Palladium nanoparticles in ionic liquids stabilized by mono-phosphines.

Catalytic applications

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Abstract

Palladium nanoparticles generated from organometallic complexes in the presence of functionalized mono-phosphines (L1-L3), in both THF and imidazolium-based ionic liquids (ImILs), were successfully synthesized. Depending on the phosphine and solvent nature, PdNPs with different extent of aggregation were observed. Actually, the ligand L1, P(CH2CH2CH2Ph)3, led to small and well-dispersed nanoparticles in both ILs, [BMI][PF6] and [EMI][HP(O)2OMe], in contrast to more agglomerated PdNPs obtained in THF. PdNPs in ILs were catalytically active and chemoselective in C-C cross-coupling (Suzuki-Miyaura and Heck-Mizoroki) and hydrogenation reactions. Well-defined Pd(0) and Pd(II) organometallic complexes containing L1, [PdCl2(L1)2] and [Pd(ma)(L1)2], were also prepared for comparative purposes.

Introduction

Imidazolium-based ionic liquids (ImILs) represent the most common molten salts applied in catalysis [1]. Especially, they have found a remarkable success in the field of nanocatalysis, where metallic nanoparticles (MNPs) are involved in the catalytic process [2]. The highly organized structures exhibited by ImILs permit the stabilization of nanoclusters in the absence of other kind stabilizers, named “ligand-free” systems [3]. The presence of ligands (in general relatively small organic entities containing donor groups, such as thiols, amines, isocyanides, phosphines…) as stabilizers other than the ImIL salts, often contributes to control the size and to improve the dispersion and solubility of MNPs, impeding their aggregation and prompting on their reactivity [4]. In particular for palladium
nanoparticles (PdNPs), the use of phosphines as stabilizers has captivated the attention of many research groups working on catalysis due to coordinating properties and versatile structural modification increasing activity and selectivity, mainly using bis-P-donor ligands (diphosphines, diphosphites) [5] or phosphines containing an additional donor center, such as thioether-phosphines [6]. However, PdNPs capped with mono-phosphines have received less attention [7]. To the best of our knowledge, PdNPs containing mono-phosphines in ILs have not been previously reported.

Results and discussion


We synthesized PdNPs in both an organic solvent (THF) and ImILs ([BMI][PF₆], [EMI][HP(O)₂OMe]), by decomposition of molecular organometallic precursors [Pd(ma)(nbd)] (ma = maleic anhydride; nbd = norbornadiene) and [Pd₂(dba)₃] (dba = dibenzylidenacetone) under dihydrogen atmosphere, and in the presence of mono-phosphines L₁-L₃ (Scheme 1) [8], based on reported methodologies [9].

![Scheme 1. Synthesis of PdNPs stabilized by monophosphines L₁-L₃ in THF and imidazolium-based ionic liquids (for L₁, the BH₃-L₁ adduct was used instead of free L₁).](image)

We chose mono-phosphines containing a second function (phenyl group in L₁ or cyano group in L₂) in order to reinforce the coordination at the metallic surface; for comparative purposes, the phosphine L₃, with a non-coordinated arm, was also considered. In fact, the phosphine L₁ containing an alky-phenyl substituent, i.e. 3-phenylpropyl arm, was envisaged based on our previous observations [10]. We evidenced a π,π'-coordination mode of the ligand 4-(3-phenylpropyl)pyridine by the two aromatic rings (phenyl and pyridyl groups) at the metallic surface of ruthenium nanoparticles [11]. Due to the air sensitivity exhibited by the trialkyl phosphine L₁, the adduct H₃B-L₁ (from now simply L₁) was used in the synthesis of PdNPs, with the aim to limit its oxidation.

For both metallic precursors, [Pd(ma)(nbd)] and [Pd₂(dba)₃], agglomeration was favored when THF was used as solvent (Fig. 1, a and b). However more dispersed systems were observed when ImILs were involved, obtaining relatively small spherical nanoparticles.
In particular for PdNPL1_{nbd,BMI} and PdNPL1_{dba,EMI} (Fig. 1, d and f, respectively); in both cases, the mean diameter was similar: 2.2-2.6 ± 0.8-0.9 nm (Fig. 1, g-h). These observations point to a better dispersion of PdNPs in ILs than in THF. Different factors can justify this behaviour, such as the template effect induced by the structural organization of ImILs or the ion interactions with the metallic surface [12].

Powder X-ray diffraction (XRD, Fig. 2) and the crystallographic planes spots observed by fast Fourier transform to the HRTEM on a single particle, proved the fcc structure exhibited by PdNPs prepared in both THF and IL, PdNPL1_{nbd,THF} and PdNPL1_{nbd,BMI} (Figs. 2 and 3, respectively) [13]. In addition, the corresponding energy dispersive X-ray analysis (EDX) proved the presence of both the phosphine and IL in the nanoparticle.
When L2 was involved as stabilizer, nanoparticles were obtained exhibiting different types of dispersion and organization depending on the nature of metallic precursor and solvent used (Fig. 4). TEM analyses for PdNPs prepared in THF showed dispersed spherical nanoparticles with no uniform size, observing at least two different populations (1.6 ± 0.6 nm and 2.3 ± 1.6 nm, Fig. 4, a and b respectively), together with sponge-like agglomerates (Fig. 4, c-d), pointing to a poor stabilization of the nanoparticles due to both the solvent and ligand effect. In both ILs, [BMI][PF6] and [EMI][HP(O)2OMe], only agglomerates could be observed, constituted by small nanoparticles like in THF (Fig. 4, e-f).

Using L3 as stabilizer in THF and in [BMI][PF6] for both metal precursors, only agglomerates could be observed (Fig. 5); in addition, 31P NMR spectra recorded from the washing phases after the synthesis of the corresponding PdNPs, showed the formation of phosphine oxide. Phosphine L3 under synthesis conditions led to Ph2PCH2CH2CH3 by hydrogenation of the C=C bond. Consequently and in contrast to L1 and L2, no additional coordination group other than phosphorus is present in its structure, fact that can explain the worse dispersion, favoring the formation of agglomerated materials.

After these results, PdNPs containing L1 were chosen as catalytic precursors for the catalytic study (see section 3).

Pd(II) and Pd(0) organometallic complexes with ligand L1 were prepared, with the aim to use them in catalysis and comparing their behavior with that observed using preformed nanoparticles as catalytic materials. These complexes, [PdCl₂(L1)₂] and [Pd(ma)(L1)₂], were synthesized in high yields (up to 85%) by conventional methods [14] and fully characterized both in solution and solid state (Scheme 2). In the case of [PdCl₂(L1)₂] only trans isomer was observed by ³¹P NMR and IR spectroscopy.

The Pd(II) complex [PdCl₂(L1)₂] was crystallized from a solution of complex in dichloromethane and slow diffusion of pentane, obtaining suitable crystals for an X-ray diffraction study. Figure 6 shows the molecular view and a selection of bond lengths and angles. The palladium atom exhibits a square-planar coordination, bonded to two phosphorus and two chlorine atoms, in a trans arrangement. The distances and angles were in the expected range for this type of complexes [15]. A weak noncovalent intramolecular Cl-π interaction could be observed, showing Cl-π distances 4.03-4.08 Å with angles of the Cl-centroid axis to the plane of the aromatic ring 82-88 °, slightly longer than those reported in the literature [16].

3. Catalytic behavior of preformed PdNPs in ImIIₗs.

PdNPs stabilized by BH₃-L₁, PdNPL₁ₐbd,BMI and PdNPL₁dba,BMI, were evaluated in the hydrogenation reaction of (E)-4-phenyl-3-buten-2-one in [BMI][PF₆] (Table 1). Both systems were active under smooth conditions (entries 1-4), leading to full conversion after 1h under 5 bar of dihydrogen pressure at 50 °C (entries 2 and 4). In any case, 4-phenyl-2-butanone was exclusively obtained, model molecule of interest for the synthesis of
some fragrances [17]. Organic compounds were quantitatively extracted from the catalytic phase (control of the recovered mass). With ligands L2 and L3, the corresponding PdNPs were much less active, and only full conversion was achieved under 40 bar during 16h of reaction (entries 5 and 6). This behavior agrees with the low stabilizing character of ligands L2 and L3 in relation to L1 (see above). In the absence of palladium, the reaction did not take place.

Table 1. Pd-catalyzed hydrogenation of (E)-4-phenyl-3-buten-2-one using preformed PdNPs as catalytic precursors.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>pH₂ (bar)</th>
<th>t(h)</th>
<th>Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdNPL1dba,BMI</td>
<td>3</td>
<td>1</td>
<td>48</td>
</tr>
<tr>
<td>2</td>
<td>PdNPL1dba,BMI</td>
<td>5</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>PdNPL1nbd,BMI</td>
<td>3</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>PdNPL1nbd,BMI</td>
<td>5</td>
<td>1</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>PdNPL2nbd,BMI</td>
<td>40</td>
<td>16</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>PdNPL3nbd,BMI</td>
<td>40</td>
<td>16</td>
<td>100</td>
</tr>
</tbody>
</table>

Data from duplicated results. Conditions: 1 mmol of (E)-4-phenyl-3-buten-2-one, 1 mL of PdNPs in [BMI][PF₆] (0.01 mmol Pd), 50 °C. * Determined by ¹H NMR.

However after catalysis, TEM analyses evidenced the agglomeration of the catalytic system (Fig. 7), in contrast to ligand-free PdNPs in [BMI][PF₆], for those nor size neither morphology changes were observed after catalysis [3b,18]. Unfortunately this behavior impedes their recycling.

PdNPs-based catalysts were also tested in Suzuki-Miyaura cross-couplings (Table 2). The nanocatalyst systems PdNPL1nbd,BMI and PdNPL1dba,BMI were active for both substrates, I and II; but the system synthetized from [Pd₂(dba)₃] precursor was relatively more active than that corresponding from [Pd(ma)(nbd)] one (entries 1-2 vs 3-4, Table 2). It is important to underline that practically no difference in reactivity was observed using electron-donor and electron-withdrawing groups (especially for PdNPL1dba,BMI, entries 1-2, Table 2) in agreement with reported data for PdNPs in conventional organic solvents, and in contrast to what is observed under homogeneous conditions (involving molecular catalysts) [19]. In addition, these systems showed a remarkable chemoselectivity, only observing a low amount of biphenyl (5-10%). However PdNPL2nbd,BMI and PdNPL2dba,BMI led to low conversions (<50%, entries 5 and 6, Table 2), favoring the formation of biphenyl; this behavior is in agreement with the formation of agglomerated palladium systems (see above).

Using [PdCl₂(L1)_2] as catalytic precursor, very low conversion could be attained.
under the same conditions (entry 7, Table 2). The Pd(0) molecular complex [Pd(ma)(L1)2] was inactive (entry 8, Table 2), probably due to the robustness that offer the phosphine ligand to the complex, avoiding thus the reactivity with the reagents. These results proved the convenience to use PdNPs stabilized by monophosphines in relation to well-defined organometallic compounds in this kind of catalytic reactions.

**Table 2.** Pd-catalyzed Suzuki-Miyaura cross-coupling reactions using preformed PdNPs as catalytic precursors.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>R</th>
<th>Conv. (%)</th>
<th>III or IV/biphenyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PdNPL1dba,BMI</td>
<td>OMe</td>
<td>93</td>
<td>19/1</td>
</tr>
<tr>
<td>2</td>
<td>PdNPL1dba,BMI</td>
<td>CF$_3$</td>
<td>100</td>
<td>100/0</td>
</tr>
<tr>
<td>3</td>
<td>PdNPL1nbd,BMI</td>
<td>OMe</td>
<td>70</td>
<td>9/1</td>
</tr>
<tr>
<td>4</td>
<td>PdNPL1nbd,BMI</td>
<td>CF$_3$</td>
<td>95</td>
<td>19/1</td>
</tr>
<tr>
<td>5</td>
<td>PdNPL2nbd,BMI</td>
<td>OMe</td>
<td>39</td>
<td>1/1</td>
</tr>
<tr>
<td>6</td>
<td>PdNPL2nbd,BMI</td>
<td>OMe</td>
<td>46</td>
<td>1.5/1</td>
</tr>
<tr>
<td>7</td>
<td>[PdCl$_2$(L1)$_2$]</td>
<td>OMe</td>
<td>15</td>
<td>n.d.</td>
</tr>
<tr>
<td>8</td>
<td>[Pd(ma)(L1)$_2$]</td>
<td>OMe</td>
<td>&lt;5</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*a Data from duplicated results. Reaction conditions: Pd / Substrate / Phenyl boronic acid / Na$_2$CO$_3$ = 0.01 / 1 / 1.1 / 2.5. 1 mL of PdNPs in [BMI][PF$_6$] (0.01 mmol Pd), 1 mL of H$_2$O, 100 °C, 16 h. b Determined by $^1$H NMR. c Determined by GC-MS (no other homocoupling products were observed).

Figure 8. TEM micrographs and size distribution diagrams observed for PdNPL1nbd,BMI before and after Suzuki-Miyaura coupling. a) and b) before catalysis ($\phi$ mean = 2.2 ± 0.8 nm; for 451 particles counted). c) and d) after catalysis, substrate = 4-bromoanisole ($\phi$ mean = 2.7 ± 0.9 nm for 1420 particles counted). e) and f) after catalysis, substrate = 4-trifluoromethyl bromobenzene ($\phi$ mean = 2.9 ± 0.9 nm for 1320 particles counted).

Based on our previous works [18,21], we wanted to carry out the one-pot sequential process, consisting in a Heck-Mizoroki coupling followed by hydrogenation to obtain 4-phenyl-2-butanone, starting form iodobenzene and 3-buten-2-one and only involving one catalytic precursor. With the aim to avoid the formation of palladium-N-heterocyclic carbene species (Pd-NHC) [22] which are inactive for the further hydrogenation step, we used [EMI][HP(O)$_2$OMe] as IL due to the basic cross-coupling process and further readsoption on nanoclusters [3a, 20].
character of the anion, permitting to work in the absence of an additional base [23].

In contrast to our previous experiences, under these “base-free” conditions, the catalytic solution for the first step (C-C coupling) was orange (formation of molecular Pd species) and no PdNPs could be reformed again under hydrogen pressure. But surprisingly, the analyses of the organic phase after the coupling (in the absence of H$_2$) led to a mixture of two products, (E)-4-phenyl-3-buten-2-one (expected Heck coupling product) and 4-phenyl-2-butanone (reduced product from the Heck coupling product), in a ratio 2/3 respectively (Scheme 3).

Scheme 3. Pd-catalyzed coupling between iodobenzene and 3-buten-2-one in [EMI][HP(O)$_2$OMe].

This catalytic behavior seems to point a molecular-like reactivity. In fact, the recently proposed mechanism suggests that the nature of the catalyst depends on both the IL nature and temperature range [6a].

Conclusions

To sum up, PdNPs were successfully synthesized by decomposition of organometallic precursors, [Pd(ma)(nbd)] and [Pd$_2$(dba)$_3$], under dihydrogen reducing atmosphere both in THF and ionic liquids ([BMI][PF$_6$] and [EMI][HP(O)$_2$OMe]), using mono-phosphines (L$_1$-L$_3$) as stabilizers. In contrast to ligands L$_2$ and L$_3$ which exhibited a trend to give agglomerated systems, small, spherical and well-dispersed PdNPs (mean diameter = ca. 2-3 nm) were obtained involving L$_1$, in particular using [BMI][PF$_6$] as solvent and starting from [Pd(ma)(nbd)].

PdNPs in ILs were applied in C=C bond hydrogenation and C-C coupling processes. Concerning hydrogenations, PdNPs-based systems containing L$_1$, L$_2$ or L$_3$ phosphines were active, exhibiting a better reactivity those based on L$_1$, which performed under smooth conditions (3-5 bar H$_2$, 50 °C, 1 mol% Pd).

The most well-dispersed systems PdNPL$_1$dba,BMI and PdNPL$_1$nbd,BMI led to full conversions and high chemoselectivity in Suzuki-Miyaura cross-couplings for bromobenzene based substrates containing electron-donor and electron-withdrawing substituents. However PdNPL$_2$dba,BMI and PdNPL$_2$nbd,BMI were less efficient probably due to their aggregated state. Well-defined organometallic complexes, [PdCl$_2$(L$_1$)$_2$] and [Pd(ma)(L$_1$)$_2$] were practically inactive. Unfortunately these systems were not recyclable, observing aggregation after catalysis, which points to a weak stabilizer character of the phosphines. It is important to underline that PdNPs systems in [EMI][HP(O)$_2$OMe] were evaluated in Heck-Mizoroki coupling, giving as main product the reduced compound in the absence of dihydrogen and in the absence of additional base. This behavior proved the multiple role of the anion.
HP(O)$_2$OMe, as partner of the solvent, base and reducing agent. This behavior permits to envisage the development of multi-task ionic liquids adapted for synthetic purposes.

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**Experimental part**

All manipulations, including the synthesis of phosphines ($L_1$-$L_3$) [8], palladium complexes, nanoparticles and catalytic reactions were performed under Ar atmosphere using Schlenk protocols. Phosphorus trichloride (PCl$_3$), diphenyl phosphate (Ph$_2$PH) and diphenylchlorophosphine (Ph$_2$PCl) (Aldrich) were used as received, solvents toluene and diethyl ether (Fisher), pentane and petroleum ether (Merck), dichloromethane, chloroform, methanol and ethanol (Riedel-de Haën), were used in analytical grade, purified prior to use according to the procedures described in the literature [24] or taken directly from a solvent machine. Palladium dichloride PdCl$_2$, [Pd$_2$(dba)$_3$] (Strem Chemicals) and [Pd(ma)(nbd)] (NanoMeps) were used as received (analytical grade). Ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, [BMI][PF$_6$] and 1-ethyl-3-methylimidazolium hydrogenomethylphosphonate [EMI][HP(O)$_2$OMe] (Solvionic) were dried under vacuum at 60 °C for 18 h before use. Reagents iodobenzene and methyl vinyl ketone, 4-bromoanisole, 1-bromo-4-trifluoromethylbenzene and phenyl boronic acid (Aldrich) and 4-phenyl-3-buten-2-one (Across) were analytical grade taken from their containers and used without purification.

Hydrogenation reactions were carried out in a stainless steel autoclave reactor Top 45 (Top Industrie) 100 mL, with a magnetic stirring and a heater belt. The reactions were analyzed by using a PerkinElmer Clarus 500 chromatograph containing a flame ionization detector and a BPX5 SGE capillary column (30 mx 0.32 mm x 0.25 mm), composed phase of 5% de phenyl methylsiloxane. Catalytic cross-coupling
reactions were carried out on Schlenk glass flasks, meanwhile processes while the use of low gas pressure required (1-5 bar) were carried out in Fisher-Porter bottles.

Chromatographic conditions for Heck and Suzuki reactions were: injector 250 °C and detector = 280 °C, carrier gas flow (helium) 30 mL / min, using the temperature program for the next column: \( T_0 = 40 \, ^\circ \text{C} \) for 2 min, increasing 10 °C / min until a \( T_1 = 300 \, ^\circ \text{C} \) where it stays for 5 min for a total run time of 25 min. Product quantification was performed using dodecane as internal standard using the CROMAT software version 1.2. Correlation studies, as well as all mathematical and statistical calculations were performed using the Origin 6.0 Microcal program.

Electron Microscopy (TEM and HRTEM) for palladium nanoparticles were performed with an electronic microscope JEOL-JEM-1400 (0.20 nm resolution, acceleration voltage of 40-120 kV) and JEOL 200 CX –T 4.5 Å of resolution, accelerating voltage of 80-200 kV), the samples were prepared by evaporation of the solvent present in a drop of colloidal solution deposited onto a copper grid coated with activated carbon. The size distributions of nanoparticles of palladium and the mean diameter were determined directly from the TEM images using Image -J program associated with a Microsoft Excel macro developed for this purpose.

**Synthesis of PdNPs in ImILs**

\[ \text{[Pd}_2(\text{dba})_3] \text{ or } [\text{Pd}(\text{ma})(\text{nb})] \] (0.05 mmols: 25.8 mg for [Pd\(_2\)(dba)\(_3\)] and 14.8 mg for [Pd(ma)(nb)]) in the presence of 0.2 equivalents of the corresponding phospine (0.01 mmol: 4.0 mg for \( \text{L1} \), 2.4 mg for \( \text{L2} \) and 2.3 mg for \( \text{L3} \)), hydrogen pressure (3 bar) and 5 mL of the corresponding ionic liquid, were mixed and stirred in a Fischer-Porter bottle at room temperature (for [Pd(ma)(nb)]) or at 60 °C (for [Pd\(_2\)(dba)\(_3\)]) for 4h. The residual gas was then released and volatiles removed under reduced pressure. The resulting colloidal solutions were directly used for characterization and catalysis purposes.

**Synthesis of PdNPs in THF**

\[ \text{[Pd}_2(\text{dba})_3] \text{ or } [\text{Pd}(\text{ma})(\text{nb})] \] (0.08 mmols: 37.0 mg for [Pd\(_2\)(dba)\(_3\)] and 24.0 mg for [Pd(ma)(nb)]) in the presence of 0.2 equivalents of the corresponding phosphine (0.016 mmol: 6.2 mg for \( \text{L1} \), 3.8 mg for \( \text{L2} \) and 3.6 mg for \( \text{L3} \)), hydrogen pressure (3 bar) and 150 mL of THF were mixed and stirred in a Fischer-Porter bottle, at room temperature for 16h. The residual gas was then released and the solvent removed under reduced pressure to obtain a black powder that was washed with pentane (10 x 5 mL) and dried under vacuum.

**Synthesis of [Pd(ma)(L1)\(_2\)]**

Phosphine \( \text{L1} \) (0.09 g; 0.23 mmol) was dissolved in THF (20 mL) and then [Pd(ma)(nb)] (0.03 g; 0.10 mmol) was added. The resulting dark green solution was filtered on a celite column and
washed with portions of THF degassed (3 x 5 mL). Diethyl ether (15 mL) was then added to give a yellow precipitate which was filtered off, washed with diethyl ether (3 x 5 mL) and dried under vacuum to obtain a dark orange solid.

Yield: 77 mg (77%). Elemental analysis found (calc.) for C_{58}H_{68}Cl_{2}P_{2}Pd: C 68.80 (70.97), H 6.30 (6.98).

\(^1\)H NMR (300 MHz, CDCl\(_3\)); (\(\delta\); ppm) 7.40 - 7.0 (m, 30H, C\(_6\)H\(_5\)); 2.7 (m, 12H, PCH\(_3\)CH\(_2\)CH\(_2\)Ph); 2.1 - 2.3 (m, 24H, PCH\(_3\)CH\(_3\)CH\(_3\)Ph).

\(^{31}\)P\(^{1}\)H NMR (121 MHz); (\(\delta\); ppm) 7.4 (s).

**Synthesis of \([\text{PdCl}_2(\text{L1})_2]\)**

PdCl\(_2\) (0.27 g; 1.5 mmol) was dissolved in hot concentrated hydrochloric acid (4 mL) to generate in situ H\(_2\)[PdCl\(_4\)]. This solution was diluted in dry ethanol (40 mL), filtered off and the filtrate was added to a solution of phosphine L1 (0.750 g; 3.2 mmol) previously dissolved in ethanol. The mixture was vigorously stirred during 4h to give a pale yellow solid which was filtered off and washed with successive portions of ethanol, water and diethyl ether (3 x 5 mL), and dried under vacuum. Yield: 170 mg (85%).

Elemental analysis found (calc.) for C\(_{54}\)H\(_{66}\)Cl\(_2\)P\(_2\)Pd: C 67.20 (67.96), H 7.06 (6.97).

\(^1\)H NMR (300 MHz, CDCl\(_3\)); (\(\delta\); ppm) 7.5 – 7.0 (m, 30H, C\(_6\)H\(_5\)); 2.6 (pseudo t, 12H, PCH\(_3\)CH\(_2\)CH\(_2\)Ph, \(J_{H-H} = 6\) Hz); 1.8 (m, 24H, PCH\(_3\)CH\(_2\)CH\(_2\)Ph).

\(^{13}\)C \(^{1}\)H NMR (75 MHz, CDCl\(_3\)); (\(\delta\); ppm) 141.3 (s, C\(_1\)); 128.5 (s, C\(_2,6\)); 128.5 (s, C\(_3,5\)); 126.1 (s, C\(_3\)); 37.2 (t, PCH\(_3\)CH\(_2\)CH\(_2\)Ph \(J_{P-C} = 7\) Hz); 25.9 (s, PCH\(_3\)CH\(_2\)CH\(_2\)Ph).

Crystal data

The X-ray data for single crystals of \([\text{PdCl}_2(\text{L1})_2]\) was obtained at a temperature of 193(2) K on a Bruker-AXS SMART APEX II diffractometer using the MoKα radiation (\(\lambda = 0.71073\) Å). Phi- and omega-scans were used. The data were integrated with SAINT [25] and an empirical absorption correction with SADABS was applied [26]. The structure was solved by direct methods, using SHELXS-97 and refined using the least-squares method on \(F^2\) with SHELXL-97 [27]. All non-H atoms were treated anisotropically. The hydrogen atoms were fixed geometrically and treated as a riding model.

CCDC-1440920 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Selected data for \([\text{PdCl}_2(\text{L1})_2]\): C\(_{54}\)H\(_{66}\)Cl\(_2\)P\(_2\)Pd, \(M = 954.30\), monolinic, space group P 2\(_1\)/c, \(a = 23.9383(7)\) Å, \(b = 10.5614(3)\) Å, \(c = 31.7091(9)\) Å, \(\beta = 111.4570(10)°\), \(V = 7461.1(4)\) Å\(^3\), \(Z = 6\), crystal size 0.70 x 0.60 x 0.08 mm\(^3\), 103710 reflections collected (15118 independent, \(R_{int} = 0.0519\)), 799 parameters, \(R1[I>2\sigma(I)] = 0.0556\), \(wR2\ [all\ data] = 0.1336\), largest diff. peak and hole : 1.256 and -0.923 eÅ\(^{-3}\).
Pd-catalyzed hydrogenation of (E)-4-phenyl-3-buten-2-one.

In a stainless steel autoclave containing a Pyrex glass beaker, a solution of synthesized PdNPs in ionic liquid (1 mL) and (E)-4-phenyl-3-buten-2-one (146 mg; 1 mmol) were added. The system was deoxygenated by three cycles of argon and heated at 50 °C. The system was then pressurized with dihydrogen to the corresponding pressure (3-40 bar) during 1h. After gas releasing, the reaction mixture was treated with cyclohexane (5 x 5 mL) for extracting the organic products, filtered through a column of celite, and the solvent removed under reduced pressure, giving a yellow oil characterized by 1H NMR and GC-MS.

General C-C Suzuki-Miyaura coupling procedure.

In a 25 mL Schlenk flask, a solution of synthesized PdNPs in ionic liquid (1 mL), Na₂CO₃ (220 mg 2.1 mmol), and 1 mmol of the appropriate aromatic halide (4-bromo-anisole: 0.187 g; 4-bromo-trifluoromethylbenzene: 0.225 g) were placed. This mixture was vigorously stirred at 100 °C in a silicone bath for 16 h. The resulting solution was washed with portions of diethyl ether (10 x 5 mL) to extract the organic products, transferred to a flask and dried on anhydrous Na₂SO₄, then filtered through a column of celite to finally remove the solvent under reduced pressure, giving a white solid characterized by 1H NMR and GC-MS.

References


[26] SADABS, Program for data correction, Bruker-AXS.