



Short communication

Tuning the hydrogen donor/acceptor behavior of ionic liquids in Pd-catalyzed multi-step reactions



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ABSTRACT

Palladium nanoparticles stabilized by thioether-phosphine ligands (**1–3**) were used as catalytic precursors in Heck–Mizoroki cross-coupling and C=C reduction reactions in ionic liquids. The ionic liquid [EMI][MeHPO₃] (**A**) exhibited an important hydrogen donor/acceptor behavior depending on the reaction conditions. Tandem or parallel pathways for C–C coupling and H-transfer reactions were observed, leading to the coupled product *trans*-4-phenyl-3-buten-2-one (**I**) and the corresponding reduced partner 4-phenylbutan-2-one (**II**) pointing to a molecular-like catalytic reactivity of the process. When the reaction was carried out under hydrogen pressure and low temperature, the reduction to **II** was inhibited by the presence of thioether-phosphine ligands.

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1. Introduction

One of the main applications of metal nanoparticles (MNP) relies on their ability to achieve homo- or heterogenous catalytic transformations [1–4]. The modulation of size, shape and catalytic performance of MNP is one of the main challenges in this area [5–8]; nevertheless, the surface-like reactivity of the MNP with organic molecules cannot be ruled out, since it has been found that PdNP activate C–S and C–P bonds' cleavage [9]. Stabilization of MNP can be achieved by the fitting combination of ligands and ionic liquids (ILs). It is well-established that the presence of ionic liquids in catalytic processes makes possible a highly efficient product separation together with successful nanocatalyst recycling [10–16]. Some of the ligands that have been employed in MNP in ILs include phenantroline [17], bipyridines [18], pyridines [19] and amines [20,21]. The most commonly used ILs stem from imidazolium cations resulting in highly stabilized and well-structured MNP, where the possible formation of NHC-carbene species on the nanoparticle surface represents a main drawback [22]. In general, IL cations are considered as non-innocent ligands in many reactions, whereas IL anions are mistakenly considered as 'spectators'. In a previous study, we investigated the reaction chemistry of palladium nanoparticles with

phosphorous ligands in the ionic liquid [EMI][MeHPO₃] (**A**) [23]. We found a unique catalytic system for a one-pot multi-step process of Heck–Mizoroki reaction followed by reduction of the coupled product in a sequential way (Scheme 1) as a result of a cooperative effect between the ligand and the ionic liquid.

We observed that the presence of ligands such as **1** (Scheme 2) in combination with ionic liquid **A** triggered tandem reactions to obtain phenylbutanones whose skeleton is commonly found in fragrances.

With the aim to get a deeper insight in the influence of thioether-phosphine ligands (**L**) on the stabilization of nanoparticles and their role in multi-step catalytic reactions in ionic liquids, we turned our attention to the study of different substituents on the thioether moiety; in addition to the aryl-derivative **1**, we explored the reactivity of palladium nanoparticles stabilized by **L** (PdNPL, **L** = **1–3**) employing a long chain hydrocarbon (**2**) to promote stabilization by steric effects, and an ethyl-ene chain containing a OH group (**3**) in order to favor the interaction with the ionic liquid. Herein, we report a systematic study of the influence of both thioether-phosphine-based ligands and the ionic liquid nature on the stabilization of PdNP as well as on the combined Heck–Mizoroki cross-coupling reaction followed by reduction of the alkene function.

2. Experimental section

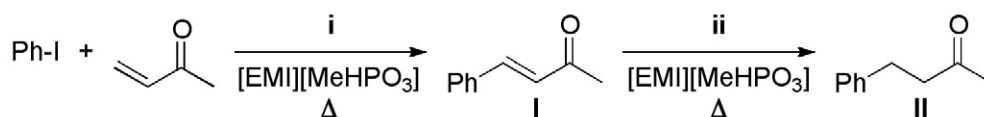
2.1. General methods

A description of all the equipments reagents used can be found in Appendix A.

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i Heck-Mizoroki cross-coupling: [Pd]/L
 ii C=C reduction: [Pd]/L, IL or H₂

Scheme 1. One-pot sequential Heck–Mizoroki cross-coupling/reduction reaction.

2.2. Synthesis of palladium nanoparticles PdNPL (L = 1–3): General methodology

[Pd₂(dba)₃]·CHCl₃ (0.05 mmol of Pd, 23 mg) and the appropriate ligand (0.01 mmol, ratio Pd/L = 1/0.2) were placed in a Fisher–Porter bottle. 5 mL of the corresponding IL (IL = A or B; A = [EMI][MeHPO₃], B = [BMP][NTf₂]) was introduced under an argon atmosphere. The system was then pressurized with H₂ (3 bar) and stirred at 50 °C overnight, leading to a black solution. After replacing the residual H₂ pressure by argon, a sample was taken for TEM and GC analyses. The solution was washed with pentane (3 × 20 mL) and dried under reduced pressure. The organic phase was concentrated and analyzed by ¹H NMR, proving the absence of free ligand.

2.3. Catalytic experiments: Heck–Mizoroki cross-coupling/hydrogen transfer concomitant reactions

Iodobenzene (204 mg, 1 mmol) and butenone (0.1 mL, 1.2 mmol) were added to 1 mL of preformed PdNPL in A (PhI/Pd = 100; L = 1, 2 or 3; A = [EMI][MeHPO₃]). The mixture was stirred at the selected temperature (90, 120 or 150 °C) for 16 h. Products were extracted from the IL phase with cyclohexane (5 × 5 mL), the organic solvent phase was filtered over celite and volatiles were removed under reduced pressure. The reaction mixture was analyzed by ¹H NMR in order to determine the conversion of the process.

In the case of PdNPL/B, (B = [BMP][NTf₂]) NEt₃ (0.35 mL, 2.5 mmol) and isopropanol (77 μL, 1 mmol) were also added as base and hydrogen transfer reagent, respectively, and the reaction mixture was treated as described above.

2.4. Catalytic experiments: hydrogen transfer. Reduction of trans-4-phenyl-3-buten-2-one (I)

A 50 mL Schlenk tube was charged with trans-4-phenyl-3-buten-2-one (I) (146 mg, 1.2 mmol) and 1 mL of preformed PdNPL in IL (I/Pd = 100; L = 1, 2 or 3; IL = A or B). The mixture was stirred at the desired

temperature (90, 120 or 150 °C) for 16 h. Products were extracted from the IL phase with cyclohexane (5 × 5 mL), the organic solvent phase was filtered over celite and volatiles were removed under reduced pressure. The reaction mixture was analyzed by ¹H NMR in order to determine the conversion of the process.

2.5. Catalytic experiments: hydrogenation. Reduction of trans-4-phenyl-3-buten-2-one (I)

A mixture of trans-4-phenyl-3-buten-2-one (146 mg, 1.2 mmol) and 1 mL of preformed PdNPL in A (I/Pd = 100; L = 1, 2 or 3) were placed in a 45 mL stainless steel reactor. The system was perfectly closed and vacuum was applied for 15 min. The reactor was stirred and heated to the desired temperature (30, 50 or 80 °C) and charged with pressure of hydrogen (20 or 40 bar). After the desired time (16 or 24 h), the reactor was cooled to room temperature, followed by depressurization. Products were extracted from the IL phase with cyclohexane (5 × 5 mL), the organic solvent phases were filtered over celite and volatiles were removed under reduced pressure. The reaction mixture was analyzed by ¹H NMR to determine the conversion of the process.

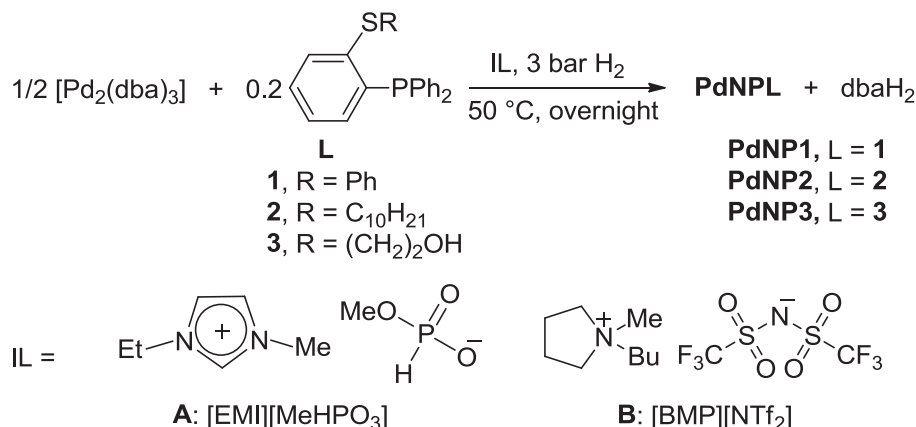
3. Results and discussion

3.1. Synthesis of PdNPL in ionic liquids

Ligands 1–2 were prepared as we reported elsewhere [9] and 3 was obtained from the thiophenol derivative and bromoethanol as a white solid and was fully characterized by conventional spectroscopic techniques (see Appendix A).

PdNPL (L = 1–3) were prepared from decomposition of [Pd₂(dba)₃]·CHCl₃ by molecular hydrogen under mild conditions (50 °C, 3 bar H₂) using [EMI][MeHPO₃] (A) and [BMP][NTf₂] (B) for comparative purposes (Scheme 2).

In all cases, the obtained black solutions were analyzed by TEM (Fig. 1) and EDX (see Appendix A). The ligands exhibited a strong influence on the size, distribution and stabilization of nanoparticles. Well-dispersed spherical nanoparticles with 2D arrays were obtained for



Scheme 2. Synthesis of palladium nanoparticles (PdNPL) in ionic liquids.

Table 1
Heck–Mizoroki cross-coupling/H-transfer concomitant reactions using PdNPL in ILs.^a

IL: **A**, [EMI][MeHPO₃]
B, [BMP][NTf₂]

Entry	Catalytic system	T (°C)	Conv. (%) ^b	I/II
1	PdNP1/A	90	61	60/40
2	PdNP1/A	120	100	80/20
3	PdNP2/A	90	71	50/50
4	PdNP2/A	120	100	78/22
5	PdNP3/A	90	61	40/60
6	PdNP3/A	120	100	73/27
7 ^c	PdNP1/B	120	100	97/3
8	PdNP/A ^d	120	100	92/8
9	PdNP1/A	150	100	20/80

^a Reaction conditions: iodobenzene/butenone/Pd, 1/1.2/0.01 mmol.

^b Determined by ¹H NMR.

^c Addition of 2.5 mmol of Et₃N and 1.0 mmol of *i*PrOH.

^d Synthesis reported in reference [23].

PdNP1/A and **PdNP3/A**. In contrast, **PdNP2/A** showed agglomerated areas and a broad size distribution, indicating lower nanoparticle stabilization in spite of the presence of a long alkyl chain on **2**. The best dispersions and narrow distributions were obtained using the thioether-phosphine containing a phenyl substituent, ligand **1**, in both ILs, **A** and **B** (Fig. 1a and d). In the absence of ligands, **PdNP/A**, displayed a well-dispersed material with a substantially higher nanoparticles size ($d_m = 3.7 \pm 0.6$ nm) compared to those observed when **1–3** were used as stabilizers (see Appendix A). Organic extracts from **PdNPL/A** solutions were analyzed by GC to determine the stability of ligands during the formation of nanoparticles (see Appendix A), since when **PdNPL** were synthesized in THF in the presence of **1** or **2**, we observed partial fragmentation of ligands [9]. Using **1–3** as stabilizers, benzene was

detected; in the case of **2**, decane and decylphenylthioether could be also observed, but in any case obtaining less than 6% fragmentation, in contrast to the 28% attained in THF [9]. These results suggest that the ionic liquid prevents the interaction between the metal surface and S–C or P–C bonds, thus avoiding their activation through oxidative addition reactions.

3.2. Palladium-catalyzed Heck–Mizoroki cross-coupling and H-transfer reactions

With the aim to test the performance of palladium nanoparticles in Heck–Mizoroki cross-coupling reaction using ionic liquids, screening catalytic experiments were carried out using iodobenzene and

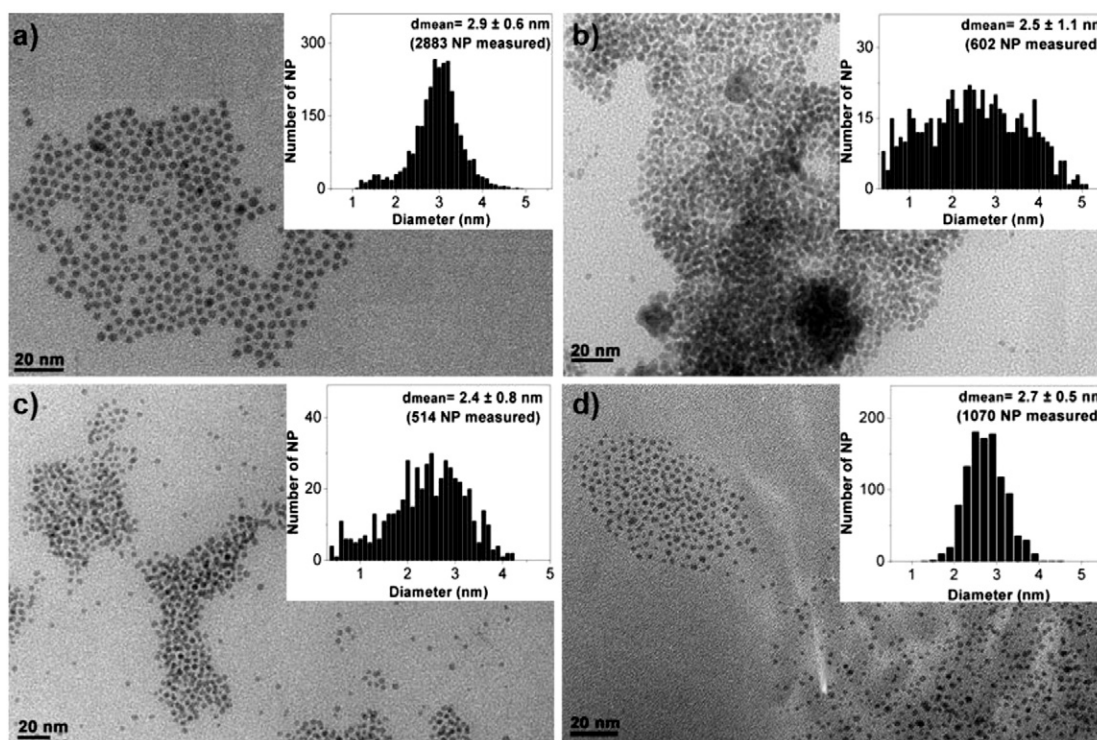


Fig. 1. TEM micrographs and size distribution histograms for: a) **PdNP1/A**; b) **PdNP2/A**; c) **PdNP3/A** and d) **PdNP1/B**.

Table 2
Hydrogen transfer reactions using PdNPLs in ILs.^a

Entry	Catalytic system	T (°C)	Conv. (%) ^b
1	PdNPL/A	90	<5
2	PdNP1/A	120	27
3	PdNP1/B	120	<5
4 ^c	PdNP1/A	120	<5
5	PdNP1/A	150	92
6	PdNP2/A	150	94
7	PdNP3/A	150	72
8	PdNP-PPH ₃ /A ^d	150	61

^a Reaction conditions: *trans*-4-phenyl-3-buten-2-one/Pd = 1/0.01 mmol.

^b Determined by ¹H NMR.

^c Addition of 2.5 mmol of Na₂CO₃.

^d Synthesis reported in reference [23].

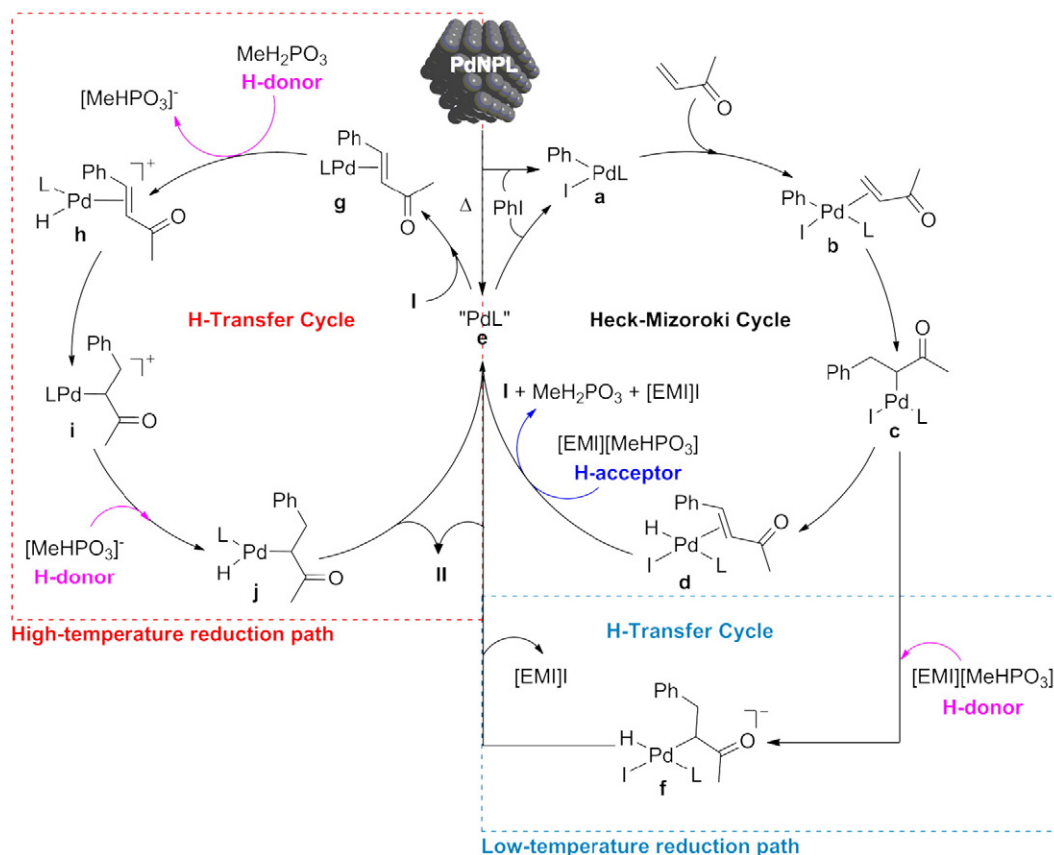
butenone to form the coupled product **I**. As we previously observed [23], phenylbutanone **II** was also generated under the reaction conditions. Selected results are collected in Table 1.

At the end of the reaction, orange colored solutions were obtained denoting that the reaction proceeded in a molecular fashion, where PdNP acted as molecular catalyst reservoirs. The resulting solutions were analyzed by TEM, revealing the absence of dispersed nanoparticles in the medium.

In general, both conversion and selectivity toward the Heck coupling product **I** increased at high temperatures (**I**/**II** = 1/1 at 90 °C; **I**/**II** = 4/

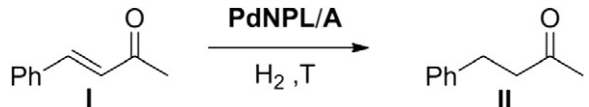
1 at 120 °C) while the nature of **L** did not significantly affect the selectivity (Table 1, entries 1, 3, 5 and 2, 4, 6). Employing [BMP][NTf₂] (**B**) as ionic liquid or in the absence of ligand, **I** was quantitatively obtained indicating that the ionic liquid **A** acts as hydrogen donor to form **II** by a hydrogen transfer reaction from the anion [23]; in addition, the presence of the thioether-phosphine ligand (**1–3**) favored this H-transfer (Table 1, entries 1–3 vs 8). When **B** was used, an external base was required to form the Heck product and the attempt to promote the hydrogen donation using isopropanol as transfer agent, was unsuccessful (Table 1, entry 7).

PdNPL were evaluated in the hydrogen transfer reaction to form the hydrogenated product **II** from **I** using [EMI][MeHPO₃] (**A**) as hydrogen donor. In all cases, yellowish orange to brown solutions were observed during the reduction reaction, pointing to the formation of palladium molecular species. Results shown in Table 2 corroborate the role of **A** as H-transfer agent (Table 2, entries 2, 5–8), which was inhibited when Na₂CO₃ was added (Table 2, entry 4). Excellent conversions were achieved at higher temperatures and the activity was related to the nature of **L**, exhibiting the following trend: **1–2** > **3** > PPh₃ (Table 2, entries 5–8). In the case of direct H-transfer, palladium species were not active to produce **II** from **I** at 90 °C in contrast to the results obtained in the apparent tandem reaction, where the selectivity was almost 1/1 for **I**/**II** (40–60% of **II**) at low temperature (Table 1, entries 1,3,5 vs Table 2, entry 1). This behavior indicates that both reactions, Heck–Mizoroki cross-coupling and H-transfer, do not proceed in a sequential mode but they are competing reactions sharing the exact same intermediate. At 120 °C, the yield obtained in the direct reduction reaction; point out to a tandem coupling/reduction process (Table 1, entry 2 vs Table 2, entry 2). In fact, when the reaction between iodobenzene and butenone was carried out at 150 °C employing PdNP1/A, full conversion and good selectivity toward the reduced product **II** were achieved (Table 1, entry 9; **I**/**II** = 20/80).



Scheme 3. Proposed mechanism for palladium-catalyzed multipath process in the ionic liquid [EMI][MeHPO₃] (**A**).

Table 3
Hydrogenation reactions of **I** using PdNPL in [EMI][MeHPO₃] (A).^a



Entry	Catalytic system	T (°C)	H ₂ (bar)	Conv. ^b (%)
1	PdNP1	50	20	32
2	PdNP	30	20	100
3 ^c	PdNP1	80	40	74
4 ^c	PdNP2	80	40	85
5 ^c	PdNP3	80	40	93

^a Reaction conditions: *trans*-4-phenyl-3-buten-2-one/Pd = 1/0.01 for 16 h.

^b Determined by ¹H NMR.

^c For 24 h.

Taking into account the overall catalytic results, we propose that three processes operate in the reaction between iodobenzene and butenone and the reaction pathway depends on both the temperature and the hydrogen donor/acceptor behavior of the ionic liquid (Scheme 3). PdNPL work as precursor of molecular species which are formed by: oxidative addition of iodobenzene to the metallic surface generating Pd(II) species **a**, via known mechanisms [24], or nanoparticle degradation by temperature. Both processes are assisted by thioether-phosphine ligands since they can bind to palladium in bi- or monodentate form, depending on the metal coordinative requirements, leading to the formation of catalytically active molecular species. The Heck–Mizoroki cross-coupling cycle proceeds by the coordination of butenone to complex **a**, further carbometallation produces the alkyl-palladium species **c**. Depending on both, the temperature and the behavior of the ionic liquid, the hydrogen transfer reaction occurs in a tandem mode or competes with the cross-coupling reaction. At relative low temperature (right dotted box), the intermediate **c** is involved in the H-transfer path, where the anion [MeHPO₃][−] acts as a hydrogen donor species giving **f** which leads to **II** by reductive elimination, regenerating the Pd(0) species **e**. In a parallel path, IL acts as hydrogen acceptor toward hydride complex **d**, which is formed by β-elimination from **c**, affording **I** and **e**. In both pathways, species **e** is stabilized by the thioether-phosphine ligand. When the temperature increases, the Heck–Mizoroki reaction path is faster than the low-temperature hydrogen transfer path (right dotted box) thus, the selectivity to **I** enhances. However, at even higher temperatures (left dotted box), **I** is converted to **II** in a tandem fashion through the coordination of **I** to Pd(0) species, generating an olefin complex **g**, which undergoes a proton addition from the conjugated acid of [MeHPO₃][−] (species **h**). Subsequent hydrometallation leads to alkyl-palladium species **i**, where hydrogen donation by [MeHPO₃][−] followed by reductive elimination, gives **II** and regenerates Pd(0) species **e**.

3.3. Palladium-catalyzed hydrogenation reactions: homogeneous versus heterogeneous catalysts

In order to explore the influence of **1–3** on PdNPL reactivity as heterogeneous catalysts, we carried out the reduction of coupled product **I** under hydrogen pressure. As it is shown in Table 3, the presence of **L** on nanoparticles inhibited the *trans*-4-phenyl-3-buten-2-one **I** reduction; therefore it was necessary to increase the temperature and also the H₂ pressure to improve the activity. The reaction proceeded in a heterogeneous fashion at moderately harsh conditions (Table 3, entries 1 and 2; black solutions were observed during all the reaction time) meanwhile, at 80 °C and 40 bar of H₂ pressure, orange colored resulting solutions suggested the formation of molecular systems which are favored by the ligand presence and high temperature (Table 3, entries 3–5). TEM studies of the orange solution revealed the absence of nanoparticles. In heterogeneous-like catalysts, the coordination of ionic liquid and the thioether-phosphine ligand hindered the interaction between **I** and the metal surface. In the case of

homogeneous-like catalysts, an H-transfer pathway is discarded because at low temperatures this process does not occur as demonstrated in Section 3.2. Therefore, we propose that an oxidative addition of molecular hydrogen on palladium takes place, and due to the presence of **L** on the surface, the sequestration of Pd atoms occurs, leading to **L**-Pd-hydride molecular species, responsible for the reduction of **I** to **II**, generating molecular LPd(0) complexes and restarting the catalytic cycle. The effect of **L** on the catalytic performance (**3** > **2** > **1**) could be explained in terms of the electronic donor properties of the sulfur substituent on LPd(0) complexes favoring the dihydrogen oxidative addition.

4. Conclusions

The Heck–Mizoroki and reduction multi-step process in the ionic liquid [EMI][MeHPO₃] (A) using PdNPL was explored; the palladium nanoparticles stabilized by thioether-phosphine ligands generate catalytically active molecular species which are involved in diverse reaction pathways depending on both reaction temperature and hydrogen donor/acceptor properties of the ionic liquid. When the ionic liquid acts as H-acceptor, the Heck–Mizoroki reaction is favored; whereas as H-donor, the hydrogen transfer reaction proceeds. A thorough analysis of the catalytic results permitted to conclude that at relative low temperature, the Heck–Mizoroki and H-transfer reactions, compete sharing the same palladium intermediate. Meanwhile, at higher temperatures both reactions complement each other through a tandem process; therefore, it is possible to modulate the mechanism pathway and the resulting product, coupled (**I**) or reduced (**II**), by selection of the appropriate ionic liquid and temperature range.

When no H-transfer reaction occurs, heterogeneous species are responsible for the reduction of the Heck product in the presence of dihydrogen under mild conditions; however, their performance diminished by the presence of ligands. In contrast, an increase in temperature led to the formation of catalytically active molecular species, presumably favored by thioether-phosphines. Under these conditions the ionic liquid acts merely as solvent.

Taking into account that imidazolium-based ionic liquids used in this work efficiently immobilize the catalyst, the scope of the coupling/reduction process including the catalytic phase recycling, is currently underway.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.10.011>. These data include MOL files and InChiKeys of the most important compounds described in this article.

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