Inorg. Chem. **2008**, *47*, 9090−9096

Inorganic Chemistry
Article

Rhodium Nanocatalysts Stabilized by Various Bipyridine Ligands in Nonaqueous Ionic Liquids: Influence of the Bipyridine Coordination Modes in Arene Catalytic Hydrogenation

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Received June 11, 2008

Rhodium nanoparticles stabilized by 2,2′-, 3,3′-, 4,4′-bipyridine ligands were prepared in various ionic liquids according to a chemical reduction approach. Zerovalent nanospecies in the size range of 2.0−2.5 nm were characterized. The nature of the bipyridine and its influence on the coordination environment of rhodium nanoparticles were investigated in various nonaqueous ionic liquids according to the cation and anion. The hydrogenation of various aromatic compounds by these colloidal suspensions was carried out at 80 °C and under 40 bar of H_2. A first structural explanation based on bipyridine coordination modes is proposed to justify the observed different activities.

Introduction

In recent years, transition metal clusters or colloidal suspensions have received increasing interest because of their unique properties and have found applications in many research areas such as in catalysis.[1,2] Nevertheless, metallic nanoparticles are thermodynamically unstable and must be stabilized by various protective agents to prevent their agglomeration.[3−8] Among the different protective agents, ionic liquids (IL) have proved to be interesting because they could play the dual role of a solvent and a stabilizing agent. Imidazolium salts such as [BMI][PF_6] or [BMI][BF_4] have particulary been used in the synthesis of Ir, Rh, and Ru nanoparticles (BMI = 1-methyl-3-butyl-methyl imidazolium).[9] However and particularly in the case of Rh(0) colloids, the precipitation of nanoparticles has been reported during catalytic applications such as the hydrogenation of substituted arene compounds.[10] Consequently, the addition of a ligand constitutes an alternative approach to increase the stability of rhodium nanospecies. Different N-donor compounds have already proved their efficiency as protective agents in the case of colloidal suspensions in nonaqueous ionic liquids. As an example, the synthesis of phenanthroline-stabilized palladium nanocatalysts and their use for olefin hydrogenation in [BMI][PF_6] media have been reported by Han and co-workers.[11] Similarly, we have recently described an efficient approach for the preparation of zerovalent Rh(0)

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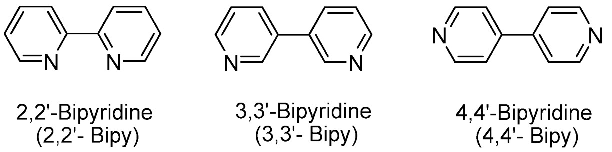
10.1021/ic8010713 CCC: $40.75

Scheme 1. Bipyridine Isomers



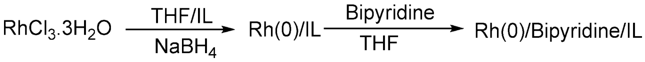
nanoparticles stabilized by 2,2′-bipyridine as a polynitrogen ligand.[12] These colloidal suspensions have shown interesting activities and selectivities for the hydrogenation of aromatic compounds in several nonaqueous ionic liquids according to the nature of the anion and cation fragments. Here, we report the efficient stabilization of Rh(0) nanoparticles by different 2,2′-, 3,3′-, 4,4′-bipyridine (Bipy) isomers. These bipyridine-stabilized Rh suspensions have been characterized by transmission electron microscopy (TEM) and evaluated in the catalytic hydrogenation of styrene. The reduction of various aromatic compounds in different ionic liquids has fully been investigated at 80 °C and under 40 bar of H_2. A mechanistic approach based on the suitable coordination of the mono- or bidentate bipyridine ligands and their analogous monodentate bipyridinium salts onto the nanoparticle surface has been proposed to justify the different observed catalytic results in terms of activity and selectivity. Finally, new rhodium nanoparticle systems with Bipy isomers as chelates have been studied. According to the reactivity and stability of the colloidal systems, the role and the coordination mode of the Bipy isomers will be discussed.

Results and Discussion

Recently, we have reported the synthesis of rhodium nanoparticles and their stabilization with 2,2′-bipyridine as an efficient N-donor ligand.[12] With an optimized ligand-to-metal ratio, the catalytic system has shown interesting activities and selectivities in the hydrogenation of substituted aromatic compounds. While leading to a weak coordination effect to the nanoparticle surface, 2,2′-bipyridine provides a major steric stabilization effect. These promising results obtained with 2,2′-Bipy-stabilized rhodium(0) nanoparticles have incited us to study the influence of the other bipyridine isomers through the nitrogen atom's position using 3,3′-bipyridine and 4,4′-bipyridine (Scheme 1). 4,4′-Bipyridine is commercial, whereas 3,3′-bipyridine has been synthesized by a palladium-catalyzed homocoupling reaction, according to a procedure described in the literature.[13]

On the basis of the method we have developed for the 2,2′-bipyridine ligand, the catalytically active suspensions of metallic rhodium(0) particles have been prepared in a similar way by the chemical reduction of rhodium trichloride salts with sodium borohydride in the presence of bipyridine and ILs (Scheme 2). The synthesis has been performed in the open air and at room temperature. A previously optimized molar ratio [Bipy]/[M] of 0.5 has been chosen, and the [BMI][PF_6] has been used as a standard ionic liquid.

Scheme 2. Synthesis of Bipy-Stabilized Rhodium Nanoparticles in Ionic Liquids



$$RhCl_3.3H_2O \xrightarrow[NaBH_4]{THF/IL} Rh(0)/IL \xrightarrow[THF]{Bipyridine} Rh(0)/Bipyridine/IL$$

The [Bipy]/[Rh] molar ratio of 0.5 has proved to be a good compromise between stability and activity of the nanocatalyst system. The Rh(0) colloids were maintained stable, without any agglomeration, over several months. They can be stored in the air without special precautions. X-ray photoelectron spectroscopy (XPS) analyses have been carried out to examine the oxidation state and the chemical environment of the 2,2′-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF_6] (Figure 1).

The XPS analyses show the presence of rhodium, fluorine, sodium, carbon (from the support), and nitrogen. It is clear that the F signal indicates that the Rh(0) nanoparticles contain a residue of the ionic liquid ([BMI][PF_6]); however, we observe no contribution of phosphorus. The sodium signal could be assigned to traces of the chemical reducing agent, sodium borohydride. The low binding energy (BE) signal (BE of 3d3/2 at 313.8 eV and Rh 3d5/2 at 308.8 eV) is consistent with Rh metal. The presence of a nitrogen atom (through the N1s signal at 403.3 eV) could be certainly assigned to the 2,2′-Bipy ligand. In fact, previous XPS analyses on Ir(0) nanoparticles stabilized by [BMI] [PF_6] have detected no nitrogen signal due to the butylmethyl imidazolium group.[14]

These nanoparticle suspensions have been characterized in [BMI][PF_6] by TEM. The size distributions were calculated from about 200 particles. Whatever the bipyridine isomer used (2,2′-, 3,3′-, or 4,4′-Bipy), the particles present a narrow size distribution with an average diameter of 2.0−2.5 nm (Figure 2). In comparison with 2,2′-Bipy, the

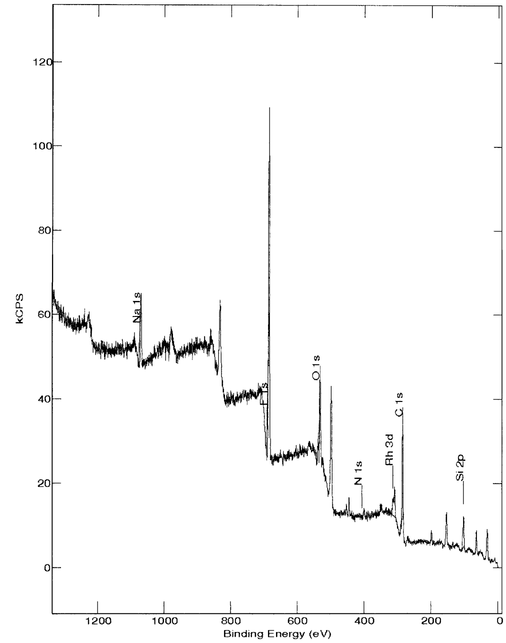


Figure 1. X-ray photoelectron spectra of 2,2′-Bipy-stabilized Rh(0) nanoparticles.

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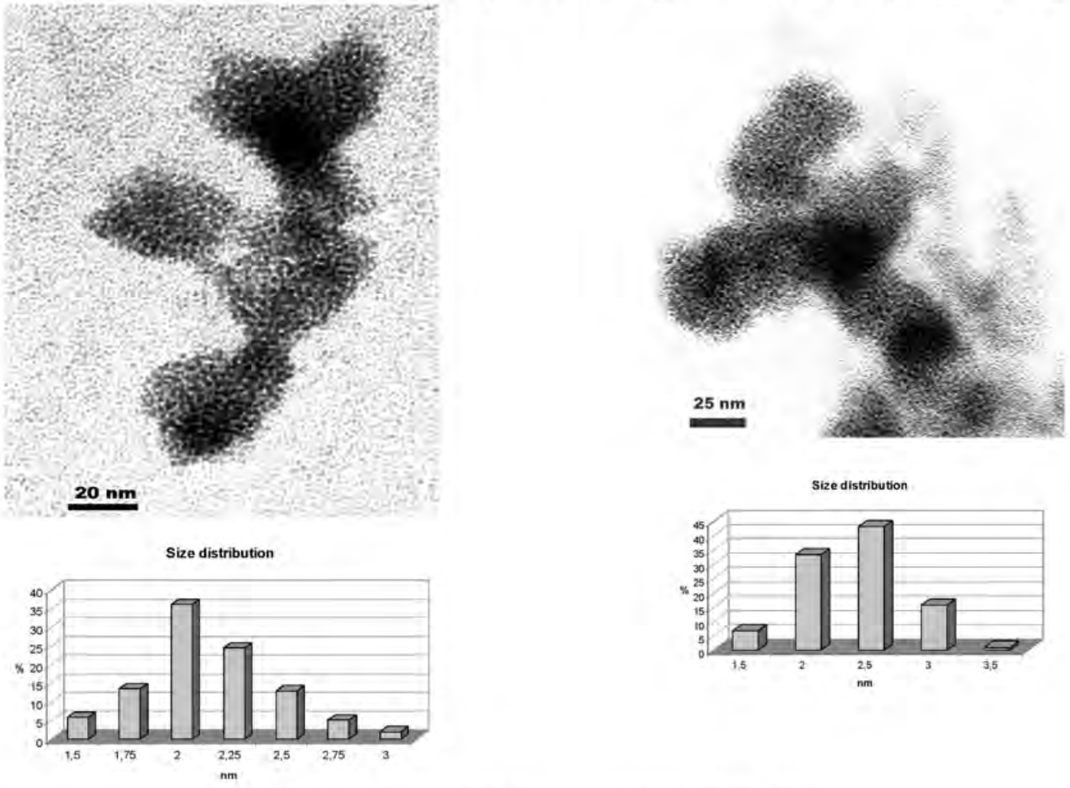


a) 2,2'-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF$_6$] b) 3,3'-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF$_6$]

c) 4,4'-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF$_6$]

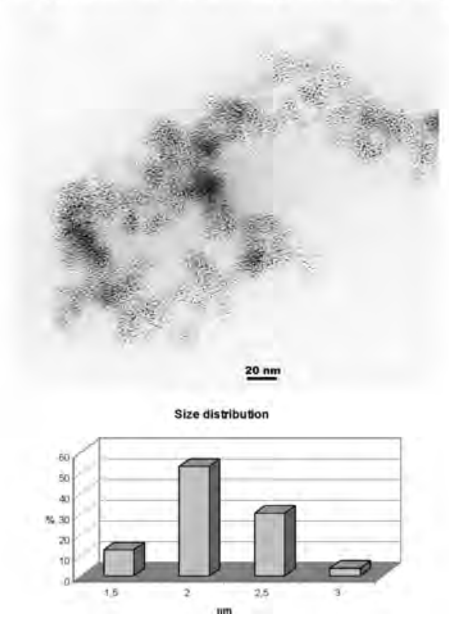


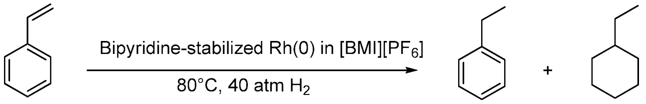
Figure 2. TEM micrographs and size distributions.

same spherical superstructures are obtained according to the observations reported by Dupont.[15] Consequently, these comparative TEM studies show that the Bipy isomers have no significant influence on the particle size and organization in the [BMI][PF$_6$] ionic liquid.

The hydrogenation of styrene has been investigated to evaluate the catalytic behavior of these Bipy systems (2,2′-, 3,3′, and 4,4′-Bipys) as protective agents providing potentially dynamic coordination of dangling bonds on the nanoparticle surface. The reaction has been performed according to the experimental conditions previously optimized such as 40 bar H_2 and 80 °C.[12] The reaction time was arbitrarily chosen to 15 h. At that time, the styrene was completely converted. The selectivity of the hydrogenation is evaluated according to the ethylbenzene and ethylcyclohexane ratios. The results are summarized in Table 1.

These experiments display the significant influence of the Bipy isomers on the catalytic selectivity of metallic nanoparticles. Undoubtedly, the best selectivities for styrene hydrogenation have been demonstrated with 3,3′-Bipy- and

Table 1. Influence of the Bipy Isomer on Catalytic Activity and Selectivity[a]



		products[b]	
entry	Bipy isomer	ethylbenzene (%)	ethylcyclohexane (%)
1	2,2′-Bipy	40	60
2	3,3′-Bipy	0	100
3	4,4′-Bipy	0	100

[a] Reaction conditions: 10 mg of Rh salt (3.8×10^{-5} mol), ligand (1.9×10^{-5} mol), [BMI][PF_6] (2 mL), styrene/Rh(0) (mol/mol) = 100, 40 bar H_2, 80 °C, $t = 15$ h, stirred at 1500 rpm. [b] Determined by GC analysis.

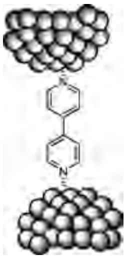
Table 2. Hydrogenation of Arene Derivatives with 4,4′- or 2,2′-Bipy-Stabilized Rh(0) Nanoparticles[a]

entry	ligand	substrate	product	conv. [%][b]
1	2,2′-Bipy	benzene	cyclohexane	100
2	4,4′-Bipy	benzene	cyclohexane	100
3	2,2′-Bipy	toluene	methylcyclohexane	100
4	4,4′-Bipy	toluene	methylcyclohexane	100
5	2,2′-Bipy	ethylbenzene	ethylcyclohexane	60
6	4,4′-Bipy	ethylbenzene	ethylcyclohexane	100
7	2,2′-Bipy	propylbenzene	propylcyclohexane	85
8	4,4′-Bipy	propylbenzene	propylcyclohexane	96
9	2,2′-Bipy	cumene	isopropylcyclohexane	10
10	4,4′-Bipy	cumene	isopropylcyclohexane	100
11	2,2′-Bipy	styrene	ethylbenzene/ethylcyclohexane	40/60
12	4,4′-Bipy	styrene	ethylcyclohexane	100

[a] Reaction conditions: 10 mg of Rh salt (3.8×10^{-5} mol), ligand (1.9×10^{-5} mol), ionic liquid (2 mL), substrate/Rh = 100 (molar ratio), 40 bar H_2, 80 °C, 15 h, stirred at 1500 rpm. [b] Determined by GC analysis.

Scheme 3. Representation of Potential Bipy Coordination Modes onto Metallic Nanoparticles (Bipy vs Nanoparticle Sizes Are Not Respected)

Scheme 4. Putative Bridging Mode between Two Nanoparticles with Symmetric 4,4′-Bipy



4,4′-Bipy-protected Rh(0) nanoparticles with complete conversion into ethylcyclohexane in 15 h (entries 2 and 3), whereas 2,2′-Bipy-stabilized Rh(0) nanoparticles lead to a total conversion of the substrate into ethylbenzene (40%) and ethylcyclohexane (60%) in the same time (entry 1).

In a second series of studies, we have investigated the hydrogenation of benzene and its monoalkyl-substituted derivatives to check the ability of 4,4′-Bipy-stabilized Rh(0) nanoparticles to reduce aromatic rings in [BMI][PF_6]. The catalytic results obtained and compared with the results already described for 2,2′-Bipy are summarized in Table 2.

The results obtained with 2,2′-Bipy-stabilized nanoparticles show that the activity tends to decrease with the bulkiness of the substituent on the aromatic ring. The conversion varies in the order cumene < propylbenzene < ethylbenzene < toluene (entries 5, 7, 9, and 11). In opposition to this behavior, all of the aromatic compounds studied are completely hydrogenated (entries 2, 4, 6, 8, 10, and 12) in 15 h with 4,4′-Bipy-stabilized Rh(0) nanoparticles. In all cases, the colloidal suspensions are stable after catalytic reactions. This difference of behavior between the Bipy isomers could be explained by the fact that increasing the steric hindrance of aromatic compounds tends to limit their access to the Bipy-stabilized nanoparticle surface. A stronger and unfavorable interaction between the substrate and bidentate 2,2′-Bipy could be proposed. In the case of 3,3′-Bipy- and 4,4′-Bipy-stabilized nanoparticles, a plausible monocoordination of the ligand could be suggested. However, with the monocoordination mode, the ligand remains a better protective agent than the ionic liquid, as a previously reported experiment[12] without a ligand in [BMI][PF_6] has shown the formation of Rh(0) aggregates after catalysis. Because of a decrease in the steric hindrance around the colloids, the substrate could have better accessibility to the nanoparticle surface. Consequently, the "poison" effect encountered with 2,2′-Bipy is less significant with 3,3′-Bipy and 4,4′-Bipy.

According to organometallic approaches described for Ru−Bipy complexes,[16] a schematic organization of the ligands around the particle is proposed in Scheme 3. This representation clearly suggests that the steric hindrance around the nanoparticles and consequently the catalytic activities could greatly be influenced by the Bipy isomer due to various chelating coordination modes.

Finally, the reactivity depends on the mono- or bidendate coordination mode of the ligand. In the case of 3,3′-Bipy, we could consider the possibility to have a dynamic coordination mode between mono- or bidentate coordination or a mixture of the two modes. Moreover, we cannot exclude the ability for 4,4′-Bipy to form a bidentate bridging system between two nanoparticles (Scheme 4). Nevertheless, on the basis of microscopy observations, no significant difference has been demonstrated. In all cases, we have observed spherical superstructures according to the literature,[17] even if slightly well-dispersed particles are observed with 4,4′-Bipy due to a monocoordination mode, leading to better catalytic activity in comparison with 2,2′-Bipy.

Typically, it is presumed that the 2,2′-Bipy isomer coordinates to nanoparticles with both N-donor atoms yielding a chelate structure. This bidentate approach results in a more steric hindrance on the particle surface and thus

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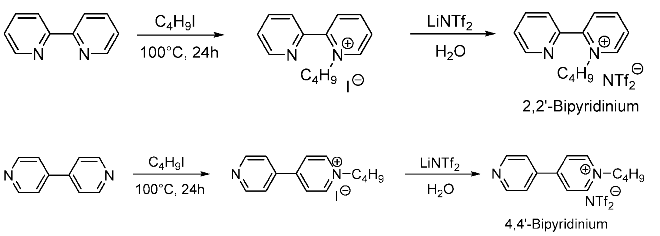
Scheme 5. Synthesis of 2,2′-Bipyridinium and 4,4′-Bipyridinium Salts

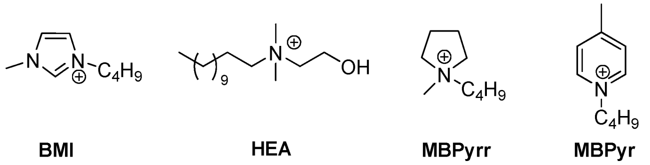


in a decrease in the catalytic activity compared to the monodentate 3,3′- and 4,4′-Bipy. To confirm the proposed organization, we have synthesized analogous 2,2′-bipyridinium and 4,4′-bipyridinium salts as monocoordinating protective agents for Rh(0) nanoparticles. These compounds have been prepared from commercial products in two steps and according to a procedure adapted from the literature.[18] The synthesis described in Scheme 5 consists of a monoalkylation of 2,2′- and 4,4′-Bipy with a butyl chain, followed by metathetic anion exchange. The 2,2′- and 4,4′-bipyridinium trifluoromethanesulfonylimide salts were isolated with a good yield of about 90%.

These new monodentate ligands have been used to stabilize efficiently rhodium(0) nanoparticles in [BMI][NTf_2] ionic liquid according to the procedure described in Scheme 2, with a similar [ligand]/[Rh] molar ratio of 0.5. The obtained catalytic systems have been tested in the hydrogenation of styrene as a model substrate. Whatever the bipyridinium salt used is, the suspensions lead to a complete conversion of styrene into ethylcyclohexane in 15 h under standard conditions (40 bar H_2, 80 °C), giving the same results as with 4,4′-Bipy. This tends to confirm that a monodentate coordination of the ligand favors the reactivity of the catalytic system, leading to a complete hydrogenation of the aromatic ring.

In a third set of studies using the efficient 3,3′-Bipy-stabilized Rh(0) nanoparticles, we have investigated the influence of various nonaqueous ionic liquids in styrene hydrogenation as a model substrate. Several associations have been studied with NTf_2 as the anion (bis-trifluoromethanesulfonylimide anion) and various cationic structures. The NTf_2 anion was chosen so that the ionic liquids could be easily and rapidly prepared and purified and could be liquid at ambient temperature. Several heterocyclic cation skeletons such as imidazolium (BMI = 1-*n*-butyl-3-methyl imidazolium), pyrrolidinium (MBPyrr = N-methyl-N-butyl pyrrolidinium), and pyridinium (MBPyr = 1-butyl-4-methyl pyridinium) rings have been tested. In the same manner, the methylbutyl-pyridinium and pyrrolidinium salts have been used to avoid the potential formation of carbenes already reported with BMI.[19,20] Finally, an ammonium salt, classically used in water, such as the easily synthetized N,N-dimethyl-N-dodecyl-N-(2-hydroxyethyl) ammonium group (HEA),[21] has also been applied. The results are presented in Table 3 and compared with those obtained for 2,2′-Bipy.

Table 3. Influence of the Cation of the Ionic Liquid in Styrene Hydrogenation[a]



entry	ligand	ionic liquid [NTf_2] salt	product	selectivity [%][b]
1	2,2′-Bipy	[BMI]	ethylbenzene/ethylcyclohexane	70/30
2	3,3′-Bipy	[BMI]	ethylcyclohexane	100
3	2,2′-Bipy	[HEA]	ethylbenzene/ethylcyclohexane	40/60
4	3,3′-Bipy	[HEA]	ethylcyclohexane	100
5	2,2′-Bipy	[MBPyr]	ethylbenzene/ethylcyclohexane	85/15
6	3,3′-Bipy	[MBPyr]	ethylcyclohexane	100
7	2,2′-Bipy	[MBPyrr]	ethylbenzene/ethylcyclohexane	70/30
8	3,3′-Bipy	[MBPyrr]	ethylcyclohexane	100

[a] Reaction conditions: 10 mg of Rh salt (3.8×10^{-5} mol), ligand (1.9×10^{-5} mol), ionic liquid (2 mL), substrate/Rh = 100 (molar ratio), 40 bar H_2, 80 °C, 15 h, stirred at 1500 rpm. [b] Determined by GC analysis.

The 3,3′-Bipy-stabilized rhodium(0) nanoparticle suspension leads to a complete conversion of styrene into ethylcyclohexane (entries 2, 4, 6, and 8), whatever the cationic skeleton is. In all cases, this new system demonstrates high efficiency and stability in various nonaqueous ionic liquids. On the contrary, as already described,[12] the 2,2′-Bipy-protected Rh(0) suspensions lead to a total conversion of the substrate in a mixture of ethylbenzene/ethylcyclohexane mixtures (entries 1, 3, 5, and 7). However, as the particles are always stable after 15 h of reaction, we could presume a complete conversion of styrene into ethylcyclohexane for longer reaction times. No significant differences have been observed, using BMI, MBPyr, or BMPyrr cations. With the HEA cation, higher yields in ethylcyclohexane have been obtained. The presence of a lipophilic chain on the ammonium could explain the formation of nearly dispersed nanoparticles with an average diameter of 3 nm with about 70% of the colloids between 2.5 and 3.5 nm, as shown by TEM analysis (Figure 3). This phenomenon has recently been reported in the literature.[22]

These results underline again the difference in terms of kinetic behavior between 2,2′- and 3,3′-Bipy isomers due to their different chelating coordination modes.

Undoubtedly, the monodentate coordination mode of 3,3′-Bipy and 4,4′-Bipy seems to be very interesting in terms of benzene derivatives’ hydrogenation activity. Consequently, we have investigated the stabilization of nanoparticles by pyridine as the N-donor chelating agent. Two rhodium(0)

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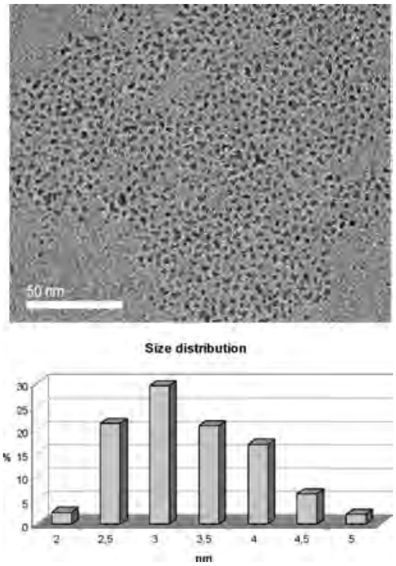

Figure 3. TEM micrograph of 2, 2′-Bipy-stabilized Rh(0) nanoparticles in [HEA][NTf$_2$].

Table 4. Influence of the Pyridine Ratio on the Catalytic Activity[a]

		products[b]	
entry	[pyridine]/[Rh] ratio	EB (%)	EC (%)
1	1	0	100
2	5	20	80

[a] Reaction conditions: 10 mg of Rh salt (3.8×10^{-5} mol), Pyridine (x eq.), [BMI][PF$_6$] (2 mL), Styrene/Rh = 100 (molar ratio), 40 bar H$_2$, 80 °C, 15 h, stirred at 1500 rpm. [b] Determined by GC analysis.

colloidal suspensions in [BMI][PF$_6$] have been synthesized with pyridine/metal molar ratios of 1 (considering the same number of pyridine patterns as in the case of the Bipy ligand) and 5. These two colloidal suspensions have been tested for the hydrogenation of styrene at 40 bar of hydrogen pressure and 80 °C. The catalytic results are presented in Table 4.

These results show a significant influence of the pyridine amount on the catalytic activity. The best result has been obtained with a pyridine/Rh molar ratio of 1 (entry 1). Nevertheless, the nanoparticles are visually destabilized at the end of the reaction. The increase of the pyridine/Rh ratio to 5 decreases the catalytic activity but increases the stability of colloids with no aggregation at the end of the reaction by steric hindrance. A good compromise could be found between these two ratios. We have checked that pyridine has not been reduced into piperidine, proving that this ligand is a good stabilizer for Rh(0) nanoparticles. This study shows the possibility of stabilizing nanoparticles by monocoordination instead of a bidentate coordination mode with an increase of the activity without any loss of stability. This approach offers several perspectives in terms of stability and activity with future-designed pyridine ligands.

Conclusion

The present work confirms the possibility to efficiently stabilize zerovalent rhodium nanoparticles with N-donor ligands. Particularly, we have shown that 2,2′-Bipy, 3,3′-Bipy and 4,4′-Bipy are good protective agents for the stabilization of Rh(0) nanoparticles in different nonaqueous ionic liquids. The synthesis mode developed in ionic liquids using chelates constitutes an alternative approach when ionic liquids such as imidazolium salts do not efficiently combine the roles of solvent and protective agent. The Bipy-stabilized Rh suspensions have proved to be efficient catalytic systems for the hydrogenation of aromatic compounds in ionic liquids. In all cases, no loss of stability at the end of the reaction has been observed. In opposition to 2,2′-Bipy, the best reactivities are obtained with 3,3′-Bipy and 4,4′-Bipy with complete conversions of styrene into ethylcyclohexane. To explain these results, we have proposed various coordination modes according to the Bipy isomer used. When a monodentate coordination mode is plausible, particularly with 4,4′-Bipy, the steric hindrance decreases on the nanoparticle surface. The substrate access therefore increases, giving a better reactivity and an efficient aromatic ring hydrogenation. We have checked the competition between mono- and bidentate coordination of the Bipy ligand by the synthesis of analogous monodentate 2,2′- and 4,4′-bipyridinium salts. Total hydrogenation of styrene has been obtained under the same catalytic conditions, justifying our proposed structural mechanism. Finally, the possibility to use a mono N-donor ligand has been shown with the use of pyridine as a protective agent. This study clearly shows, thanks to pyridine tests, that a simple monocoordination of a N ligand is sufficient to increase the activity of nanoparticles without any precipitation of colloids. Consequently, our strategy offers an interesting approach in terms of activity and selectivity such as enantioselectivity with easily chiral pyridine derivatives. This opens the field to a diversification of the protective agents that could be considered for the stabilization of nanoparticles in ionic liquids.

Experimental Section

General. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen in oven-dried glassware. THF was distilled from sodium/benzophenone. Rhodium chloride hydrate was obtained from Strem Chemicals. Sodium borohydride, 2,2′-bipyridine, 4,4′-bipyridine, and all arenes were purchased from Aldrich, Acros, or Alfa Aesar and were used without further purification. 3,3′-Bipyridine was synthetized according to a known procedure.[13] Water was distilled twice before use by conventional methods. The [BMI][PF$_6$] ionic liquid was prepared according to a known procedure,[23] dried under vigorous stirring for 6 h at 70 °C and under a vacuum. Its chloride content was checked by a AgNO$_3$ test and the purity by ^{1}H NMR and ^{31}P NMR spectra. The [BMI][NTf$_2$],[22] [MBPyrr][NTf$_2$],[24] and [MBPyr][NTf$_2$][25] ionic liquids were synthesized from already described procedures. The [HEA][NTf$_2$] was easily prepared by a procedure developed in our laboratory.[21] The 2,2′- and 4,4′-bipyridinium salts were obtained according to a procedure already described in the literature.[18]

Synthesis of the Rhodium(0) Suspension. Colloidal suspension was prepared at ambient temperature and in the open air. RhCl$_3$·3H$_2$O (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,

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9.5×10^{-5} mol, 2.5 equiv) dissolved in water (2 drops) was quickly added to the mixture under vigorous stirring. Immediately, Bipy (2.9 mg, 1.9×10^{-5} mol, 0.5 equiv/Rh) 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 for 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.

General Procedure for Hydrogenation under Hydrogen Pressure. The stainless steel autoclave was charged with 2 mL of a Bipy-stabilized Rh(0) colloidal suspension in [BMI][PF_6], and a magnetic stirrer was added. 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}) for 10 min for the precipitation of nanoparticles. The sample was analyzed by gas chromatography. All analyses were performed using a Carlo Erba GC 6000 with a 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; detector temperature, 250 °C.

X-Ray Photoelectron Spectroscopy Analysis. XPS measurements were performed using a Vacuum Generators Escalab 220XL spectrometer at CNRS UMR 8181 (UCCS, Université des Sciences et Technologies de Lille). A monochromatized aluminum source was used for excitation (Al Ka = 1486.6 eV). The binding energies were referenced to the photopeak C 1s at 285 eV. The catalyst solid form was obtained after the precipitation of metal nanoparticles by centrifugation, followed by various washings with acetone and dichloromethane and vacuum drying for 24 h.

TEM Analysis. The transmission electronic microscopic studies were conducted using an FEI Technaï G2 Sphera at 200 kV (Cathode LaB6) or a Philips CM12 at 100 kv for 3,3′-Bipy and 4,4′-Bipy-stabilized nanoparticles suspensions (UMR CNRS 6226-University of Rennes I). TEM studies were also performed on a Jeol 2100 F at 200 kV at IFP (Solaize, France).

Samples of 2,2′-Bipy-stabilized rhodium(0) nanoparticles were prepared by dropwise addition onto a copper sample mesh covered with carbon. The colloidal 2,2′-Bipy suspension was partially removed after 1 min using cellulose before transferring to the microscope. The picture is obtained at ×80.000 with a video GATAN USC1000 (CCD detector 2048 × 2048) and associated software DIGITAL Micrograph. Measurement of 155 particles was made with the program SCION Image (NIH) and was analyzed with the Excel program providing the histograms of the nanoparticles' size distribution. The sample of 2,2′-Bipy-stabilized Rh(0) nanoparticles in [HEA][NTf_2] was prepared according to the same procedure, and the size was manually calculated by the measurement of about 200 particles with the program SCION Image (NIH).

Samples of 3,3′- and 4,4′-Bipy-stabilized rhodium(0) nanoparticles were prepared by dropwise addition onto carbon-covered copper grids. The colloidal suspension was partially removed after 1 min using cellulose before transferring to the microscope. The histograms of the size distribution of the nanoparticles were estimated after the original negative had been digitally scanned for more occurate resolution. Measurement of about 200 particles was manually made with the program SCION Image (NIH).

Acknowledgment. We thank Institut Français du Pétrole and CNRS for financial support. We also thank Léon Gengembre from ≪Unité de Catalyse et de Chimie du Solide≫ at the ≪Université des Sciences et Technologies de Lille≫ for XPS measurements.

IC8010713