temperature, hydrogen pressure, methanol addition, catalyst recycling, and Hg^0 and dibenzo[*a*,*e*]cyclooctatetraene (DCT) tests to distinguish homogeneous from heterogeneous catalysis were studied (Table 2). It was not possible to investigate the effect of acidic or basic conditions on the reactivity and selectivity of the catalysts because the metal complexes are only soluble in aqueous media at basic pH, and they precipitate in acidic pH or even in pH close to 7. In most experiments, both complexes led predominantly to C=C hydrogenation and the formation of **6**. However, the formation of **6** was much higher with rhodium complex **4a** than with ruthenium complex **4b**; the ruthenium complex also led to substantial C=O hydrogenation and the formation of **7**.

Effect of Catalyst Concentration

The concentration of the metal complex in the aqueous solution used in catalysis was 0.2 or 1.0 mM. Under identical conditions (60 °C, 100 bar H_2), a higher catalyst concentration of **4a** increased the reaction rate and the selectivity for **6**, while the formation of **8** decreased (Table 2, entry 1 vs. 2). For **4b** on other hand, increasing the catalyst concentration from 0.2 to 1.0 mM (60 °C, 100 bar H_2), dramatically decreased the formation of **6** (no **6** was observed at 1.0 mM), while **7** and **8** increased with selectivities of 32 and 68%, respectively (Table 2, entry 10 vs. 11). Further increasing the concentration of **4b** to 2.0 mM did not affect the selectivity (Table 2, entry 12).

Effect of Reaction Temperature

The effect of the reaction temperature was investigated for 30 and 60 °C with a catalyst concentration of 1.0 mM in the aqueous solution and 100 bar hydrogen pressure. For both complexes, it was found that a higher temperature increased the conversion of **5**: 36% at 30 °C versus 100% at 60 °C for **4a** (Table 2, entry 6 vs. 2), and 44% at 30 °C versus 100% at 60 °C for **4b** (Table 2, entry 16 vs. 11). Although for **4a**, the selectivity towards the formation of **6** increased slightly at a lower temperature (Table 2, entry 6 vs. 2), it was not a true effect of the temperature because the conversion of **5** was much lower at 30 °C (only 36%) compared with quantitative hydrogenation at 60 °C. Indeed, at 30 °C with a longer reaction time (72 h), which led to 65% conversion of **5**, the selectivity for **6** was found to be 48% compared with 72% at 60 °C (Table 2, entry 7 vs. 2). For **4b**, a lower temperature increased the selectivity for **6** (no **6** at 60 °C vs. 49% at 30 °C) and the selectivities for **7** and **8** decreased (Table 2, entry 16 vs. 11).

Table 2. Aqueous–organic biphasic hydrogenation of *trans*-cinnamaldehyde catalyzed by porphyrin complexes **4a**/Et_3N and **4b**/Et_3N.[a]

Entry	[M] in water [mM]	*T* [°C]	*P* [bar][b]	Conversion [%][c]	Selectivity **6/7/8** [%][c]
Rh complex **4a**					
1	0.2	60	100	94	52:–:48
2	1.0	60	100	100	72:2:26
3	1.0	60	30	95 (cycle 1)	82:–:18 (cycle 1)
				95 (cycle 2)	82:–:18 (cycle 2)
				98 (cycle 3)	81:–:19 (cycle 3)
4 (Hg test)[d]	1.0	60	30	62	88:5:7
5 (DCT test)[e]	1.0	60	30	22	86:4:10
6	1.0	30	100	36	78:7:15
7[f]	1.0	30	100	65	48:17:35
8	1.0	30	30	17	68:16:16
9[g]	1.0	30	30	32	73:13:14
Ru complex **4b**					
10	0.2	60	100	100 (cycle 1)	60:8:32 (cycle 1)
				91 (cycle 2)	64:11:25 (cycle 2)
				88 (cycle 3)	68:7:25 (cycle 3)
11	1.0	60	100	100	–:32:68
12	2.0	60	100	100	–:31:69
13 (Hg test)[d]	1.0	60	100	100	–:39:61
14 (DCT test)[e]	1.0	60	100	100	23:13:64
15	1.0	60	30	76	44:17:39
16	1.0	30	100	44	49:19:32
17[g]	1.0	30	100	78 (cycle 1)	34:25:41 (cycle 1)
				74 (cycle 2)	43:20:37 (cycle 2)

[a] Reaction conditions: metal complex/Et_3N = 1:150; cinnamaldehyde/metal complex = 100:1; $H_2O/PhCH_3$ (v/v) = 1:1; 24 h. [b] Initial H_2 pressure at room temp. [c] Determined by ^1H NMR spectroscopy. [d] About 30 equiv. (with respect to metal complex) of Hg were added. [e] 1 equiv. (with respect to metal complex) of DCT was added. [f] 72 h. [g] 40% MeOH as a co-solvent was added to the aqueous solution.

Effect of Hydrogen Pressure

The effect of hydrogen pressure was considered for experiments performed at 100 and 30 bar at 60 °C with a catalyst concentration 1.0 mM in the aqueous solution (Table 2, entry 2 vs. 3, and 11 vs. 15). The reactivity of both complexes increased at a higher pressure because the solubility of hydrogen in the solvent system increased with pressure. For both complexes, a decrease in the hydrogen pressure led to higher selectivity for **6** and lower selectivities for **7** and **8**; this was probably due to changes in the molecular distributions of the metal among its various hydride species.[10j]

Effect of Methanol as Co-solvent

The effect of adding MeOH (40% v/v in the aqueous phase), instead of using just water, was also investigated and a considerable improvement in the activity of both complexes was found, which led to a higher conversion of **5** (Table 2, entry 8 vs. 9, and 16 vs. 17). The improvement could be attributed to the role of MeOH as a co-solvent, in which all species are partially soluble, enhancing the solubility of **5** and hydrogen in the aqueous phase. However, no firm conclusion on selectivity could be reached because the differences were not really significant and the conversions in these experiments were not quantitative.

Catalyst Recycling

The feasibility of recycling and reusing catalysts **4a**/Et_3N and **4b**/Et_3N was also examined in three of the experiments (Table 2, Rh: entry 3; Ru: entries 10 and 17). After completion of the reaction, the organic and the aqueous phase were easily separated and the substrate and the products were recovered from the toluene layer. Since the porphyrin complexes studied were not air sensitive, all manipulations were performed in air thus facilitating the workup process. The organic layer remained colourless, indicating that no metal leached from the aqueous phase. In two experiments, metal leaching was measured quantitatively with inductive coupled plasma mass spectrometry (ICP–MS) analysis of the organic layers, and it was negligible (0.020 $\mu g\,mL^{-1}$ Table 2, Rh, entry 7; 0.044 $\mu g\,mL^{-1}$ Ru, entry 12). To test the stability of the catalysts, two more catalytic runs were repeated, recycling the same aqueous phase. No significant change was observed in the stability of the complexes. Small deviations in the reaction rates and selectivities are due to the small-scale process.

Mercury Poisoning Experiment and Crabtree's Test

Aqueous biphasic hydrogenation of cinnamaldehyde catalyzed by complexes **4a**/Et_3N and **4b**/Et_3N was also performed in the presence of an excess of metallic mercury (ca. 30 equiv.) (Table 2, entries 4 and 13) or 1 equiv. of DCT (Table 2, entries 5 and 14) under some representative reaction conditions. Hg was present in the stirred solution in the autoclave throughout the reaction (24 h). With both **4a** and **4b**, at the end of the reaction metallic Hg was visible at the bottom of the autoclave and no darkening of the solution took place, indicating that no metallic precipitate was formed as evidence homogeneous catalysts. Crabtree's test for Rh and Ru catalysis was performed by the addition of DCT, the catalytic system and the substrate to the autoclave, which was immediately pressurized with hydrogen, without pre-stirring of DCT with the catalyst. Although this test might fail for a metal–porphyrin complex,[27] and inhibition of a homogeneous catalyst proceeds slowly, which requires DCT and the catalyst to be stirred for hours in the absence of hydrogen,[27] both Rh and Ru catalysis are affected by DCT. For **4a** under identical reaction conditions (60 °C, 30 bar), Hg decreased the conversion of **5** from 95 to 62% (Table 2, entry 4 vs. 3) and DCT decreased the conversion from 95 to only 22% (Table 2, entry 5 vs. 3) without any significant affect on the selectivity. These results provide evidence that catalysis is mainly homogeneous; however, partial heterogeneous catalysis should not be excluded. For **4b** under identical reaction conditions (60 °C, 100 bar), the conversion of **5** remained quantitative in the absence or the presence of Hg without any significant difference in the selectivity (Table 2, entry 13 vs. 11). DCT did not affect the conversion of **5** probably due to a slow binding with the metal complex and/or the harsh conditions (60 °C, 100 bar); however, the selectivity was affected by the presence of DCT (Table 2, entry 14 vs. 11), indicating that Ru catalysis was presumably homogeneous.

Conclusions

New phosphane-free porphyrin complexes with rhodium and ruthenium were synthesized and characterized. The complexes were completely soluble in water in the presence of a base (KOH or Et_3N) and were used as catalysts for the hydrogenation of *trans*-cinnamaldehyde. Catalysis was more efficient with the ammonium salts of the complexes rather than the corresponding potassium carboxylate salts, preferably in an aqueous–organic biphasic system instead of in neat water. Further investigation into the hydrogenation of cinnamaldehyde by these complexes in the presence of triethylamine in water/toluene as a solvent led to interesting conclusions. The activity of both complexes increased with increasing catalyst concentration, reaction temperature or hydrogen pressure. The addition of methanol as a co-solvent also improved the activity. For **4a**, the selectivity towards hydrogenation of the C=C bond and formation of **6** (max. 88%) was enhanced by (1) increasing the catalyst concentration, (2) increasing the temperature and (3) decreasing the hydrogen pressure. For **4b**, the selectivity towards the hydrogenation of the C=O bond and formation of **7** was improved by (1) increasing the catalyst concentration, (2) increasing the temperature and (3) increasing the hydrogen pressure. At 60 °C and 100 bar of pressure with 1.0 mM of ruthenium in water, no **6** was observed and the selectivity for **7** was 32%, while the majority of the substrate (68%) was hydrogenated at both C=C and C=O bonds. Moderate selectivity was also reported by Joó and Fekete in the Ru-catalyzed transfer hydrogenation of cinnamaldehyde using a phosphane-free ligand.[14] Although the mechanism and the intermediate active species for the Ru-catalyzed aqueous biphasic selective hydrogenation of cinnamaldehyde using hydrophilic phosphanes has been investigated in detail,[9,10e,10f,10i,18] no mechanistic study for the phosphane-free analogues has been performed, and perhaps the intermediate species play a crucial role in regioselectivity.

The catalysts could be easily recycled by simple phase separation and were reused without any significant change in activity and selectivity. A combination of mercury and Crabtree's tests provided evidence that catalysis was presumably homogeneous. The phosphane-free catalytic systems reported herein are air stable in the solid state, water soluble in the presence of a base, and convenient for catalysis in aqueous media. This is the first study of the application of porphyrins as ligands for the hydrogenation of cinnamaldehyde, and also one of the very few investigations concerning phosphane-free ligands in the aqueous biphasic hydrogenation of α,β-unsaturated aldehydes. The results provide important information on the catalytic activity of these systems, which should be useful to those in the scientific community actively researching the area of aqueous catalysis, and perhaps for a wide range of reactions.

Experimental Section

General: Porphyrin **1** was prepared by a known procedure.[24] All other chemicals were commercially available. Hydrogenation studies were performed in a stainless-steel autoclave (300 mL) with magnetic stirring. FTIR spectra were recorded on a Thermo-Electron Nicolet 6700 instrument. NMR spectroscopy measurements were made by using Bruker AMX-500, Bruker DPX-300 or Varian 300 spectrometers. UV/Vis spectra were recorded on a Shimadzu MultiSpec-1501 spectrometer. Gas chromatography was undertaken by using a Varian Star 3400 CX instrument equipped with a 30 m × 0.53 mm DB5 column. Electron impact GC–MS was carried out by using a Varian Saturn 2000 spectrometer equipped with a 30 m × 0.25 mm DB5-MS column. HRMS were determined by using a Thermo Scientific LTQ Orbitrap Velos (ESI) spectrometer for **2a**,**b** or a Bruker ultrafleXtreme MALDI–TOF/TOF spectrometer for **4a**,**b**. Metal leaching into the organic layer was measured by ICP–MS performed on a Thermo Scientific X series ICP–MS instrument equipped with an impact bead spray chamber and a pneumatic nebulizer. A peristaltic pump was used to deliver samples and to add an indium internal standard solution through a T connection into the sample stream. For Rh detection, a sample of the organic layer was dried in vacuo, and then a 2% aqueous solution of HNO_3 was added. For Ru detection, after drying a sample of the organic layer, concentrated HNO_3 was added and the sample was dried in vacuo then a 5% aqueous solution of HCl was added.

Rh/Porphyrin Complex 2a: Porphyrin **1** (150 mg, 132 μmol) was dissolved in benzonitrile (35 mL) under a nitrogen atmosphere and heated at reflux for 5 min. Then, $RhCl_3$ (55 mg, 264 μmol) was added and the solution was heated at reflux for an additional 3 h, cooled, and dried under vacuum with heating. Then, CH_2Cl_2 (40 mL) was added and the mixture was washed with an aqueous solution of NaCl (2× 30 mL). The organic layer was dried with Na_2SO_4, filtered, concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOH, 100:1) to obtain **2a** as a dark red solid (164 mg, 98%). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.94 (s, 8 H, Ar), 8.17 (d, J = 6.5 Hz, 4 H, Ar), 8.03 (d, J =

7.0 Hz, 4 H, Ar), 7.27 (d, J = 6.0 Hz, 8 H, Ar), 4.29 (m, 16 H, CH_2), 2.72 (t, J = 7.5 Hz, 8 H, CH_2), 2.33 (q, J = 6.5 Hz, 8 H, CH_2), 1.36 (t, J = 7.0 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.3 (CO), 158.6, 142.1, 135.7, 135.0, 132.2, 120.5 and 112.6 (Ar*C* and porphyrin ring *C*), 67.0 (CH_2), 60.5 (CH_2), 29.9 (CH_2), 24.8 (CH_2), 14.2 (CH_3) ppm. UV/Vis (CH_2Cl_2): λ (ε, $\mathrm{mM}^{-1}\mathrm{cm}^{-1}$) = 427 (71.2), 537 (9.1), 574 (5.6) nm. HRMS (ESI^+): calcd. for $C_{68}H_{68}ClN_4O_{12}Rh[M]^+$ 1271.3604; found 1271.3582.

Ru/Porphyrin Complex 2b: A mixture of porphyrin **1** (150 mg, 132 µmol), $[Ru_3(CO)_{12}]$ (150 mg, 235 µmol) and decalin (50 mL) under a nitrogen atmosphere was heated at reflux for 2 h, after which time, it was cooled and dried under vacuum with heating. Then, CH_2Cl_2 (40 mL) was added and the mixture was washed with an aqueous solution of NaCl (2× 30 mL). The organic layer was dried with Na_2SO_4, filtered, concentrated and the residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOH, 100:0.3) to obtain **2b** as a dark red solid (158 mg, 95%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.74 (s, 8 H, Ar), 8.12 (dd, J = 8.4, J = 2.1 Hz, 4 H, Ar), 8.01 (dd, J = 8.3, J = 2.1 Hz, 4 H, Ar), 7.14 (m, 8 H, Ar), 4.03 (m, 8 H, CH_2), 3.85 (m, 8 H, CH_2), 2.24 (m, 8 H, CH_2), 1.98 (m, 8 H, CH_2), 1.15 (t, J = 7.2 Hz, 12 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.9 (Ru-*C*O), 173.2 (ester CO), 158.2, 144.3, 135.3, 135.1, 134.8, 131.6, 121.4, 112.6 and 112.4 (Ar*C* and porphyrin ring *C*), 66.8 (CH_2), 60.4 (CH_2), 30.5 (CH_2), 24.5 (CH_2), 14.0 (CH_3) ppm. UV/Vis (CH_2Cl_2): λ (ε, $\mathrm{mM}^{-1}\mathrm{cm}^{-1}$) = 415 (97.7), 531 (10.1), 563 (5.6) nm. HRMS (ESI^+): calcd. for $C_{69}H_{68}N_4O_{13}Ru[M]^+$ 1262.3841; found 1262.3843.

Rh/Porphyrin Complex 4a: A solution of **2a** (100 mg, 79 µmol) in THF (100 mL), methanol (61 mL) and aqueous 0.5 M KOH (67 mL) was stirred at room temperature for 24 h. Then, the solution was evaporated to dryness to afford the potassium salt **3a** as a red solid, which was used further without any purification. An amount of 90% of the weight of this solid was dissolved in distilled water (100 mL), and a 2 N aqueous solution of HCl was added dropwise until the pH reached 3 and a precipitate formed. It was filtered and washed several times with distilled water. Then, it was dried under vacuum to afford **4a** as a purple solid (80 mg, 97%). ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 12.21 (br. s, 4 H, COOH; appeared on a high enlargement of the spectrum), 8.93 (m, 8 H, Ar), 8.14 (m, 8 H, Ar), 7.41 (m, 8 H, Ar), 4.30 (m, 8 H, CH_2), 2.56 (m, 8 H, CH_2), 2.14 (m, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 174.3 (CO), 158.4, 141.6, 134.9, 131.9, 121.1 and 112.9 (Ar*C* and porphyrin ring *C*), 66.5 (CH_2), 30.4 (CH_2), 24.5 (CH_2) ppm. UV/Vis (H_2O/Et_3N): λ (ε, $\mathrm{mM}^{-1}\mathrm{cm}^{-1}$) = 422 (130.4), 535 (22.4), 572 (9.7) nm. HRMS (MALDI–TOF): calcd. for $C_{60}H_{52}N_4O_{12}Rh[M - Cl]^+$ 1123.2631; found 1123.2649.

Ru/Porphyrin Complex 4b: A solution of **2b** (100 mg, 79 µmol) in THF (100 mL), methanol (60 mL) and aqueous 0.5 M KOH (70 mL) was stirred at room temperature for 24 h. Then, the solution was evaporated to dryness to afford **3b** as a red solid, which was used further without any purification. It was dissolved in distilled water (100 mL), and a 2 N aqueous solution of HCl was added dropwise until the pH reached 3 and a precipitate formed. It was filtered and washed several times with distilled water. Then, it was dried under vacuum to afford **4b** as a purple solid (87 mg, 96%). FTIR: $\tilde{\nu}$ = 3227 (OH), 1926 (C=O attached to Ru), 1695 (C=O carboxylic), 1229 (C–O carboxylic) cm^{-1}. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 12.19 (br. s, 4 H, COOH), 8.60 (s, 8 H, Ar), 8.08 (d, J = 7.8 Hz, 4 H, Ar), 7.96 (d, J = 8.1 Hz, 4 H, Ar), 7.32 (m, 8 H, Ar), 4.28 (t, J = 6.0 Hz, 8 H, CH_2), 2.56 (m, 8 H, CH_2), 2.13 (t, J = 6.6 Hz, 8 H, CH_2) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 180.2 (Ru-*C*O), 174.2 (ester CO), 158.1, 143.4, 134.8, 133.9, 131.3, 121.1 and 112.6 (Ar*C* and porphyrin ring *C*), 66.8 (CH_2), 30.3 (CH_2), 24.5 (CH_2) ppm. UV/Vis (CH_2Cl_2): λ (ε, $\mathrm{mM}^{-1}\mathrm{cm}^{-1}$) = 413 (143.4), 533 (11.9), 569 (6.7) nm. HRMS (MALDI–TOF): calcd. for $C_{60}H_{52}N_4O_{12}Ru[M - CO]^+$ 1122.2620; found 1122.2611.

General Experimental Procedure for the Hydrogenation of Cinnamaldehyde: In a typical experiment, metal complex (4.0 µmol), triethylamine (80 µL, 0.6 mmol) and distilled water (4 mL) were mixed in a Schlenk flask under argon and stirred at room temperature for 2–3 min, until a red (Rh) or brown (Ru) homogeneous solution formed. Then, cinnamaldehyde (50 µL, 0.4 mmol) and toluene (4 mL) were added, and the reaction mixture was transferred by using a syringe under argon to the autoclave, which was then closed, pressurized with hydrogen (30 or 100 bar) and brought to the appropriate temperature (30 or 60 °C). After 24 h of stirring, the autoclave was cooled to room temperature, the pressure was carefully released, and the organic phase was separated, washed with water, dried with Na_2SO_4, filtered, passed through Celite and analyzed by GC, GC–MS and ^1H NMR spectroscopy. Conversions and selectivities were determined by ^1H NMR spectroscopy. Some of the characteristic ^1H NMR chemical shifts are given in Scheme 2. For the reuse of the catalyst, the aqueous phase of the reaction mixture was separated, washed with toluene, degassed, treated again with triethylamine, cinnamaldehyde and toluene under argon, and the reaction mixture was transferred to the autoclave for the next cycle as described above.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra for the new compounds **2a**, **2b**, **4a** and **4b**.

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[1] B. Cornils, W. A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds, A Comprehensive Handbook in Three Volumes*, 2nd ed., Wiley-VCH, Weinheim, **2002**.

[2] B. Cornils, W. A. Herrmann, I. T. Horvath, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt (Eds.), *Multiphase Homogeneous Catalysis*, Wiley-VCH, Weinheim, **2005**.

[3] For selected books and reviews, see: a) P. T. Anastas, J. C. Warner (Eds.), *Green Chemistry: Theory and Practice*, Oxford University Press, **1998**; b) B. Cornils, W. A. Herrmann "Aqueous-Phase Catalysis" in *Multiphase Homogeneous Catalysis* (Eds. B. Cornils, W. A. Herrmann, I. T. Horvath, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt), Wiley-VCH, Weinheim, **2005**, vol. 1, pp. 25–308; c) P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, *39*, 301–312; d) V. Polshettiwar, A. Decottignies, C. Len, A. Fihri, *ChemSusChem* **2010**, *3*, 502–522.

[4] a) E. G. Kuntz, *Chemtech* **1987**, *17*, 570–575; b) B. Cornils, E. Kuntz, *J. Organomet. Chem.* **1995**, *502*, 177–186.

[5] K. Bauer, D. Garbe in *Ullman's Encyclopedia*, 3rd ed., VCH, New York, **1988**, vol. A11, p. 141.

[6] A. Müller, J. Bowers (First Chemical Corporation), WO 99/08989, **1999**.

[7] M. Lashdaf, A. O. I. Krause, M. Lindblad, M. Tiitta, T. Venäläinen, *Appl. Catal. A* **2003**, *241*, 65–75.

[8] For a review, see: X. Wu, J. Xiao, *Chem. Commun.* **2007**, 2449–2466.

[9] For a review, see: F. Joó, *Acc. Chem. Res.* **2002**, *35*, 738–745.

[10] For selected papers, see: a) J. M. Grosselin, C. Mercier, G. Allmang, F. Grass, *Organometallics* **1991**, *10*, 2126–2133; b) D. J. Darensbourg, N. W. Stafford, F. Joó, J. H. Reibenspies, *J. Organomet. Chem.* **1995**, *488*, 99–108; c) A. Andriollo, J. Carrasquel, J. Mariño, F. A. López, D. E. Páez, I. Rojas, N. Valencia, *J. Mol. Catal. A* **1997**, *116*, 157–165; d) R. A. Sánchez-Delgado, M. Median, F. López-Linares, A. Fuentes, *J. Mol. Catal. A* **1997**, *116*, 167–177; e) F. Joó, J. Kovács, A. C. Bényei, Á. Kathó, *Catal. Today* **1998**, *42*, 441–448; f) F. Joó, J. Kovács, A. C. Bényei, Á. Kathó, *Angew. Chem. Int. Ed.* **1998**, *37*, 969–970; g) F. López-Linares, M. G. Gonzalez, D. E. Páez, *J. Mol. Catal. A* **1999**, *145*, 61–68; h) A. Fukuoka, W. Kosugi, F. Morishita, M. Hirano, L. McCaffrey, W. Henderson, S. Komiya, *Chem. Commun.* **1999**, 489–490; i) G. Papp, J. Kovács, A. C. Bényei, G. Laurenczy, L. Nádasdi, F. Joó, *Can. J. Chem.* **2001**, *79*, 635–641; j) G. Papp, J. Elek, L. Nádasdi, G. Laurenczy, F. Joó, *Adv. Synth. Catal.* **2003**, *345*, 172–174; k) K. Nuithitikul, M. Winterbottom, *Chem. Eng. Sci.* **2004**, *59*, 5439–5447; l) K. Nuithitikul, M. Winterbottom, *Catal. Today* **2007**, *128*, 74–79.

[11] Z. Yang, M. Ebihara, T. Kawamura, *J. Mol. Catal. A* **2000**, *158*, 509–514.

[12] M. Marchetti, F. Minello, S. Paganelli, O. Piccolo, *Appl. Catal. A* **2010**, *373*, 76–80.

[13] J. Blum, I. Pri-Bar, H. Alper, *J. Mol. Catal.* **1986**, *37*, 359–367.

[14] M. Fekete, F. Joó, *Collect. Czech. Chem. Commun.* **2007**, *72*, 1037–1045.

[15] Y. Himeda, N. Onozawa-Komatsuzaki, S. Miyaxawa, H. Sugihara, T. Hirose, K. Kasuga, *Chem. Eur. J.* **2008**, *14*, 11076–11081.

[16] X. Wu, C. Corcoran, S. Yang, J. Xiao, *ChemSusChem* **2008**, *1*, 71–74.

[17] X. Wu, J. Liu, X. Li, A. Zanotti-Gerosa, F. Hancock, D. Vinci, J. Ruan, J. Xiao, *Angew. Chem. Int. Ed.* **2006**, *45*, 6718–6722.

[18] a) G. Kovács, G. Ujaque, A. Lledós, F. Joó, *Organometallics* **2006**, *25*, 862–872; b) A. Rossin, G. Kovács, G. Ujaque, A. Lledós, F. Joó, *Organometallics* **2006**, *25*, 5010–5023.

[19] Y. Önal, P. Claus, *Top. Organomet. Chem.* **2008**, *23*, 163–191.

[20] Recent selected reviews: a) H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 1011–1021; b) L. Cuesta, J. L. Sessler, *Chem. Soc. Rev.* **2009**, *38*, 2716–2729; c) C.-M. Che, J.-S. Huang, *Chem. Commun.* **2009**, 3996–4015; d) C. J. Medforth, Z. Wang, K. E. Martin, Y. Song, J. L. Jacobsen, J. A. Shelnutt, *Chem. Commun.* **2009**, 7261–7277; e) M. Jurow, A. E. Schuckman, J. D. Batteas, C. M. Drain, *Coord. Chem. Rev.* **2010**, *254*, 2297–2310; f) S. Mohnani, D. Bonifazi, *Coord. Chem. Rev.* **2010**, *254*, 2342–2362.

[21] For recent selected papers and reviews, see: a) W. Mori, S. Takamizawa, C. N. Kato, T. Ohmura, T. Sato, *Microporous Mesoporous Mater.* **2004**, *73*, 31–46; b) T. Sato, W. Mori, C. N. Kato, E. Yanaoka, T. Kuribayashi, R. Ohtera, Y. Shiraishi, *J. Catal.* **2005**, *232*, 186–198; c) X.-B. Jiang, L. Lefort, P. E. Goudriaan, A. H. M. de Vries, P. W. N. M. van Leeuwen, J. G. de Vries, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2006**, *45*, 1223–1227; d) E. Nelkenbaum, I. Dror, B. Berkowitz, *Chemosphere* **2007**, *68*, 210–217; e) K. Junge, K. Schröder, M. Beller, *Chem. Commun.* **2011**, *47*, 4849–4859.

[22] For selected papers, see: a) G. A. Spyroulias, A. P. Despotopoulos, C. P. Raptopoulou, A. Terzis, D. de Montauzon, R. Poilblanc, A. G. Coutsolelos, *Inorg. Chem.* **2002**, *41*, 2648–2659; b) E. M. Davoras, A. G. Coutsolelos, *J. Inorg. Biochem.* **2003**, *94*, 161–170; c) D. Daphnomili, C. Raptopoulou, J.-H. Agondanou, S. Bénazeth, A. Terzis, A. G. Coutsolelos, *Inorg. Chem.* **2004**, *43*, 4363–4371; d) K. Ladomenou, G. Charalambidis, A. G. Coutsolelos, *Tetrahedron* **2007**, *63*, 2882–2887; e) G. Charalambidis, K. Ladomenou, B. Boitrel, A. G. Coutsolelos, *Eur. J. Org. Chem.* **2009**, 1263–1268.

[23] a) D. Kovala-Demertzi, P. N. Yadav, M. A. Demertzis, J. P. Jasinski, F. J. Andreadaki, I. D. Kostas, *Tetrahedron Lett.* **2004**, *45*, 2923–2926; b) I. D. Kostas, F. J. Andreadaki, D. Kovala-Demertzi, C. Prentjas, M. A. Demertzis, *Tetrahedron Lett.* **2005**, *46*, 1967–1970; c) I. D. Kostas, G. A. Heropoulos, D. Kovala-Demertzi, P. N. Yadav, J. P. Jasinski, M. A. Demertzis, F. J. Andreadaki, G. Vo-Thanh, A. Petit, A. Loupy, *Tetrahedron Lett.* **2006**, *47*, 4403–4407; d) I. D. Kostas, B. R. Steele, A. Terzis, S. V. Amosova, A. V. Martynov, N. A. Makhaeva, *Eur. J. Inorg. Chem.* **2006**, 2642–2646.

[24] I. D. Kostas, A. G. Coutsolelos, G. Charalambidis, A. Skondra, *Tetrahedron Lett.* **2007**, *48*, 6688–6691.

[25] For a review, see: J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317–341.

[26] For selected papers, see: a) G. M. Whitesides, M. Hackett, R. L. Brainard, J. P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown, E. M. Staudt, *Organometallics* **1985**, *4*, 1819–1830; b) A. N. Lewis, *J. Am. Chem. Soc.* **1986**, *108*, 743–749; c) R. van Asselt, C. J. Elsevier, *J. Mol. Catal.* **1991**, *65*, L13–L19; d) Y. Lin, R. G. Finke, *Inorg. Chem.* **1994**, *33*, 4891–4910; e) K. S. Weddle, J. D. Aiken III, R. G. Finke, *J. Am. Chem. Soc.* **1998**, *120*, 5653–5666; f) J. Schulz, A. Roucoux, H. Patin, *Chem. Eur. J.* **2000**, *6*, 618–624; g) G. Süss-Fink, M. Faure, T. R. Ward, *Angew. Chem. Int. Ed.* **2002**, *41*, 99–101.

[27] D. R. Anton, R. H. Crabtree, *Organometallics* **1983**, *2*, 855–859.

[28] S. S. Eaton, G. R. Eaton, *Inorg. Chem.* **1976**, *15*, 134–139.

[29] M. Kumar, P. Neta, T. P. G. Sutter, P. Hambright, *J. Phys. Chem.* **1992**, *96*, 9571–9575.

[30] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**, pp. 213–220.

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