

# Palladium nanoparticles obtained from palladium salts and tributylamine in molten tetrabutylammonium bromide: their use for hydrogenolysis-free hydrogenation of olefins†

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Carbon-carbon double bonds have been selectively hydrogenated at room temperature in the presence of benzyloxy groups using an atmospheric pressure of hydrogen, toluene or [bmim]PF<sub>6</sub> as the solvent and palladium nanoparticles stabilized with tetrabutylammonium bromide. The system [bmim]PF<sub>6</sub>/palladium nanoparticles can be recycled without noticeable decrease of activity.

## Introduction

Ionic solvents are nowadays considered as potential alternatives to more conventional solvents in organic processes,<sup>1</sup> and some of us have described the oxidation of benzylic alcohols,<sup>2</sup> the Heck arylation<sup>3</sup> and the isomerization<sup>4</sup> of allylic alcohols using palladium chloride as the initial catalyst and molten *n*-Bu<sub>4</sub>NBr as solvent. Subsequently, we have detected traces of tributylamine by GC analysis from a sample of *n*-Bu<sub>4</sub>NBr heated at 120 °C, that is at the temperature we used for the above Pd-catalyzed reactions. Since alcohols<sup>5</sup> and tertiary alkylamines<sup>6</sup> are able to reduce palladium chloride, we suspected the involvement of Pd<sup>0</sup> species and effectively, the analysis of the recovered solvent by transmission electron microscopy (TEM) showed the presence of palladium nanoparticles.<sup>7</sup>

Transition-metal nanoparticles have attracted a great deal of attention in the last ten years<sup>8</sup> and the stabilization of Pd<sup>0</sup> nanoparticles by ammonium salts is documented.<sup>9,10</sup> These stabilized species are obtained from Pd<sup>II</sup> salts, often by using a carboxylate anion to play the role of reductant.<sup>10</sup> Over the last years, a few reports have described the hydrogenation of C=C bonds using palladium nanoparticles in ionic liquids but only simple olefins have been exposed to these procedures.<sup>11</sup> Otherwise, conventional Pd-catalyzed hydrogenations are rather nonchemoselective: in particular the hydrogenolysis of benzyloxy groups is often either concomitant<sup>12</sup> to the reduction of the C=C bonds or more effective,<sup>13</sup> especially with an alcohol as solvent.<sup>14</sup> Here, we report that palladium nanoparticles, denoted as Pd<sub>CL,N</sub> and Pd<sub>OAc,N</sub>, prepared from a mixture of *n*-Bu<sub>4</sub>NBr, *n*-Bu<sub>3</sub>N and PdCl<sub>2</sub> or Pd(OAc)<sub>2</sub> are catalytically active for the chemoselective hydrogenation of carbon-carbon double bonds in the presence of benzyloxy groups.

## Experimental

PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, *n*-Bu<sub>4</sub>NBr, *n*-Bu<sub>3</sub>N and [bmim]PF<sub>6</sub> (1-butyl-3-methylimidazolium hexafluorophosphate) were from Acrôs Organics. Substrates were obtained by benzylation of the corresponding acids or alcohols using standard procedures.

### Preparation of Pd<sub>CL,N</sub> and Pd<sub>OAc,N</sub>

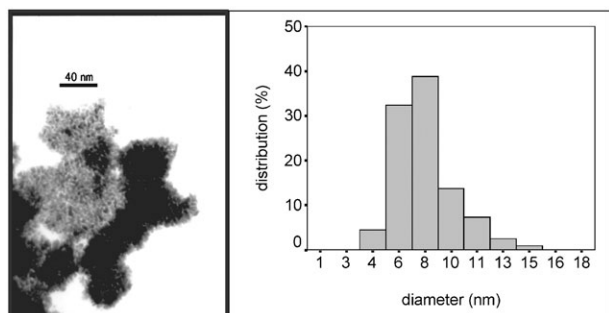
A mixture of PdCl<sub>2</sub> (101.5 mg, 0.57 mmol) and *n*-Bu<sub>4</sub>NBr (738 mg, 2.29 mmol) was stirred under vacuum (0.1 mbar) at 120 °C for 2 h. Then, the mixture was placed under an argon atmosphere and *n*-Bu<sub>3</sub>N (318 mg, 1.72 mmol) was added with a syringe. After stirring at 120 °C for an additional period of 3 h, the mixture was cooled to room temperature and then washed with diethyl ether (5 ml × 4). Drying the residue overnight under vacuum (0.1 mbar) gave Pd<sub>CL,N</sub> (742 mg); black powder, m.p. 90–92 °C. The IR spectrum was similar to that of *n*-Bu<sub>4</sub>NBr; <sup>1</sup>H and <sup>13</sup>C NMR spectra were identical to those of *n*-Bu<sub>4</sub>NBr. Elemental analysis: C, 55.37; H, 10.78; N, 4.26; Pd, 6.26; Br, 20.15; Cl, 2.77%. TEM analysis: see Fig. 1.<sup>15</sup>

The same procedure was used to prepare Pd<sub>OAc,N</sub> (dark grey powder, m.p. 114–116 °C). The IR spectrum was similar to that of *n*-Bu<sub>4</sub>NBr; <sup>1</sup>H and <sup>13</sup>C NMR spectra were identical to those of *n*-Bu<sub>4</sub>NBr. Elemental analysis: C, 53.92; H, 10.83; N, 3.85; Pd, 6.83; Br, 22.26%. TEM analysis: see Fig. 2.

### Hydrogenation in an organic solvent

A mixture of substrate (1.0 mmol), palladium nanoparticles (14 mg) or palladium on carbon (Pd/C, 5%; 1% mol equiv.) in methanol or toluene (3.0 ml) was stirred in a 50 ml round-bottomed flask under hydrogen atmosphere (gas bag) at room temperature for the stipulated time. Petroleum ether was added and after filtration the products were purified by column chromatography (silica; petroleum ether–AcOEt 95:5) and then analyzed in each case by <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, TMS standard) and/or GC-MS studies.

† Electronic supplementary information (ESI) available: electron diffraction pattern of Pd<sub>CL,N</sub>. See <http://www.rsc.org/suppdata/nj/b4/b409604e/>



**Fig. 1** (left) TEM micrograph of Pd<sub>Cl,N</sub> nanoparticles. (right) Particle size distribution of Pd<sub>Cl,N</sub> (215 particles; mean particle size distribution:  $7.5 \pm 1.7$  nm).

### Hydrogenation in [bmim]PF<sub>6</sub>

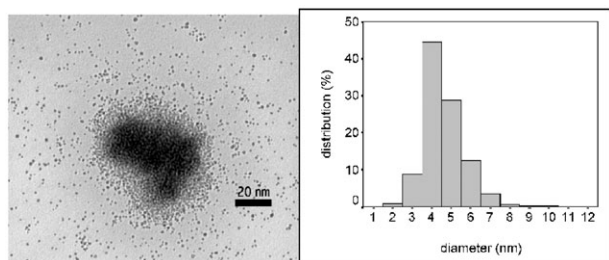
A similar procedure as described above was used but with [bmim]PF<sub>6</sub> (2.0 ml) as the solvent. At the end of the reaction, the mixture was extracted with dry diethyl ether ( $5 \times 5$  ml). The organic phase was concentrated and purified as described above. The ionic liquid was dried on a rotary evaporator, then used for recycling experiments or stored in the freezer.

### TEM analysis of a recovered sample (Fig. 3)

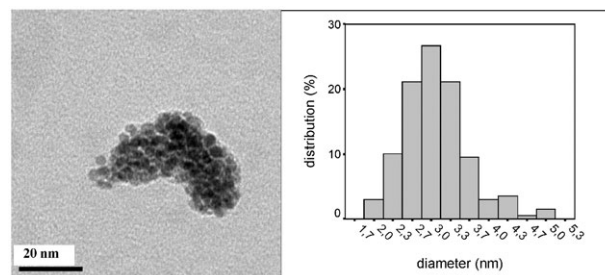
The quantity of ionic liquid in the sample was so large that observation of the nanoparticles by TEM was precluded. Separation of the ionic liquid and the nanoparticles was then performed as follows: the sample was suspended in acetone and sonicated for 5 min, then centrifuged and the supernatant phase was removed; this procedure was repeated three times until the acetone was colourless. The resulting black solid was suspended in acetonitrile and sonicated for 3 min. A drop of the suspension was placed on the specially produced structureless carbon support film with a thickness of 4–6 nm and dried in air.

### Results and discussion

Preliminary hydrogenation studies were carried out in methanol using benzyl propenoate as the reaction substrate, the palladium nanoparticles described in the experimental and, for comparison, 5% Pd/C (Table 1, runs 1–4). Both Pd<sub>Cl,N</sub> and Pd<sub>OAc,N</sub> selectively produced benzyl propanoate, even with a prolonged reaction time, while palladium on charcoal afforded propanoic acid. Since the chemical yield was higher with Pd<sub>OAc,N</sub> than Pd<sub>Cl,N</sub>, subsequent experiments were carried out with the former. As shown in Table 1, the hydrogenation of the double bond is also chemoselective from  $\beta$ -substituted- $\alpha,\beta$ -unsaturated esters (runs 5 and 6) and an unconjugated benzyl unsaturated ester (run 7). In contrast, cleavage of the benzyloxy group was observed when using benzyl benzoate and benzyl *o*-fluorobenzoate (runs 8 and 9). The formation of benzyl ethers being commonly used to protect alcohols and phenols, their stability was examined: aryl benzyl ether groups



**Fig. 2** (left) TEM micrograph of Pd<sub>OAc,N</sub> nanoparticles. (right) Particle size distribution of Pd<sub>OAc,N</sub> (1063 particles; mean particle size distribution:  $4.1 \pm 1.0$  nm).



**Fig. 3** (left) TEM micrograph of recovered Pd<sub>OAc,N</sub> nanoparticles. (right) Particle size distribution of recovered Pd<sub>OAc,N</sub> (199 particles; mean particle size distribution:  $3.1 \pm 0.6$  nm).

are not cleaved under these conditions (runs 10 and 11) while both hydrogenation of the double bond and hydrogenolysis of the *O*-benzyl bond are observed from cinnamyl or geranyl benzyl ethers (runs 12 and 13) and an alkenyl benzyl ether (run 14). As expected,<sup>16</sup> replacing methanol by toluene as the solvent prevents the hydrogenolysis of the allyl benzyl ethers (runs 15 and 16).

Following these results, we looked for a procedure that would allow recycling of both the catalyst and the solvent. Our interest in reactions taking place in neoteric solvents led us to examine the use of [bmim]PF<sub>6</sub> (Table 2) rather than *n*-Bu<sub>4</sub>NBr since the above hydrogenations were performed at room temperature. The hydrogenation of benzyl propenoate in [bmim]PF<sub>6</sub> required a longer reaction time than in MeOH (runs 2 and 17); a high chemical yield was also obtained and interestingly, four successive recyclings have been carried out without noticeable modification of the chemoselectivity and yield (90–99%). As in MeOH, 1-benzyloxy-2-allylbenzene led cleanly to 1-benzyloxy-2-propylbenzene (run 18). In contrast, the benzyl ether of cinnamyl alcohol was reluctant to react but, as in toluene (run 15), led selectively to 3-phenylpropyl benzyl ether (run 19). Hydrogenation of the benzyl ether of 9-decenol was not completed after 20 h; nevertheless, the decyl benzyl ether was selectively obtained after 40 h (run 20) while the free alcohol was produced in MeOH (run 14).

Five successive experiments were then performed using different substrates and the same batch of Pd<sub>OAc,N</sub> and [bmim]PF<sub>6</sub> (Table 3): the recycling was efficient, affording results in agreement with those above described, and we noted that the increase of the reaction time allowed a high conversion of the benzyl ether of cinnamyl alcohol while preserving the selectivity (cycle 4).

The analysis by TEM of the catalyst recovered after one run in [bmim]PF<sub>6</sub> showed that the size of the nanoparticles was similar to the original Pd<sub>OAc,N</sub> (*cf.* Figs. 2 and 3). We have also observed that the sample recovered from this TEM analysis has an efficiency and selectivity similar to the original Pd<sub>OAc,N</sub> for the hydrogenation of benzyl propenoate. Since the hydrogenations and the TEM analysis were carried out in Reims and Barcelona, respectively, the above results support the good stability of these palladium nanoparticles.

In conclusion, we have developed a mild and selective hydrogenation method of carbon-carbon double bonds using recyclable palladium nanoparticles in an ionic liquid.

### Acknowledgements

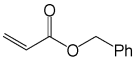
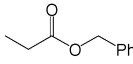
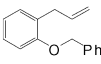
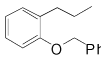
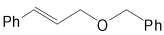
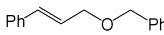
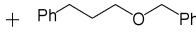
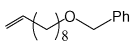
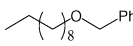
Financial support from the PAI ‘‘Picasso’’, Spanish Ministry of Science and Technology (Project 2002BQU-04002), the Generalitat de Catalunya (Project 2001SGR00181), the CNRS for a fellowship to D. K. M., the Socrates Programme for the ‘‘stage’’ of S. G. and the Ministry of Education, Culture and Sports of Spain for a predoctoral scholarship to M. T., is gratefully acknowledged.

**Table 1** Hydrogenation reactions with various palladium catalysts in methanol or toluene<sup>a</sup>

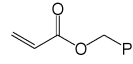
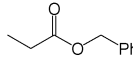
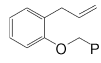
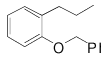
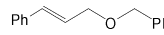
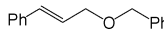
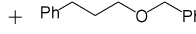
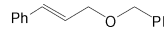
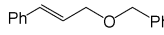
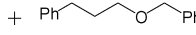
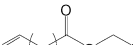
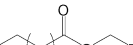
Run	Substrate	Catalyst	Solvent	Time/h	Products	% Yield
1		PdCl <sub>2</sub> N	MeOH	4		89
2		PdOAc <sub>2</sub> N	MeOH	4		96
3		5% Pd/C <sup>b</sup>	MeOH	4		40 <sup>c</sup>
4		PdOAc <sub>2</sub> N	MeOH	20		95
5		PdOAc <sub>2</sub> N	MeOH	20		84
6		PdOAc <sub>2</sub> N	MeOH	16		87
7		PdOAc <sub>2</sub> N	MeOH	20		98
8		PdOAc <sub>2</sub> N	MeOH	16		95
9		PdOAc <sub>2</sub> N	MeOH	22 <sup>b</sup>		87
						11
10		PdOAc <sub>2</sub> N	MeOH	20	N. R. <sup>d</sup>	
11		PdOAc <sub>2</sub> N	MeOH	22		94
12		PdOAc <sub>2</sub> N	MeOH	18		86
13		PdOAc <sub>2</sub> N	MeOH	18		78
14		PdOAc <sub>2</sub> N	MeOH	20		96
15		PdOAc <sub>2</sub> N	PhMe	42		96
16		PdOAc <sub>2</sub> N	PhMe	47	N. R. <sup>d</sup>	

<sup>a</sup> Reactions carried out at room temperature using a balloon filled with hydrogen and 0.01 equiv. of catalyst. <sup>b</sup> From Janssen Company. <sup>c</sup> The low isolated yield is due to the volatility of this acid. <sup>d</sup> N. R. indicates that more than 90% of the starting substrate was recovered.

**Table 2** Hydrogenation reactions in [bmim]PF<sub>6</sub> using Pd<sub>OA</sub>c,N as catalyst

Run	Substrate	Time/h	Products	% Yield
17		20		97
18		22		98
19		20	 + 	82 17
20		40		92

**Table 3** Hydrogenation reactions with different substrates carried out with recycled [bmim]PF<sub>6</sub> and Pd<sub>OA</sub>c,N<sup>a</sup>

Cycle	Substrate	Time/h	Products	% Yield
1		20		97
2		23		97
3		21	 + 	81 18
4		120	 + 	9 90
5		20		90

<sup>a</sup> Reactions carried out at room temperature using a balloon filled with hydrogen, 0.01 equiv. of catalyst, 2 ml of [bmim]PF<sub>6</sub> for 1 mmol of substrate.

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- Electronic diffraction showed the characteristic pattern of Pd<sup>0</sup> species: face-centred cube with average *d*-spacing values of 2.246, 1.938 and 1.358 Å (see Electronic supplementary information).
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