Sulfonated Phosphine Ligands in the Ruthenium Catalyzed Biphasic Hydrogenation of Unsaturated Hydrocarbons

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Abstract

The hydrogenation of monocyclic aromatic hydrocarbons by ruthenium catalysts has been investigated in the presence of sulfonated monophosphine ligands with different stereoelectronic properties under biphasic conditions. The effects of (i) the number of sulfonate groups, (ii) the steric demand of the ligand and (iii) the σ -donor ability of the phosphorus atom have been investigated in the catalytic reactions. The TEM analysis of the catalytically active systems revealed that in situ formed soluble ruthenium nanoparticles (RuNPs) are responsible for the catalytic turnover. The Ru/sulfonated phosphine system with the properly tuned ligand exhibited high activity (8800 h^{-1}) and selectivity in the hydrogenation of benzene to cyclohexane. Furthermore, the aqueous phase containing RuNPs could be recycled four times without a considerable loss of activity.

Graphic Abstract

Keywords Ruthenium nanoparticle · Sulfonated phosphine · Arene hydrogenation · Biphasic hydrogenation

1 Introduction

Transition metal catalyzed reactions performed in aqueous–organic biphasic media represent a fruitful approach to the highly efficient and sustainable synthesis of organic

chemicals [1, 2]. Water is an attractive solvent due to its low cost, easy availability, nontoxic and nonflammable nature [3–5]. Moreover, the application of biphasic catalytic conditions represents a promising alternative for the easy recovery and recycling of the expensive transition metal catalyst. Water-soluble transition metal catalysts can be obtained by combining the corresponding metal precursor with a water-soluble ligand [6]. Amongst these types of ligands sulfonated phosphine sodium-salts can be mentioned as interesting examples due to their structural versatility, high solubility in the aqueous phase and straightforward

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synthesis. The most representative member of this ligand family, trisulfonated triphenylphosphine sodium salt (TPPTS) is industrially applied in the aqueous-organic hydroformylation of propene and butene [7] as well as in the Suzuki–Miyaura coupling of aryl bromides [8]. Despite the impressive progress in the synthesis and catalytic application of sulfonated phosphines in the last decade, a significant number of novel applications have been developed recently. Thus, sulfonated phosphines are extensively used in hydroformylation [9–13], Suzuki–Miyaura coupling [14, 15], hydrogenation of unsaturated esters [16], hydrogenation of levulinic acid to γ -valerolactone in aqueous media [17, 18], catalytic hydrogenation of bicarbonate [19], hydrogenation of aldehydes [20] or heteroaromatic compounds [21]. A challenging application of transition metal catalysts modified by water-soluble phosphines is the hydrogenation of aromatic hydrocarbons under biphasic conditions.

The complete hydrogenation of aromatic hydrocarbons to cycloparaffins represents a great deal of interest that can mainly be attributed to the growing demand for diesel fuels with low aromatic content [22, 23]. The aromatic compounds can be responsible for low cetane number of diesel fuels, the high smoke point in jet fuels, and most importantly for the particulate emissions in the exhaust gas. Additionally, the growing concerns about the high carbon dioxide concentration in the atmosphere render fuels with high hydrogen to carbon ratio more suitable [24, 25]. Moreover, cyclohexane, that is produced mainly by the catalytic benzene hydrogenation, is a key intermediate for the synthesis of industrially relevant raw materials such as cyclohexanone, cyclohexanol, caprolactone and caprolactam [26]. Furthermore, cyclohexane is an excellent non-polar solvent and is considered to be greener than *n*-pentane and *n*-hexane [27].

The complete hydrogenation of benzene and its alkylated derivatives to (alkyl)cycloparaffins is realized mainly by heterogeneous supported metal catalysts. It is however, important to note that these processes suffer from several drawbacks. As benzene hydrogenation is strongly exothermic,

reaction conditions (pressure, temperature, residence time) must precisely be controlled in heterogeneous catalytic reactions to achieve complete conversion. Additionally, heterogeneous catalysts such as supported noble metal catalysts or Raney-Ni, frequently used in benzene hydrogenation, can easily be poisoned by sulfur containing feedstocks [28]. The high pressure and temperature required for the hydrogenation process may also promote several side-reactions as hydrocracking or isomerization leading to alkylated cycloparaffins as byproducts. The difficulties connected to the safe handling of several highly pyrophoric heterogeneous catalyst (Raney-Ni or Ziegler-type catalysts based on triethylaluminum with a nickel or cobalt salt) may also raise serious concerns.

As a result, the development of stable, active, selective and safer catalytic systems for the hydrogenation of aromatic rings is highly desirable. The additional aim of such research is to increase the energy efficiency and to decrease the environmental impact of the hydrogenation process. In this context, the neat aromatic hydrogenation by using water-soluble transition metal catalysts under biphasic conditions represents a fruitful approach towards the synthesis of cycloparaffins. Ruthenium catalysts drew a considerable attention in the field of aromatic hydrogenation as they are highly active and selective catalysts [29] and the precursors are relatively inexpensive compared to the corresponding rhodium or platinum containing compounds [30].

The application of sulfonated phosphines is highly popular in ruthenium catalyzed reactions. Interestingly, however, in arene hydrogenation the use of sulfonated phosphines is less preceded [31–36] and the ligand scope is rather narrow (Fig. 1) despite their promising catalytic properties. In recent years, Papadogianakis and coworkers reported the use of simple Rh/TPPTS complex for the homogeneous hydrogenation of benzene under biphasic conditions [37]. Extremely high catalytic activity ($> 204,000 \text{ h}^{-1}$) could be obtained under optimized conditions. Philippot et al. described the synthesis and catalytic application of ruthenium nanoparticles (RuNPs) stabilized by tetrasulfonated diphosphines of different tether length (Fig. 1) [35]. It has been found that the activity of the catalyst increased with the length of the ligand backbone. Bajaj and coworkers reported on the application of a newly developed sulfonated phosphine, BiphTS [38], in the ruthenium catalyzed hydrogenation of benzene [36]. The in situ prepared catalyst proved to be highly active and could be recycled four times without considerable loss of activity.

Despite the fact that the use of sulfonated phosphines represents an elegant approach for the aqueous–organic biphasic hydrogenation of arenes, no clear interpretation of the steric and electronic factors influencing their catalytic activity has been available yet in such reactions.

Fig. 1 Sulfonated phosphines used in ruthenium catalyzed arene hydrogenation

Undoubtedly, through the understanding of these factors the stereoelectronic properties of the ligands could be fine-tuned to enhance catalytic performance in these catalytic processes.

The present report focuses on the investigation of the stereoelectronic features of sulfonated phosphine ligands in the ruthenium catalyzed arene hydrogenation under biphasic conditions. In order to shed light on the structure–activity relationships we have evaluated a series of sulfonated monophosphine ligands with different stereoelectronic properties. Specifically, eight mono-, di- and trisulfonated systems were used to study (i) the effect of sulfonation degree, (ii) the influence of electron-donating substituents and (iii) the steric demand of the ligand on catalytic activity (Fig. 2).

2 Results and Discussion

2.1 Characterization of the Phosphine Ligands

Sulfonated monophosphine ligands **1–3** (Fig. 2) with different stereoelectronic properties have been used to evaluate their catalytic properties in the aqueous biphasic hydrogenation of aromatic hydrocarbons. Ligands **1–3** were synthesized according to the literature procedures [39–42]. In order to rationalize their catalytic behavior we characterized their stereoelectronic nature. Ligand sets **1**, **2** and **3** differ in their sulfonation degree that strongly affects their steric and electronic properties. The sulfonate group can be identified as an electron withdrawing substituent, therefore the electron donating ability of the phosphine is reduced by enhancing the number $-\text{SO}_3^-$ substituents [43]. Additionally, the introduction of a sulfonate group in the *meta*

position increases the Tolman cone angle [44] significantly (eg. **1a** vs. **3a**, Table 1) [45, 46]. It is therefore not surprising that *o*-methyl substituents even more strongly affect the steric demand of the ligands [45]. In compounds with *ortho*- or *diortho*-substituted rings, the Tolman cone angle is drastically increased compared to the parent sulfonated phosphines [47]. (It is interesting to note that the effect of their increased steric demand on their catalytic properties is documented in other homogeneous catalytic reactions [48, 49].) As the steric congestion around the phosphorus is significantly increased, it is reasonable to assume that in these cases the lone pair of the phosphorus atom is less available to coordination. It is also important to mention that ligands with *p*-substituents show no significant difference in the cone angles compared to their unsubstituted analogues [50]. Ligand **2c** with methyl-substituent connected directly to phosphorus is assumed to have smaller cone angle than other phosphines presented in this study.

A simple way of evaluating the σ -donor ability of the phosphorus functionalities is by measuring the magnitude of the $^1J(^{77}\text{Se}-^{31}\text{P})$ coupling constant in the ^{77}Se isotopomer of the corresponding phosphine-selenide [51, 52]. This value is roughly inversely proportional to the basicity of the phosphine. Thus, to evaluate the electronic nature of the ligands we have synthesized their selenides in the reaction of the phosphines with elemental selenium. The corresponding $^1J(^{77}\text{Se}-^{31}\text{P})$ coupling constants are summarized in Table 1. As expected, (i) the introduction of sulfonate substituents decreased the basicity (eg. ligands **1a**, and **3a**), (ii) the presence of methyl or methoxy groups increased the σ -donor character of the ligands. Enhanced σ -donor ability makes the phosphorus lone pair more available to coordination to the transition metal.

2.2 Catalytic Hydrogenations

The catalytic activity of ruthenium catalysts modified by water-soluble ligands **1–3** was studied in the aqueous biphasic hydrogenation of aromatic hydrocarbons and several olefins. The Ru/sulfonated phosphine system was synthesized in situ, by simply mixing the corresponding ligand with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ precursor in water. At first, the ligands were screened at a phosphine/ruthenium molar ratio of 4, at 120 °C and 50 bar H_2 pressure in the hydrogenation of neat benzene under biphasic conditions using non-ionic surfactant Brij-L4, according to literature procedure [36].

In the first set of experiments, the effect of the ligands' structure was evaluated in the catalytic reaction. The results achieved by using ligands **1–3** are compiled in Table 2. Catalysts modified with sterically less demanding and/or more basic ligands (**1a**, **1b**, **2c**, **3c**) resulted in very low turnover (entries 1 and 8) or no catalytic activity (entries 2 and 5). In contrast, sulfonated phosphines with considerable steric

Fig. 2 Ligands used in the ruthenium catalyzed hydrogenation of arenes

Table 1 Cone angles of the ligands and the $^1J(^{31}\text{P}, ^{77}\text{Se})$ coupling constants [Hz] observed for their selenides (L(Se))

Ligand (L)	Cone angle (°)	$^1J(^{31}\text{P}, ^{77}\text{Se})$ coupling constant of L(Se) [Hz] ^c
1a	151 [45]	695.6
1b	—	670.5
2a	—	658.7
2b	—	663.8
2c	—	677.3
3a	166 ^a [45]	707.1
3b	196 or 210 [48]	660.9
3c	~166 ^b	681.4

^aThe cone angle of ligand **3a** (TPPTS) has been proposed in a wide range (from 129° to 178°) [46]

^bApproximation based on the fact that *p*-substituents do not influence the cone angle

^cThe NMR spectra were recorded in D₂O at 25 °C

demand (**2a**, **2b**, **3b**) or decreased σ -donor ability (**3a**) formed highly active catalysts (entries 3, 4, 7 and 6, respectively) with ruthenium.

Based on these results and literature findings [33] we decided to investigate the nature of the catalytically active species in the case of ligands **2a–b** and **3a–b** providing high activity. Initially, control experiments were performed in the presence of mercury under the same conditions. Basically no conversion could be observed in either case suggesting that the catalytically active species are not homogeneous complexes. In the next experiments, the catalytic reaction was repeated with ligands **3a** and **b** without addition of mercury to check the reproducibility of the reaction. The catalytic

systems modified with **3a** and **b** provided similar results in the control experiments, 39 and > 99% conversions could be achieved, respectively. Using these reaction mixtures, samples were taken from the aqueous phase and analyzed by transmission electron microscopy (TEM). The TEM analysis revealed the presence of well dispersed ruthenium nanoparticles in the aqueous phase. Interestingly, the size distribution and the mean diameter of the nanoparticles formed in the two systems were nearly identical despite the significant difference in their catalytic activity. This suggests that the remarkable differences in their catalytic properties can be correlated to the stereoelectronic features of the phosphine ligands used (Fig. 3).

In other words, high catalytic activity and nanoparticle formation could be achieved with sterically more demanding sulfonated phosphines. This also suggests that ligands with less steric demand or with higher basicity do not facilitate nanoparticle formation under catalytic conditions or simply function as catalyst poisons through a strong coordination to the surface of the nanoparticles. The first case is corroborated by the fact that sterically more demanding phosphines [53–55] or ligands with more negative charge [56–58] form less stable or coordinatively unsaturated complexes due to interligand repulsions and thus may facilitate nanoparticle formation. Consequently, sterically less demanding ligands with stronger σ -donor ability can stabilize homogeneous complexes more effectively. The second possibility is the consequence of the fact that phosphines with strong coordinating ability block the catalytically active sites of the nanoparticle preventing the coordination of the substrate [59]. However, it cannot be excluded that both of these phenomena play an

Table 2 Screening of sulfonated phosphines in the hydrogenation of benzene under biphasic conditions

Entry	Ligand	Conversion (%)
1	1a	2
2	1b	0
3	2a	60
4	2b	56
5	2c	0
6	3a	31
7	3b	> 99
8	3c	1

Reaction conditions: 0.011 mmol of RuCl₃·3H₂O, 0.044 mmol of sulfonated phosphine in 15 mL of water. Brij-L4: 11 mmol/L, benzene/Ru molar ratio: 2000, pressure: 50 bar, temperature: 120 °C, reaction time: 1 h. Conversion has been determined by GC

important role in reduced catalytic activity. Nevertheless, the application of phosphines with considerable steric bulk (**2a**, **2b** and **3b**) resulted in the formation of highly active ruthenium catalysts. In contrast, ligands **1a**, **1b**, **2c** and **3c** are possibly too basic and not hindered enough to promote the formation of catalytically active nanoparticles. Finally, even if sterically not hindered, ligand **3a** provided an intermediate conversion (31%, Table 2, entry 6) that can be due to its low σ -donor ability ($^1J(^{31}\text{P}, ^{77}\text{Se}) = 707.1 \text{ Hz}$, Table 1).

Encouraged by the catalytic results achieved with ligand **3b**, we performed further catalytic tests to obtain a deeper insight into the optimal working conditions of the catalytic system (Table 3). The conversion remained > 99 while decreasing the temperature from 120 to 60 °C. At 50 °C, however, the activity drastically decreased to 17%. Likewise, decreasing the L/Ru molar ratio resulted in a decreased turnover. It is, however, important to note that a TOF value of $\sim 8800 \text{ h}^{-1}$ could be obtained at 120 °C at a substrate/catalyst molar ratio of 6000.

The catalyst Ru/**3b** was also assessed in the hydrogenation of more challenging aromatic substrates as well as in the hydrogenation of several alkenes (Table 4). Amongst aromatic hydrocarbons the highest turnover frequency could be obtained with benzene as a substrate. Lower TOF values were achieved with different alkyl-benzenes. The number and the length of the alkyl substituents strongly affected the activity. Alkenes could readily be hydrogenated under the conditions applied.

The main purpose of using water-soluble phosphines in the biphasic hydrogenation reactions is the easy separation

of the aqueous phase containing the catalysts from the product and its recycling to the next catalytic run. In the next set of experiments the recycling of the catalyst was investigated with benzene/Ru molar ratio of 8000 at 80 °C and 50 bar pressure using Brij-L4 as non-ionic detergent. After each catalytic run the upper organic layer of the reaction mixture was separated and the lower aqueous layer was recycled. The catalyst was reused three times with a marginal drop of its activity. The conversion decreased from 20 to 18% during the four runs indicating that the catalyst can be reused without significant deactivation or leaching from the aqueous to the organic phase (Diagram 1). Ligand **3b** with weak coordination ability promotes the formation of ruthenium nanoparticles and may contribute to their stabilization. The careful stereoelectronic fine-tuning of the phosphine ligand led to a highly active and recyclable in situ formed catalysts in the hydrogenation of aromatic hydrocarbons. The utilization of this strategy in the hydrogenation of heteroatom-containing aromatic compounds is currently in progress.

3 Conclusion

Several water-soluble phosphines were characterized and tested in the biphasic aqueous–organic hydrogenation of aromatic hydrocarbons. It has been shown that the steric and electronic properties of the ligands strongly influence the activity of the catalytic system. Water-soluble phosphines with considerable steric demand or low basicity promoted the formation of ruthenium nanoparticles under catalytic conditions. These ligands proved to be labile enough to ensure the binding of the substrate to certain sites on the nanoparticle surface and at the same time they were able to facilitate efficient recycling of the catalyst. Consequently, this study shows the high potential of stereoelectronic fine-tuning in biphasic nanoparticle chemistry which we believe can be a fruitful approach in other types of catalytic reactions to achieve high activity, selectivity and successful recovery of the catalyst.

4 Experimental

4.1 General Experimental Details

All synthetic manipulations were carried out under argon using Schlenk techniques. Solvents were purified, dried and deoxygenated by standard methods. Sulfonated phosphines **1a–b**, **2a–b**, **2d** and **3a–c** were synthesized according to the literature procedures [39–42]. All other starting materials were purchased from Aldrich.

Fig. 3 TEM images and size distributions of RuNPs formed in the presence of ligands **3a** (a) and **3b** (b)

Table 3 Hydrogenation of benzene with Ru/**3b** catalyst at different reaction conditions

Entry	Temperature (°C)	L/Ru	Conversion (%)
1	40	4	0
2	50	4	17
3	60	4	> 99
4	80	4	> 99
5	120	4	> 99
6 ^a	120	4	> 99
7	120	2	48
8	120	6	> 99
9 ^b	120	4	49

Reaction conditions: 0.011 mmol of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, the desired amount of sulfonated phosphine in 15 mL of water. Brij-L4: 11 mmol/L, benzene/Ru molar ratio: 2000, reaction time: 1 h. Conversion has been determined by GC

^aWithout using Brij-L4

^bBenzene/Ru molar ratio: 6000

Table 4 Aqueous biphasic hydrogenation of several unsaturated (aromatic and aliphatic) hydrocarbons to the corresponding alkanes

Entry	Substrate	Conversion (%)
1		> 99
2		90
3		57
4		53
5		23
6		> 99
7		> 99
8		> 99

Reaction conditions: 0.011 mmol of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 0.044 mmol of sulfonated phosphine in 15 mL of water. Brij-L4: 11 mmol/L, benzene/Ru molar ratio: 2000, pressure: 50 bar, temperature: 120 °C, reaction time: 1 h. Conversion has been determined by GC

4.2 Characterization Techniques

$^1\text{P}\{^1\text{H}\}$ NMR measurements were carried out on a Bruker Avance 400 spectrometer (NMR Laboratory, University of Pannonia) operating at 161.98 MHz. Samples for TEM analyses were prepared by slow evaporation of a drop of colloidal aqueous solution deposited onto lacey carbon-covered copper grids. Transmission electron microscopy analyses were performed at the Nanolab, University of Pannonia. TEM images were obtained with an FEI Talos F200X transmission electron microscope (equipped with X-FEG electron source and Super-X energy disperse X-ray spectrometer) working in parallel illumination (TEM) mode and scanning transmission (STEM) mode. The acceleration voltage was 200 kV. TEM bright field, HRTEM, and STEM images, chemical analysis and elemental maps were taken during the measurements. Statistical size distribution and the mean diameter of the nanoparticles were obtained by the manual analysis of the TEM micrographs by using ImageJ software.

4.3 Synthesis of Phosphine-selenides

The selenides were synthesized in D_2O in the reaction of the corresponding phosphine and elemental selenium at room temperature or in the case of ligands **2a–c** and **3b** at 90 °C. The reaction mixtures were stirred for 8 h, filtered and then analyzed by NMR. (The product selenides were not isolated or purified due to the high toxicity of elemental selenium.)

Diagram 1 Recycling of catalyst Ru/**3b**. Reaction conditions: 0.011 mmol of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 0.044 mmol of sulfonated phosphine in 15 mL of water. Brij-L4: 11 mmol/L, benzene/Ru molar ratio: 8000, pressure: 50 bar, temperature: 80 °C, reaction time: 1 h. Conversion has been determined by GC, it is <20% in each case. TOF has been calculated as moles of double bonds hydrogenated per moles of Ru per hour

4.4 Catalytic Hydrogenation

A mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and the water-soluble phosphine in 15 mL of water was stirred for 10 min and Brij-L4 was added to the mixture. (The water used in the catalytic experiments was doubly distilled and thoroughly deoxygenated by argon bubbling and sonication.) The resulting solution and the unsaturated hydrocarbon were charged into a 100 mL stainless steel autoclave equipped with a glass inlet and a robust magnetic stirring bar. The reactor was then flushed with argon, pressurized with H_2 and brought to the desired temperature. The reaction was initiated by stirring (1200 rpm). After the reaction stirring was stopped, the reactor was cooled down with an external water-cooling system and then carefully depressurized. The composition of the upper layer was determined with GC using an Agilent 7820A, equipped with a Supelcowax 10 fused silica capillary column (30 m $\times$ 0.25 mm, film thickness = 0.25 μm , carrier gas: N_2 at 1.14 mL/min) or an SPB-1 capillary column (30 m $\times$ 0.25 mm, film thickness = 0.25 μm , carrier gas: N_2 at 200 kPa), a split/splitless injector at 250 $^\circ\text{C}$ and a FID at 250 $^\circ\text{C}$. The chromatography method using the Supelcowax column for the determination of the conversion of benzene, toluene, ethylbenzene, *m*-xylene and 1,3,5-trimethylbenzene consists of 5 min at 50 $^\circ\text{C}$ and a ramp of 5 $^\circ\text{C min}^{-1}$ to 200 $^\circ\text{C}$. Retention times are 6.1 min for cyclohexane and 8.2 min for benzene, 8.2 min for methylcyclohexane and 11.6 min for toluene, 8.6 min for ethylcyclohexane and 13.1 min for ethylbenzene, 7.5 min for 1,3-dimethylcyclohexanes and 13.3 min for *m*-xylene, 8.1 min for 1,3,5-trimethylcyclohexanes and 16.3 min for 1,3,5-trimethylbenzene. The same column was used for the determination of the conversion of cyclohexene and cyclooctene at 30 $^\circ\text{C}$ constant temperature. Retention times are 8.6 min for cyclohexane and 10.1 min for cyclohexene, 21.4 min for cyclooctane and 24.6 min for cyclooctene. The SPB column was used for the determination of the conversion of 1-octene at 30 $^\circ\text{C}$ constant temperature. The retention times are 6.9 min for 1-octene and 7.6 min for octane. Conversions were calculated as the following: the peak area of the product was divided by the sum of the peak areas of the product and the substrate. TOF values have been calculated as moles of double bonds hydrogenated per moles of Ru per hour. In the mercury poisoning tests 300 mg of Hg (~1.5 mmol) was used.

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Compliance with Ethical Standards

Conflict of interest The authors declare that there are no conflicts of interest regarding the publication of this paper.

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