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Imidazolium-functionalized bipyridine derivatives: a promising family of ligands for catalytical Rh(0) colloids

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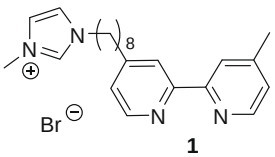
ABSTRACT

A new imidazolium-monofunctionalized bipyridine ligand has been synthesized and efficiently used as a protective agent for Rh(0) nanoparticles. Preliminary results in arene hydrogenation have been obtained.

In the last decades, transition-metal nanoparticles have proved to be highly efficient catalytic systems in various reactions[1] and are particularly known as a relevant catalyst for arene hydrogenation.[2] As they are thermodynamically unstable, the protective agents should be chosen according to the nature of the metallic species and the reaction media to avoid their aggregation.[3] Among them, ionic liquids are promising, as they can play the dual role of solvent and protective agent.[4] Rh, Ru, Ir, and Pd nanoparticles have been easily prepared in various ionic liquids and have proved to be efficient catalysts for olefin or arene hydrogenation reactions.[5] Nevertheless, Rh(0) and Ir(0) nanocatalysts in simple imidazolium ionic liquids tend to aggregate after reactions such as hydrogenation of aromatic compounds or ketones with loss of catalytic activity.[6] In that context, more stable catalytic systems could be obtained by the addition of an extra-protective agent, such as PVP[7] or 1,10-phenanthroline,[8] which has proved to play a synergistic effect on the activity and durability of the catalyst. Moreover, as the commonly used organic stabilizers present low solubility in ionic liquids, new ionic copolymers containing imidazolium units, which could act as soluble bifunctional costabilizers when dissolved in ionic liquids, have been designed.[9] Recently, our team have described the stabilization in ionic liquids of Rh(0) nanoparticles by *N*-donor ligands, such as 2,2′-bipyridine[10] or triazine and pyrazine derivatives,[11] and their application in arene hydrogenation. In order to improve the solubility of the 2,2′-bipyridine ligand in ionic liquids and also to induce new interactions between the protective agent and the reaction media, we have designed an imidazolium-monofunctionalized bipyridine **1** as precursor of a promising family of ligands (Scheme 1). In this Letter, we report the synthesis of this new ligand **1** based on 2,2′-bipyridine, which has proved to be efficient for the stabilization of Rh(0) nanoparticles. Catalytic results in terms of activity and selectivity in arene hydrogenation are compared with 2,2′-Bipyridine-protected Rh(0) colloids.

The new bipyridine ligand bearing an imidazolium tag **1** is synthesized starting from 4,4′-dimethyl-2,2′-bipyridine **2** by a procedure adapted from the literature.[12,13] The route is described in Scheme 2. Reaction of 4,4′-dimethyl-2,2′-bipyridine **2** with BuLi in THF generates the monolithiated intermediate, which is quenched with 1,7-dibromoheptane. The resulting 4-bromooctyl-4′-methyl-2,2′-bipyridine **3** reacted with 1-methylimidazole in toluene at 90 °C for 7 days to yield 4-(1-methylimidazolium-



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Scheme 1. Imidazolium-monofunctionalized bipyridine ligand **1**.

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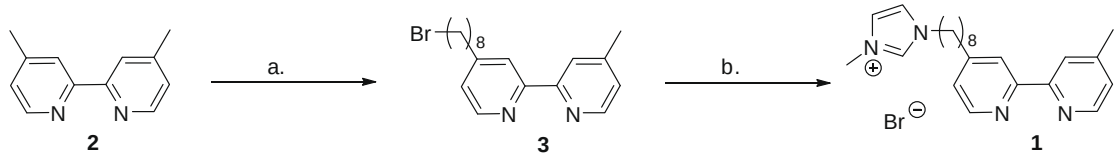


Scheme 2. Synthesis of imidazolium-functionalized bipyridine ligand **1**. Reagents and conditions: (a) (i) diisopropylamine, BuLi, THF, −78 °C; (ii) 1,7-dibromoheptane, THF, −78 °C and (b) methylimidazole, toluene, 90 °C, 7 days.

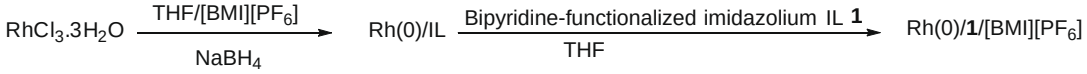
3-yloctyl)-4′-methyl-2,2′-bipyridine bromide **1** with an overall non-optimized yield of 36%.[14]

On the basis of the method previously developed for the synthesis of Rh(0) nanoparticles stabilized by 2,2′-bipyridine,[10a] the colloidal Rh(0) suspensions have been prepared by the chemical reduction of rhodium trichloride salt with an excess of sodium borohydride in a monophasic tetrahydrofuran-ionic liquid media.[15] Immediately after reduction, the protective agent **1**, dissolved in THF, was added to the pre-stabilized metallic Rh(0) nanoparticles, according to the procedure described in Scheme 3. The reduction, which is characterized by a color change from red to black, has been performed in the open air and at room temperature occurring instantaneously. A previously optimized molar ratio [protective agent]/[M] of 0.5, which has already proved to be a good compromise between stability and activity of the nanocatalyst, has been chosen and [BMI][PF_6][16] has been used as a standard ionic liquid.

The catalytic activity of the imidazolium-functionalized bipyridine ligand **1**-protected Rh(0) nanoparticles in [BMI][PF_6] has been evaluated in the hydrogenation of benzene and monofunctionalized derivatives according to the experimental conditions previously optimized (40 bar H_2, 80 °C) in an arbitrarily chosen time (15 h).[17] The conversion was determined by gas chromatography analysis. The catalytic results are summarized in Table 1 and compared with the results already described for 2,2′-Bipy.[10a]

The results clearly show that the catalytic performances of imidazolium-functionalized bipyridine ligand **1**-protected Rh(0) nanospecies in the hydrogenation of monofunctionalized aromatic substrates are quite similar to those of 2,2′-Bipyridine-stabilized Rh(0) colloids with turnover number (TON) up to 300. The turnover number (TON) was established according to the amount of rhodium introduced, taking into account the true number of active metal sites. Thus, we could presume that TON may be underestimated.[18] In both cases, in the series of benzene, toluene, and ethylbenzene (entries 1–6), the decrease in catalytic activity is typical of the influence of the increasing steric hindrance as usually observed with other catalysts.[19] As the colloidal suspensions are always stable after the catalytic reaction, we could presume that the complete hydrogenation of aromatic rings such as toluene (entry 3), ethylbenzene (entry 5), and styrene (entry 7) could be achieved for longer reaction times and that the catalytic system could be easily recycled by simple liquid–liquid extraction with diethylether. Thus, similar catalytic activities have been obtained for the two catalytic systems, showing that the imidazolium cation tagged to the bipyridine has no significant influence on the substrate approach on nanoparticles surface. Moreover, in the absence of bipyridine ligand, styrene was totally converted in ethylcyclohexane in 15 h; however, the colloidal suspension is unstable after catalytic reaction with formation of aggregates.[10a] Thus, this preliminary work is promising as this new synthesized compound **1** offers the opportunity to develop a new class of functionalized ionic liquids by simple anion-exchange reactions, as recently described in the literature.[20] Moreover, according to the possibility to access 3,3′- and 4,4′-bipyridines and to modify the chain length, this class of new ligands could significantly be increased.

In conclusion, a new imidazolium-monofunctionalized bipyridine ligand **1** has been easily prepared in two steps starting from commercial 4,4′-dimethyl-2,2′-bipyridine and has proved to be an efficient protective agent for the stabilization of Rh(0) nanoparticles in [BMI][PF_6]. These ligand **1**-stabilized Rh(0) colloids are efficient and stable catalysts for arene hydrogenation in ionic liquids. The use of ligands as nanoparticles protective agent is a promising alternative to avoid aggregation in some hydrogenation reactions. Finally, a new class of functionalized ionic liquids could be easily prepared starting from this imidazolium-functionalized bipyridine ligand **1** in order to improve, for example, the performances of these nanocatalysts in terms of activity and selectivity with asymmetric tags.



Scheme 3. Synthesis of Rh(0) nanoparticles stabilized by bipyridine-functionalized imidazolium IL **1** in ionic liquids.

Table 1
Hydrogenation of arene derivatives with Rh(0) nanoparticles stabilized by imidazolium-functionalized bipyridine ligand **1** or 2,2′-bipyridine[a]

Entry	Ligand	Substrate	Product	Conversion[b] (%)	TON[c]
1	**1**	Benzene	Cyclohexane	100	300
2	2,2′-Bipy	Benzene	Cyclohexane	100	300
3	**1**	Toluene	Methylcyclohexane	85	255
4	2,2′-Bipy	Toluene	Methylcyclohexane	100	300
5	**1**	Ethylbenzene	Ethylcyclohexane	60	180
6	2,2′-Bipy	Ethylbenzene	Ethylcyclohexane	60	180
7	**1**	Styrene	Ethylbenzene (35)/ethylcyclohexane (65)	100	300
8	2,2′-Bipy	Styrene	Ethylbenzene (40)/ethylcyclohexane (60)	100	300

[a] Reaction conditions: Rh (3.8×10^{-5} mol), ligand (1.9×10^{-5} mol), [BMI][PF_6] (2 mL), substrate/Rh(0) (mol/mol) = 100, 40 bar H_2, 80 °C, 15 h, stirred at 1500 rpm.
[b] Determined by GC analysis.
[c] Turnover number defined as the number of moles of consumed H_2 per mole of introduced rhodium.

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14. *Experimental procedure for the synthesis of 4-(bromooctyl)-4′-methyl-2,2′-bipyridine* **3**: 1.2 mL (1.3 mmol, 1.2 equiv) of BuLi was added dropwise to an anhydrous solution of diisopropylamine (190 μL, 1.3 mmol, 1.2 equiv) in THF (2 mL) at −78 °C. The resulting solution was maintained under vigorous stirring at −78 °C for 30 min. Then, 203 mg (1.1 mmol, 1 equiv) of 4,4′-dimethyl-2,2′-bipyridine in THF (6 mL) was added to the mixture dropwise at −78 °C. The reaction mixture was vigorously stirred at −78 °C for 1 h. 743 μL (4.3 mmol, 4 equiv) of 1,7-dibromoheptane in THF (2 mL) was added to the mixture which was slowly warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of 2 mL of water. Subsequently, 8 mL of phosphate buffer (pH 7) was added and the reaction mixture was extracted with diethyl ether. The organic layer was dried over magnesium sulfate, and the ether was removed under reduced pressure at room temperature. The resulting yellow-brown oil was purified by column chromatography (neutral aluminum oxide, petroleum ether/ diethyl ether 9/1) yielding **3** as a white solid (143 mg, 36%); R_f = 0.2 (petroleum ether/diethyl ether 9/1); ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.60 (s, 2H), 8.40 (d, 2H), 7.02 (d, 2H), 3.30 (t, 2H), 2.55 (t, 2H), 2.37 (s, 3H), 1.79 (st, 2H), 1.62 (st, 2H), 1.29 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 157.9, 157.2, 150.5, 149.8, 148.3, 147.7, 123.2, 122.6, 121.3, 120.7, 36.1, 34.1, 32.9, 32.4, 30.3, 29.9, 29.3, 28.7, 21.2. *Preparation of 4-(1-methylimidazolium-3-yloctyl)-4′-methyl-2,2′-bipyridine bromide* **1**: 35.7 mg (0.43 mmol, 1.1 equiv) of distilled methylimidazole was added to 143 mg (0,39 mmol) of 4-(bromooctyl)-4′-methyl-2,2′-bipyridine **3** in toluene (10 mL). The reaction mixture was stirred under inert atmosphere at 90 °C for a week. Toluene was removed under reduced pressure at ambient temperature and the final product 1 (60 mg) was obtained with a nearly quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.,92 (s, 3H), 8.42 (d, 2H), 7.76 (d, 1H), 7.71 (d, 1H), 7.19 (d, 2H), 4.39 (s, 3H), 4.04 (t, 2H), 2.62 (t, 2H), 2.36 (s, 3H), 1.74 (m, 2H), 1.59 (m, 2H), 1.33 (m, 2H), 1.29 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 156, 155.7, 152.9, 149.7, 149, 147.7, 136.2, 123.6, 122.2, 121.3, 120.7, 123.2, 122.6, 51.8, 36.1, 34.2, 32.4, 30.3, 30, 29.9, 28.1, 21.2, 13.5.
15. *Synthesis of ligand-stabilized Rh(0) nanoparticles in ionic liquid*: $RhCl_3{\cdot}3H_2O$ (10 mg, 3.8×10^{-5} mol, 2.5 equiv) was dispersed in a mixture of THF (5 mL) and ionic liquid (2 mL). $NaBH_4$ (3.6 mg, 9.5×10^{-5} mol, 2.5 equiv) dissolved in water (two drops) was quickly added to the mixture under vigorous stirring. Immediately, the ligand **1** (1.9×10^{-5} mol, 0.5 equiv/Rh) that was considered and dissolved in 5 mL of THF was quickly added under vigorous stirring to the mixture. Then, THF was removed under reduced pressure and the colloidal suspension was dried under vacuum during 2 h. The reduction occurs instantaneously and is characterized by a color change from red to black. The obtained suspensions are stable for several weeks.
16. [BMI][PF_6] was prepared from a procedure described in the literature (*Adv. Synth. Catal.* **2006**, *348*, 243–248) and was dried under vigorous stirring for 6 h at 70 °C and under vacuum. Its chloride content was checked by $AgNO_3$ test and the chloride content's purity by ^{1}H NMR and ^{31}P NMR spectra.
17. *General procedure for hydrogenation under hydrogen pressure*: the stainless steel autoclave was charged with 2 mL of ligand-stabilized Rh(0) colloidal suspension in [BMI][PF_6] and a magnetic stirrer. The appropriate substrate (3.8×10^{-5} mol, 100 equiv) was added into the autoclave and dihydrogen was admitted to the system at constant pressure up to 40 atm. The mixture was heated to 80 °C and stirred for 15 h. After cooling to ambient temperature, the mixture was dispersed into 10 mL of CH_3CN and centrifuged (g = 20152 m s^{-2}) during 10 min for the precipitation of nanoparticles. The sample was analyzed by gas chromatography, using Carlo Erba GC 6000 with FID detector equipped with a Factor Four column (30 m, 0.25 mm i.d.). Parameters were as follows: temperature, 80 °C; injector temperature, 220 °C; and detector temperature, 250 °C.
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