DOI: 10.1002/cctc.201300079



Water-Soluble, 1,3,5-Triaza-7-phosphaadamantane-Stabilized Palladium Nanoparticles and their Application in Biphasic Catalytic Hydrogenations at Room Temperature

Maria Caporali,*^[a] Antonella Guerriero,^[a] Andrea lenco,^[a] Stefano Caporali,^[b] Maurizio Peruzzini,^[a] and Luca Gonsalvi^{*[a]}

Water-dispersible Pd nanoparticles stabilized by the hydrophilic cage-like aminophosphine ligand 1,3,5-triaza-7-phosphaadamantane and its N-methyl derivative were synthesized and fully characterized in the colloidal state by TEM, and NMR and UV spectroscopy and in the solid state by X-ray photoelectron spectroscopy and powder XRD. The three different nanoparti-

Introduction

Dr. L. Gonsalvi

Metal nanoparticles (MNPs) have received an increased attention in the last decade as they show a high surface-to-volume ratio and quantum size effects owing to their small size, which make them attractive in many technologically relevant applications.^[1] For instance, MNPs can have better catalytic performances than the corresponding bulk metals owing to their higher surface activities^[2] and they can also reach high enantioselectivities induced by the presence of chiral ligands on the metal surface. In this regard, examples of hydrogenation,^[3] C-C coupling,^[4] hydrosilylation,^[5] and allylic alkylation^[6] reactions that use modified MNPs as catalysts have been published. Nowadays, there is a resurgent interest in performing catalytic processes in water as the reaction medium^[7] because of its advantages compared to organic solvents, such as low cost, availability, and safe use. However, one of the main obstacles to the widespread use of water in catalysis is the need to convey the active catalysts into the water phase, often obtained by modification of ancillary ligands, which in turn can make the approach economically unviable. Moreover, the relatively low stability of the catalyst under forcing conditions can be an issue as water often behaves as a noninnocent medium towards transition metal complexes. A possible alternative approach is the preparation of stable MNPs dispersible in water.^[8] cles obtained showed a narrow distribution range with average core sizes of 2.8, 3.2, and 3.5 nm. The activity of some of these Pd nanoparticles as catalysts in the biphasic hydrogenation of organic substrates under mild conditions has been tested, and good results and excellent reusability (up to nine catalytic runs) were obtained.

Recently, efforts have been reported towards the preparation of water-soluble transition metal nanoparticles (NPs), either using highly hydrophilic capping agents, such as cyclodextrins,^[9] or suitable amines, that is, 4-(dimethylamino)pyridine,^[10] or coating the nanocrystals with an amphiphilic polymer shell derived from maleic anhydride,^[11] poly(ethylene glycol),^[4b] or others.

Herein we describe the use of a known water-soluble cagelike aminophosphine ligand 1,3,5-triaza-7-phosphaadamantane (PTA) and its N-alkylated derivative 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane (mPTA) as stabilizing agents for watersoluble Pd NPs.^[12] Pd is one of the most important metals in organic synthesis, in particular for C-C coupling reactions and the hydrogenation of unsaturated substrates, and water-dispersible Pd NPs have found useful applications in sustainable approaches to catalysis in organic synthesis and the production of fine chemicals. The results obtained by using some of the water-soluble Pd NPs described above in the catalytic biphasic hydrogenation of organic substrates under mild conditions are described.



(mPTA)

Consiglio Nazionale delle Ricerche Istituto di Chimica dei Composti Organometallici (ICCOM-CNR) Via Madonna del Piano 10, 50019 Sesto Fiorentino (Italy) E-mail: maria.caporali@iccom.cnr.it l.gonsalvi@iccom.cnr.it [b] Dr. S. Caporali Universita' degli Studi di Firenze Dipartimento di Chimica Via della Lastruccia 3, 50019 Sesto Fiorentino (Italy)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300079.

[a] Dr. M. Caporali, Dr. A. Guerriero, Dr. A. Ienco, Dr. M. Peruzzini,

Results and Discussion

Synthesis of water-soluble Pd NPs

The preparation of Pd NPs capped by the water-soluble aminophosphine ligand PTA in different metal-to-ligand ratios was performed in a stepwise fashion by following two general methods that are detailed in the Experimental Section. In the first method, the Pd NPs protected by tetraoctylammonium

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bromide (TOAB) were prepared by the so-called two-phase reduction method. In our case, the metal precursor K₂PdCl₄, dissolved in water and transferred into toluene by means of TOAB, was reduced at room temperature by an aqueous solution of NaBH₄ according to a known procedure.^[13] In the second step, the exchange of capping agent was performed simply by the addition of a diluted aqueous solution of PTA $(3.78 \times 10^{-3} \text{ M})$ to a colloidal solution of Pd@TOAB NPs in toluene, to obtain a Pd/PTA ratio of 1:4. This Pd/phosphine ratio was chosen initially according to literature data, which showed that high stabilization and water solubility can be obtained in such a way.^[12] Under these conditions, PTA worked as an efficient transfer agent and the Pd NPs were transferred quantitatively from the organic phase to the water layer within few minutes without significant changes in size or shape as evidenced by comparative TEM analyses, which showed the presence of Pd NPs of 3.2 ± 0.4 nm for both materials (Figures 1 and S8). An alternative method to replace TOAB with PTA was to add the solid phosphine directly to a solution of Pd@TOAB NPs in toluene. In this way, the Pd NPs became insoluble in the organic phase and precipitated as a black microcrystalline powder that could be extracted into water to leave TOAB in the organic layer. The efficacy by which PTA displaces TOAB can be attributed to the better ligand properties of the tertiary phosphine towards Pd than the tetraalkyl ammonium salt, which is a weakly coordinating ligand.^[14] The ³¹P NMR spectrum of an aliquot of Pd@PTA (1:4) (1) in D₂O showed the presence of a singlet at approximately -5.2 ppm owing to the formation of PTA oxide, PTA(O), as described by Chaudret et al. for M@PTA systems (M=Ru, Pt).^[12] The ¹³C NMR spectrum showed a doublet at 52.6 ppm with ${}^{1}J_{PC} = 53.3$ Hz attributed to PCH_2N and a doublet at 69.8 ppm with ${}^{3}J_{PC} = 9.4$ Hz from NCH₂N, which corresponds to free PTA(O), together with two very broad, low-intensity signals at 56.7 and 70.8 ppm (Figure S5). Similar signal broadening and slight variations in chemical shifts have been observed for Au, Pt, and Ru colloids^[10] and are well known for ligands coordinated to the surface of MNPs,^[15,16] which confirms the coordination of PTA at the surface of the Pd NPs through the P atoms.

Attempts were performed to prepare Pd NPs directly with PTA(O) and the sulfide analog PTA(S) by using the same meth-

odology described above, however, no transfer of Pd NPs from the organic to the water layer was observed.

At this point, we were interested in decreasing the Pd/PTA ratio to investigate its effect on the morphology and stability of the Pd NPs. We reasoned that stable Pd@PTA NPs with a low phosphine coverage may be endowed with a different activity in catalytic applications because of the increased amount of exposed Pd atoms available for substrate activation (see below). Thus, another Pd nanoscale material was prepared from Pd@TOAB NPs with a Pd/TOAB ratio of 1:2 by an exchange reaction between TOAB and PTA to obtain new NPs with a Pd/PTA ratio of 1:1. The new material **2** showed a lower ligand surface coverage than **1**, as confirmed by TEM, which revealed an average core size of 2.8 ± 0.4 nm, smaller than that of **1**. NMR spectra of **2** in D₂O showed the presence of PTA(O), which was also seen for **1**.

Finally, we decided to verify if positively charged, water-soluble ligands with electronic and steric properties $^{\left[17\right] }$ similar to those of PTA could also act as stabilizing agents for Pd NPs. A cationic derivative of PTA, (mPTA)I, prepared by quaternization of one of the three N atoms with Mel,^[18] was thus tested as a capping agent for Pd NPs. A 0.1 M aqueous solution of (mPTA)I was added to a toluene colloidal solution of Pd@TOAB NPs. After stirring at room temperature (RT) for 30 min, the color of the organic phase faded and the water layer became dark brown. TEM measurements confirmed the transfer of Pd NPs to the water layer owing to the exchange of capping agents from TOAB to (mPTA)I. The average size of these NPs was 3.5 nm. Moreover, as TOAB is insoluble in water, the organic phase contained pure TOAB that can be recovered and reused. The ³¹P NMR spectrum of Pd@(mPTA)I (3) in D₂O at RT showed a singlet at -1.5 ppm, which corresponds to m(PTA)I oxide, similar to that observed for PTA-capped Pd NPs, accompanied by a singlet at -48.6 ppm likely because of the formation of [Pd(mPTA)₄]I₄ by comparison with values observed for Pd(PTA)₄ (-59.3 ppm).^[19]

The long-term stability of Pd NPs protected by PTA and (mPTA)I at different temperatures was evaluated. Above 50° C, 1 started to aggregate and formed a black precipitate. This phenomenon has been observed for related Pd colloids that showed poor stability at high temperatures, which prevented



Figure 1. Bright-field TEM image of 1 and the related size-distribution histogram. Scale bar = 100 nm.

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es that require heating.^[20] Samples of 1 could be stored for a week at 4°C without significant changes. After this time, ³¹P NMR spectra evidenced the slow formation of $Pd(PTA)_4$. TEM analysis showed also the formation of aggregates with diameters ranging from 40–100 nm (Figure 2). Compound **3** was less stable; a material likely to be Pd black started to form

their use as catalysts in process-

after only 24 h at 4°C. Previous

studies^[21] have shown that N-

quaternization of PTA as in

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Figure 2. Bright-field TEM image of aggregates of 1 after the colloidal solution was kept at 4° C under air for one month. Scale bar = 200 nm.

(mPTA)I decreases the Lewis basicity and donor power of the P atom, which in turn may cause weaker coordination to the surface of the Pd NPs.

Structural and spectroscopic characterization of Pd NPs capped by TOAB, PTA, and (mPTA)I

TEM

TEM is one of the most effective tools to characterize NPs. By using TEM, we are able to determine the average size of the NPs and discriminate between

NPs and metal aggregates. In the case of 1, TEM measurements showed that these NPs have an average diameter of 3.2 ± 0.4 nm with a narrow size distribution (Figure 1) similar to that of their precursor Pd@TOAB (1:4), which suggests that upon ligand exchange and transfer from toluene into water the physical properties were maintained. Compound 1 was found to be stable for several days if stored under N₂ at RT. If the solutions were exposed to air at RT, characteristic hrowntheir yellow color faded within few hours, however, fading took longer (1 week) at 4 $^\circ\text{C}.$ TEM measurements of the colorless hydrosol showed that the Pd NPs formed aggregates of various dimensions ranging from 40-100 nm in diameter (Figure 2).

TEM analysis of freshly prepared **2** revealed that the NPs are monodispersed and the average core size of the Pd NPs is 2.8 ± 0.4 nm (Figure 3). With regard to air sensitivity and stability in solution, **2** behaved similarly to **1**. TEM analysis of **3** showed that the nanomaterial is monodispersed with an average core diameter of 3.5 ± 0.4 nm (Figure 4). The stability of **3** was limited in the presence of air even at low temperature. However, if kept under N₂ at 4°C, it was stable for a few days.

UV/Vis spectroscopy

UV/Vis spectroscopy is often used to determine the formation of MNPs from Pd molecular precursors. In some cases, it has been applied to explain the deactivation processes of homogeneous Pd catalysts if it is suspected that NP formation was responsible for a decrease in catalytic activity. For example, Tromp et al. used time-resolved UV/Vis spectroscopy to show that during allylic substitution reactions the molecular catalyst [Pd(dppe)(C₅H₉)]OTf (dppe =1,2-bis(diphenylphosphino)ethane) rearranged into Pd dimers and trimers (with absorptions at 430 and 490 nm, respectively) upon the addition of piperidine, which decomposed to Pd colloidal species, characterized by a strong absorption at approximately 390 nm with the disappearance of the bands over 400 nm.^[22] In the case of Pd nanoclusters formed from the reaction of K₂PdCl₄ with watersoluble poly(4-styrenesulfonic acid-co-maleic acid) (PSSA-co-



Figure 3. Bright-field TEM image of 2 and the related size-distribution histogram. Scale bar = 100 nm.



Figure 4. Bright-field TEM image of 3 and the related size-distribution histogram. Scale bar = 100 nm.

MA), the absorption bands at 308 and 415 nm observed initially for the Pd precursors disappeared upon reduction to give a new absorption band at 264 nm, which was attributed to the formation of Pd nanoclusters.^[23] Similar behavior was observed upon the reaction of H₂PdCl₄ with a solution of glutathione, characterized by metal-to-ligand charge transfer (MLCT) bands at 420 and 302 nm and ligand-to-metal charge transfer (LMCT) bands at 237 and 208 nm. The formation of glutathione-stabilized Pd NPs was confirmed by the disappearance of bands at 420, 302, and 237 nm and the appearance of a broad band at approximately 270 nm.^[24] Similarly, water-soluble Pd NPs obtained from Pd(NO₃)₂ upon reduction and stabilization with seminatural cellulose do not have any surface plasmon bands because of the small particle size. The d-d transition band at 380 nm attributed to the Pd^{II} precursor in the spectra before reduction was replaced by a broad absorbance in the range 400-700 nm upon formation of Pd NPs.^[25] In the case of thiolate-capped Pd NPs, the reaction of an aqueous (D₂O) solution of K₂PdCl₄ with TOAB in CDCl₃ in the presence of sodium S-dodecylthiosulfate ($C_{12}S$) caused a shift of the initial intense band at 430 nm attributed to the metal precursor to 445 nm (in the organic phase) because of the formation of [TOA]₂[PdCl₄]. Upon reduction with NaBH₄, NPs were formed and no bands were observed in the UV/Vis spectrum in the range 300-900 nm.^[26] In our case, and also in analogy to that commonly observed for colloidal dispersions of Pd NPs in organic solvents,^[10] the UV/Vis spectrum of **1** suspended in water (Figure 5) did not show a surface plasmon band in the range 300-700 nm, which was expected because of the formation of very small particles and the extension of interband transitions into the visible region.^[27]



Figure 5. UV/Vis spectrum of a colloidal solution of 1 in water.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that allows us to discern between elements in different chemical environments. We performed XPS on samples of Pd@PTA NPs to elucidate the chemical environment of the P and Pd atoms located at the surface of the NPs, which are likely involved in the catalytic process. Figures 6 and 7 display high-resolution XPS spectra of Pd and P atoms, respectively, collected from **1**. The Pd 3d core transaction is characterized by



Figure 6. Curve fitting of the Pd 3d XPS spectra recorded from a dry sample of 1. The experimental values and the contributions attributed to Pd^0 and Pd^{II} are indicated as circles, blue, and red lines, respectively.



Figure 7. Curve fitting of the P2p XPS spectrum recorded from a dry sample of 1.

a doublet attributed to spin-orbit coupling, namely, the $3d_{5/2}$ and $3d_{\scriptscriptstyle 3/2}$ components. However, the experimental spectrum requires at least two different components to be fitted. These two components are attributed to Pd in different chemical environments. The component responsible for the larger amount of the signal, located at lower binding energy (B.E.) values (B.E. $3d_{5/2} = 335.1 \pm 0.1$ eV), in accordance with literature data, is attributed to bulk metallic Pd.^[28] Consequently, the signal located at the higher binding energy (B.E. $3d_{5/2} = 337.5 \pm 0.1$ eV) is consistent with chemically bound Pd.^[29] The presence of Pd in two different chemical environments at the surface of the NP is a common phenomenon for Pd NPs protected by tetraalkylammonium cations and aliphatic amines as capping agents.^[30] The layer of complexed Pd atoms on the surface of the NPs likely acts as a stabilizer to create an electrostatic repulsion between the NPs and prevent their aggregation. As the area under the peaks is proportional to the amount of Pd atoms present in the sample, the evaluation of the relative concentration of the two species is straightforward and gives a metallic Pd/ complexed Pd ratio of 2:1 for 1. The chemical environment of this component cannot always be unambiguously determined by the evaluation of its binding energy as size, extra-atomic relaxation, and core-hole screening effects can lead to different binding energies for NPs with respect to the same bulk species. Generally, components at energy values higher than 336 eV are ascribed to partially oxidized Pd.^[31]

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Other studies have evidenced that Pd^{0} complexes such as palladium tetrakis(triphenylphosphine) ($Pd(PPh_{3})_{4}$) and bis(dibenzylideneacetone) palladium ($Pd(dba)_{2}$) have binding energies similar to those observed in this study.^[32] However, palladium oxide (PdO) has a higher binding energy (338.1 eV). Therefore, in light of these considerations, the component at 337.5± 0.1 eV is more likely attributable to the Pd atoms chemically bound to the aminophosphine ligand. XPS measurements also confirmed the presence of PTA as a capping agent. The highresolution XPS spectrum of P. displayed in Eigure 7 provider

resolution XPS spectrum of P displayed in Figure 7 provides evidence of a $2p_{3/2}$ core-transition peak located at very high energy (131.7±0.1 eV). This value is reasonably attributed to P^V in PTA(O). These data agree well with the NMR spectra described above and with observations by other authors that concern the role of PTA as a capping agent.^[12]

The XPS data obtained in this study are in line with results described for related Pd NPs. Values in the range 335–336 eV were measured for Pd 3d_{5/2} for NPs stabilized by cellulose.^[31a] Another study reported on Pd NPs supported on a sulfonate-functionalized triphenylphosphine ligand by ion–ion interactions with an imidazolium-modified SBA-15.^[33] XPS data for the hybrid material Pd@SBA-15 so-obtained showed values of 336.3 (Pd 3d_{5/2}), 341.6 (Pd 3d_{3/2}), and 133.4 (P 2d), which were considered to be borderline between molecular Pd⁰ species^[34] and small NPs.^[35] XPS analysis of Pd NPs capped by glutathione gave binding energies in the range 335.2–335.7 eV (Pd 3d_{5/2}) for Pd⁰ species accompanied by peaks in the range 336.8–337.4 eV for oxidized Pd.^[24]

The nature of the ligand that coordinates Pd has an influence on the electrophilicity of the metal, and this can be appreciated by XPS studies. For example, Lee et al.[36] reported values of $Pd3d_{5/2}$ binding energies of 336.9–336.7 eV for a mixed N-heterocyclic carbene (NHC)-phosphino Pd complex cis-[PdCl₂(L)(PR₃)] (L=NHC; R=Ph, Cy) and concluded that such low binding energies were attributable to the "very strong electron-donating nature of the phosphine/carbene ligand set". A study by Dupont et al.^[37] on the formation of stable small Pd NPs obtained by heating Pd(OAc)₂ in ionic liguids (ILs), such as 1-butyronitrile-3-methylimidazolium-N-bis(trifluoromethane sulfonyl)imide ((BCN)MI·NTf₂), established that the Pd 3d_{5/2} binding energies of Pd(OAc)₂ were 337.7 eV with a small shift to a higher binding energy (338.4 eV) if dispersed in the IL and that after heating at 120 $^\circ\text{C}$ for 48 h, only a minor shift was observed (338.7 eV). By comparison with the isolated Pd NPs (B.E. = 335.1 eV), the authors concluded that only small quantities of Pd⁰ NPs were contained in the IL layer, and the major amount present in the inner region of the IL was not accessible to XPS.

Powder XRD

Powder XRD (PXRD) analysis was performed to obtain further structural information on the Pd@NPs prepared in this study. Analysis of a microcrystalline sample of **3** and its precursor, Pd@TOAB (1:4), prepared on addition of ethanol to the colloidal sample and cooled to -30 °C for 24 h to precipitate the NPs, showed the presence of characteristic diffraction peaks

that corresponding to the *hkl* planes of the face-centered cubic (fcc) lattice of Pd (Figures S2 and S1, respectively). These results confirm that the Pd in **3** is nanostructured. In particular, the peak at 40° (2θ) indicates the crystallographic plane (111) typical of the fcc lattice of Pd. This peak is related to the diameter of the NPs according to Scherrer's equation.^[38] By applying this equation to the measured PXRD spectra, an estimation of the average core diameter of the NPs was obtained with values of 5.2 nm for Pd@TOAB (1:4) and 8.0 nm for **3**, respectively. These values are slightly larger than those obtained by measuring a colloidal sample of the same NPs by using TEM. This discrepancy could be because of precipitation of the NPs from the colloidal solution to favor an aggregation process.

Pd water-soluble NPs as hydrogenation catalysts

MNPs have found various applications, in particular, as catalysts for metal-mediated chemical transformations. $^{\mbox{\tiny [2b]}}$ M@PTA (M = Ru, Pt) NPs are effective catalysts for the hydrogenation of unsaturated substrates by using H₂, ranging from terminal olefins to arene rings.^[12] In these recent examples, the reactions were performed in water under mild conditions with temperatures and H_2 pressures typically 20 °C and 1–10 bar. Moderate to good conversions were observed using a substrate-to-catalyst ratio of 100. Inspired by these results, we tested our Pd@PTA NPs in the aqueous biphasic catalytic hydrogenation of selected unsaturated organic substrates, such as alkynes, alkenes, and dienes. The reactions were performed in a carousel-modified, home-built stainless-steel autoclave that contained glass vials at RT under 10 bar of H₂ with magnetic stirring. The catalyst resided in the water phase, immiscible with the organic phase, which contained the reagent and the products. Therefore, at the end of the reaction, the products could be separated easily from the catalyst by simple phase separation. The results of the catalytic tests obtained with 1 and 2 are summarized in Tables 1 and 2, respectively.

The turnover numbers (TONs) and turnover frequencies (TOFs), defined as the amount of consumed substrate [mmol] per amount of initial Pd [mmol], were corrected by the number of exposed surface atoms. These were estimated from the TEM experimental values obtained for the mean diameter of the NPs (idealized as spheres) by applying the magic-numbers approach^[39] and considering a fcc lattice for Pd.^[40] The calculations allowed us to estimate the percentage of exposed Pd atoms as 34.6% for **1** and **3** and 39.0% for **2**.

In the case of **3**, the transfer from the organic to the water layer required a larger excess of phosphine ligand, probably because of the electrostatic repulsion between the positively charged phosphine ligand and the cationic tetraoctylammonium surfactant that forms the outer shell of the Pd NPs suspended in toluene. Therefore, it is expected that the density of the capping agent at the NP surface is much higher for **3** in comparison to that of Pd@PTA, which in turn may decrease the active metal surface exposed to the reagent and make this material unsuitable for catalytic applications. Similar behavior has been described for systems based on alkanethiolatecapped Pd NPs,^[26] for which a systematic investigation on the

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Table 1. Hydrogenations catalyzed by 1. ^[a]								
Entry	Substrate	t [h]	Substrate/ catalyst	Products (Yield [%]) ^[c]	TON ^[d]	TON _{exp} ^[e]	TOF ^[f]	$TOF_{exp}^{[g]}$
1	diphenylacetylene ^[b]	24	100	diphenylethane (100)	100	289	4.2	12.0
2	1,5-cyclooctadiene	24	1000	cyclooctane (99.9)	999	2887	41.6	120.3
3	1-dodecene	24	1000	dodecane (99.9)	999	2887	41.6	120.3
4	cis-4-hepten-1-ol	24	100	heptan-1-ol (100)	100	289	4.2	12.0
5	cinnamyl alcohol	18	100	3-phenyl-1-propanol (100)	100	289	5.6	16.1
6	benzylidene acetone ^[b]	24	100	4-phenyl-2-butanone (100)	100	289	4.2	12.0
[a] Conditions: $P_{\rm H_2} = 10$ bar, 25 °C, 1 (1.96×10 ⁻⁴ mmol), neat substrate added by microsyringe, H ₂ O (1.0 mL),								

[a] conditions: $P_{H_2} = 10$ bar, 25 C, 1 (1.96 × 10⁻¹ mmol), near substrate added by microsyringe, H_2O (1.0 mL), Pd@PTA (1.96 × 10⁻⁴ m). [b] The substrate was dissolved in dichloromethane (800 µL) prior to addition to the catalyst dispersion in water. [c] Determined by GC by comparison with pure products. [d] Defined as mmol_{consumed substrate} mmol_{initial Pd}⁻¹. [e] Defined as mmol_{consumed substrate} mmol_{initial Pd}⁻¹h⁻¹. [g] Defined as mmol_{consumed substrate} mmol_{exposed Pd atoms}⁻¹h⁻¹.

Table 2. Hydrogenations catalyzed by 2. ^[a]								
Entry	Substrate	t [h]	Substrate/ catalyst	Products (Yield [%]) ^[c]	TON	TON_{exp}	TOF	TOF_{exp}
1	1-dodecene	24	4000	dodecane (74.5)	2980	7641	124.2	318.4
2	1-dodecene	24	3000	dodecane (89.4, 92.1 ^[d])	2682,	6877,	111.8,	286.6,
					2763	7085	115.1	295.2
3	1-dodecene	1	300	dodecane (85.8)	257	660	257.4	660.0
4	diphenylacetylene ^[b]	1	400	diphenylethane (89.9)	360	922	359.6	922.1
5	diphenylacetylene ^[b]	1	200	diphenylethane (95.0)	190	487	190.0	487.2
6	cis-4-hepten-1-ol	24	200	heptan-1-ol (49.6)	99	254	4.1	10.6
7	cinnamyl alcohol	24	200	3-phenyl-1-propanol (15.1, 61.6 ^[d])	30,	77,	1.3,	3.2,
					123	316	5.1	13.2
8	benzylidene acetone ^[b]	24	200	4-phenyl-2-butanone (67.9, 82.3 ^[d])	136,	348,	5.7,	14.5,
					165	422	6.9	17.6
[a] Co	[a] Conditions: $P_{\rm H} = 10$ bar, 25 °C, 2 (9.18×10 ⁻⁴ mmol), neat substrate added by microsyringe, H ₂ O (0.5 mL).							



relationship between the catalytic properties and the surface ligand density/core size showed that Pd NPs with a lower surface ligand coverage afforded higher activity and selectivity in the isomerization of various allyl alcohols. TOFs as high as 449 h⁻¹ were reached in the isomerization of allyl alcohol to 1-propanal (90% selectivity) by using Pd NPs with a large mean diameter (3.38 ± 0.95 nm) and low surface coverage (34%) in CDCl₃ at RT in the presence of Pd NPs at 5% Pd loading. Under the same conditions, NPs with smaller mean diameters (1.51 ± 0.46 nm) and higher surface ligand coverage (75%) reached a TOF of 61 h⁻¹, which confirms the initial hypothesis.

Following this work, Shon et al. showed that allylic alcohol could be preferentially hydrogenated rather than isomerized if polar solvents such as MeOH and water were used in the presence of C_{12} S-alkanethiolate-capped Pd NPs because of the sterically induced formation of a linear P–alkyl intermediate.^[41]

A similar effect of the NP-size dependence on the catalytic hydrogenation of allylic alcohols was observed by Crooks et al., who found that the kinetics was dominated by electronic effects for the smallest particles (< 1.5 nm diameter) and by geometric effects for the larger particles (> 1.5–1.9 nm diameter).^[42]

We chose to screen the activity of **1** and **2** towards the hydrogenation of structure-sensitive (alkynes)^[43] and structure-insensitive substrates (alkenes, allylic alcohol, and α , β -unsaturated alcohols and ketones).^[44]

By comparison of the results shown in Tables 1 and 2, it can be observed that the catalytic activity of the Pd@PTA NPs depends on the Pd/PTA ratio. For instance, 2, which has a PTA lower content and, therefore, a less hindered surface, was more active for the reduction of structure-insensitive long-alkylchain alkenes such as 1-dodecene. Diphenylacetylene was chosen as a structure-sensitive substrate, which was reduced quantitatively to diphenylethane by 2 in 1 h at a substrate/catalyst ratio of 400, whereas 1, which has a larger mean particle diameter, reached the same conversion at substrate/catalyst ratio of 100 after 24 h. TOFs up to 257 and 360 h^{-1} (660 and 922 h⁻¹ if corrected for the amount of exposed Pd atoms) were obtained for the conversion of 1-dodecene to dodecane and diphenylacetylene to diphenylethane, respectively, by using 2.

Dupont et al. reported a TOF of 13 h⁻¹ (74 h⁻¹, exposedatoms corrected), for the chemoselective hydrogenation of diphenylacetylene to cis-stilbene (87% conversion after 6.5 h) by using Pd NPs obtained from Pd(OAc)₂/(BCN)MI·NTf₂ under a H₂ pressure of 1 bar. The authors concluded that the high chemoselectivity depended on the H₂ pressure as reduction to alkanes was observed at values higher than 4 bar.^[37] Marin-Astorga et al. found that the stereoselective hydrogenation of 3-hexyne over catalysts with low Pd loadings (1%) supported on mesostructured materials such as SBA-15 gave cis-hexene at substrate-to-Pd ratios as high as 11000 (at 25 °C and 3 bar H₂ pressure), which was highly metal-dispersion dependent. However, TOFs as high as 2538 s⁻¹ were measured if toluene was used as the reaction medium.^[45] Similarly, Pd NPs supported on SBA-15 modified by electrostatically grafted triphenylphosphine sulfonate applied in the reduction of linear (1-octene, trans-stilbene, 3-phenylprop-2-en-1-ol) and cyclic (cyclooctene) alkenes and α , β -unsaturated ketones (cyclohex-2-enone, chalcone) gave high conversions with 1 mmol of substrate and 0.2% of Pd catalyst at RT under 1 bar of H₂ for 8-12 h in toluene, but no recycling experiments were described.[33] Highly stable and active polymer-supported Pd NPs generated on gel-type ion-

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exchange resins under catalytic conditions were used by Barbaro et al. to achieve the partial hydrogenation of various unsaturated substrates, which included the reaction of hex-3-yn-1-ol to *cis*-3-hexen-1-ol a with a TOF of 322 h⁻¹ by using 1.25% Pd loading under 1 bar of H₂ at RT after 1 h in CH₃OH. Recycling experiments showed that the selectivity and activity were maintained after three consecutive cycles. Flow conditions were also applied, and in the case of the partial reduction of cyclooctadiene to cyclooctene, a productivity of 1.30 kg L⁻¹ h⁻¹ was obtained, which corresponds to an overall TON of 1700 after 4.7 h and a TOF of 395 h⁻¹.^[46]

Pd-NP-based catalysts applied to water-phase hydrogenation of unsaturated substrates are also known. For example, Astruc et al. reported the use of a series of water-soluble Pd NPs stabilized by sulfonated 1,2,3-triazolyl dendrimers, which were active in the hydrogenation of allyl alcohol to 1-propanol at 0.01% mol Pd at 25°C in water under 1 bar H₂. TOFs in the range of 8088-5173 h⁻¹ were obtained, which decreased with increasing dendrimer size characterized by mean diameters from 2.3-3.0 nm.^[8c] Highly water soluble Pd NPs (1.9 nm average diameter) were obtained by using the amphiphilic poly(ethylene glycol)-functionalized dicationic imidazolium-based IL C12Im-PEG to form micelles over the critical micelle concentration (CMC) in water.^[47] Styrene hydrogenation was achieved by using a substrate-to-Pd molar ratio of 10000 under 10 bar H_2 at 25 $^{\circ}$ C in 1 h with a TOF of 12300 h⁻¹, and this system showed excellent recyclability. Similarly, Pd NPs preformed by water-in-oil microemulsions deposited on carbon, silica, and cellulose supports endowed with different hydrophobic and textural properties showed high activities in the liquid-phase hydrogenation of styrene. The highest rate for styrene hydrogenation (0.0114 mol_{H₂}min⁻¹ g^{-1}_{cat}) was achieved with a solvated Pd/SiO₂ that had a specific surface area of 445 m^2g^{-1} and pore diameter of 4.9 nm.[31a]

Acetylene was effectively hydrogenated to ethene by Pd NPs stabilized by seminatural, water-soluble cellulose, such as sodium carboxymethyl cellulose, under mild reaction conditions in flow systems. At 40 °C, at a maximum conversion of 74%, the highest selectivity to ethene (63%) was observed.^[25]

In our system, it was observed that the yields of hydrogenation products for certain substrates in the first run were lower than that after recycling. Indeed, the conversion of cinnamyl alcohol to 3-phenyl-1-propanol was only 15.1% in the first run, whereas the second run became quantitative. Similarly, cis-4hepten-1-ol reached a conversion to heptanol of only 49% in the first run and went to completion (100%) in the second run. A possible explanation could be that in the first run (24 h at RT, 10 bar of H_2) some Pd^{II} that decorates the nanomaterial is reduced to Pd⁰, which makes the material more active in the second run. To validate this hypothesis, 2 was pretreated in an autoclave with 10 bar of H₂ for 24 h at RT, after which the desired substrate (1-dodecene, cinnamyl alcohol, or benzylidene acetone; Table 2) was added and the autoclave was repressurized with 10 bar of H₂ and the mixtures were stirred for 24 h at RT. The results showed that conversions after 24 h were increased (Table 2, entries 2, 7, and 8) to 92.1, 61.6, and 82.3%, respectively, which confirms our hypothesis.

Finally, it was shown that solutions of 1 could be recycled after up to nine hydrogenation runs. After each run, the workup was performed simply by adding an equal volume of dichloromethane to the aqueous phase, followed by decantation of the organic layer, which contained the products and the unreacted substrate if present, and addition of fresh substrate to the aqueous solution to start a new run. The results for selected tests are summarized in Tables 3 and 4. Interestingly, the conversion of 1-dodecene to dodecane did not change after the ninth recycle (Table 3), which suggests the high stability of 1, and with a substrate/catalyst ratio of 100, afforded an overall TON of 869. On using a 1-dodecene/1 ratio of 200 (Table 4), the catalytic performance increased slightly after each run, from 70.2% (run 1) to a quantitative yield in run 5 and successive runs to afford an overall TON of 1728. The water dispersion of Pd NPs was checked by TEM after nine runs, which showed the presence of NP aggregates with core diameters ranging from 7.0-11.0 nm (Figure 8). The recycling test was extended to other unsaturated substrates, such as diphenylacetylene, 1,5-cyclooctadiene, cis-4-hepten-1-ol, cinnamol, and benzylidene acetone. The catalyst was stable in all cases and gave the same conversion in the second and third runs.

Table 3. Recycling experiments for the hydrogenation of 1-dodecene catalyzed by 1 . Substrate/catalyst molar ratio = 100 . ^[a]							
Run	Conversion [%]	Yield [%] ^[b]	TOF	TOF_{exp}			
1	96.2	89.5	96.2	278.0			
2	94.4	91.4	94.4	272.8			
3	93.9	89.3	93.9	271.4			
4	94.7	92.5	94.7	273.7			
5	100.0	100.0	100.0	289.0			
6	100.0	100.0	100.0	289.0			
7	100.0	100.0	100.0	289.0			
8	94.7	88.1	94.7	273.7			
9	95.0	92.6	95.0	274.6			

[a] Conditions: $P_{\rm H_2}$ = 10 bar, 25 °C, 1 (3.92×10⁻⁴ mmol), 1 h, substrate (3.92×10⁻² mmol), H₂O (2.0 mL). [b] Yield of dodecane determined by GC by comparison with pure product. The remaining products are isomerized alkenes as determined by GC–MS.

Table 4. Recycling experiments for the hydrogenation of 1-dodecene catalyzed by 1. Substrate/catalyst molar ratio = 200.^[a]

Run	Conversion [%]	Yield [%] ^[b]	TOF	TOF_{exp}
1	83.7	70.2	167.4	483.8
2	89.6	78.6	179.2	517.9
3	97.0	87.6	194.0	560.7
4	96.5	90.3	193.0	557.8
5	100.0	99.7	200.0	578.0
6	100.0	99.5	200.0	578.0
7	100.0	99.2	200.0	578.0
8	97.2	96.5	194.4	561.8
9	100.0	99.8	200.0	578.0
1.1.6		=		1

[a] Conditions: $P_{H_2} = 10$ bar, $25 \,^{\circ}$ C, 1 (3.92×10^{-4} mmol), 1 h, substrate (7.84×10^{-2} mmol), H₂O (2.0 mL). [b] Yield of dodecane determined by GC analysis by comparison with pure product. The remaining products are isomerized alkenes as determined by GC–MS.

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Figure 8. Bright-field TEM image of 1 after nine catalytic cycles. Scale bar = 200 nm.

Catalyst **2** was also recycled in proof-of-concept tests in the hydrogenation of 1-dodecene, cinnamyl alcohol, and *cis*-4-hepten-1-ol under the conditions described in Table 2 (see entries 2, 6, and 7 for the first runs) to obtain the hydrogenated products in 87.5, 100, and 94.4% yields, respectively, in the second runs. The overall TONs considering the first and second runs are 5307, 220, and 299, respectively.

Conclusions

An efficient and reproducible method for the preparation of water-soluble Pd nanoparticles (NPs) from widely available starting materials is described. The new materials have been characterized in solution and in the solid state by TEM, inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray photoelectron spectroscopy (XPS), and UV/Vis and NMR spectroscopy. The distribution of NPs was found to be generally in a narrow range, with mean diameters of 2.8, 3.2, and 3.5 nm, respectively, for Pd@PTA (1:4) (1), Pd@PTA (1:1) (2), and Pd@(mPTA)I (3). The aqueous colloidal suspensions of PTA-stabilized Pd NPs 1 and 2 were tested as catalysts in the biphasic hydrogenation of selected unsaturated substrates in water at room temperature under 10 bar of H₂, which showed moderate to good conversions and TOFs of 257 and 360 h⁻¹ in the hydrogenation of 1-dodecene and diphenylacetylene, respectively. The catalytic system 1 shows excellent recyclability, up to nine times, to afford an overall TON of 1728. Work is in progress to expand the scope of the catalytic system to other substrates.

Experimental Section

All chemicals used were of analytical grade. Potassium tetrachloropalladate (K₂PdCl₄) and TOAB were purchased from Aldrich and used as received. PTA,^[18] (mPTA)I,^[48] and Pd(dba)₂^[49] (dba = dibenzylideneacetone) were prepared according to known procedures. Pd NPs capped by TOAB were prepared following a variation of the method previously developed by Brust^[15] and Gittins and Caruso.^[10] TEM studies were performed by using a Philips instrument operating at an acceleration voltage of 100 kV. A few drops of the Pd colloidal suspension, obtained by using either toluene or water, were placed on the TEM lacy copper/carbon grid or copper/ Formvar grid, respectively, air dried, and measured. The XPS measurements were performed by using an ultrahigh vacuum (UHV, 10^{-9} mbar) system equipped with a VSW HAC 5000 hemispherical electron-energy analyzer and a non-monochromatized MgK_a X-ray source (1253.6 eV). The source power was 100 W (10 kV × 10 mA) and the spectra were acquired in the constant-pass-energy mode at $E_{\text{pas}} = 44 \text{ eV}$. The overall energy resolution was 1.2 eV as a fullwidth at half maximum (FWHM) for the Ag $3d_{5/2}$ line of a pure Ag reference. The recorded spectra were fitted by using XPS Peak 4.1 software that employed Gauss-Lorentz curves after subtraction of a Shirley-type background. The powder sample was introduced in the UHV system through a loadlock under inert gas (N₂) flux, to minimize the exposure to air contaminants, and kept in the introduction chamber for at least 12 h before the measurements. UV/ Vis spectra were recorded by a Perkin-Elmer UV/VIS/NIR Spectrometer Lambda 19 by using a 1 cm quartz cuvette. The solvent used was water, and the concentration of the solution was approximately 5.6×10^{-4} m. PXRD data were collected by using an X'Pert PRO diffractometer with CuK_{α} radiation ($\lambda = 1.5418$). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed by using an ICP-OES dual vision Perkin-Elmer instrument at the Department of Chemistry of the University of Florence. The samples were measured in the axial mode to increase sensitivity. GC analyses were performed by using a Shimadzu 2010 gas chromatograph (with polar column) equipped with a flame ionization detector (FID) and a VF-WAXms capillary column (30 m, 0.25 mm internal diameter, 0.25 μm film thickness) and a Shimadzu GC-14A gas chromatograph (with apolar column) equipped with an FID and a SPB-1 Supelco fused silica capillary column (30 m, 0.25 mm internal diameter, 0.25 µm film thickness).

Preparation of TOAB-capped Pd NPs, Pd@TOAB (1:4)

To a solution of K_2PdCl_4 (80.0 mg, 2.45×10^{-2} mmol, 1 equiv.) in water (8.16 mL, 3.0×10^{-2} M) was added a solution of TOAB (587.0 mg, 1.07 mmol, 4.4 equiv.) in toluene $(21.4 \text{ mL}, 5.0 \times 10^{-2} \text{ M})$. Under an inert atmosphere and after stirring at high speed for 30 min, the transfer of [PdCl₄]²⁻ from the aqueous phase to the organic layer was completed as revealed by the decoloration of the water phase and the red-brown color of the organic phase. The water phase was removed by syringe, and a freshly prepared NaBH₄ aqueous solution (6.1 mL, 0.1 M, 23.2 mg, 0.613 mmol, 2.5 equiv.) was added dropwise over 1 h with vigorous stirring. The reaction mixture gradually darkened and, after stirring for 2 h at RT, the colorless water phase was discarded and the organic phase was recovered, washed with HCl solution (20 mL, 0.1 M), NaOH solution (20 mL, 0.1 M), and deionized water (3×20 mL). The organosol was dried over anhydrous Na2SO4 and stored at 4°C. The formation of Pd@TOAB NPs was confirmed by TEM analysis, which gave an average diameter of 3.2 ± 0.4 nm. The molar concentration of Pd in the colloidal toluene solution was measured by ICP-AES.

Preparation of PTA-capped Pd NPs Pd@PTA (1:4) (1)

Method A: Firstly, a solution of PTA (19.3 mg, 1.23×10^{-2} mmol, 3.78×10^{-3} m, 4 equiv.) in degassed water (32.5 mL) was prepared and divided into two aliquots of approximately 16.2 mL each. The first aliquot was added to a dark brown sol of Pd@TOAB (1:4) (10 mL, 3.08×10^{-3} m, 1 equiv.) in toluene, prepared as described above. After stirring at RT for 10 min, the two phases were allowed to separate, the aqueous phase was removed by using a syringe under N₂ and placed in a separate Schlenk flask, and the second aliquot of the PTA solution was added to the organic layer left after the phase separation. After stirring at RT for an additional 10 min, the color of the organic phase faded completely. The brown–yellow water phase so-obtained was removed by syringe under N₂ and combined with the previous water phase.^[50] The re-

sulting brown–yellow hydrosol of Pd NPs capped by PTA was stored under N_2 at 4 $^\circ\text{C}.$

Method B: Solid PTA (19.3 mg, 1.23×10^{-2} mmol, 4 equiv.) was added directly to the toluene solution of Pd@TOAB (1:4) (10 mL, 3.08×10^{-3} m, 1 equiv.) to precipitate the NPs as black microcrystal-line powder, which was isolated by filtration and easily resuspended in water (10 mL).^[51] Yield: 45% based on Pd (ICP-AES analysis); average NP diameter: 3.2 ± 0.4 nm (TEM analysis); ¹H NMR (300.13 MHz, D₂O, 20°C): $\delta = 3.95$ (d, ¹J_{HP} = 10.1 Hz, 6H, PCH₂N), 4.25 ppm (AB system, J_{AB} =13.1 Hz, 6H, NCH₂N); ³¹P{¹H} NMR (121.49 MHz, D₂O, 20°C): $\delta = -5.2$ ppm (s); ¹³C{¹H} NMR (100.61 MHz, D₂O, 20°C): $\delta = 52.6$ (d, ¹J_{PC} = 53.3 Hz, PCH₂N of free PTA(O)), 56.7 (br s, coordinated PTA).

Preparation of TOAB-capped Pd NPs, Pd@TOAB (1:2)

To a solution of K₂PdCl₄ (40.0 mg, 0.122 mmol, 1.0 equiv.) in water (4.1 mL, 3.0×10^{-2} M) was added a solution of TOAB (134.0 mg, 0.245 mmol, 2.0 equiv.) in toluene (6.0 mL). Under an inert atmosphere of N₂ with stirring at high speed for 30 min, the transfer of $\left[\text{PdCl}_4 \right]^{2-}$ from the aqueous phase to the organic layer was completed as revealed by the decoloration of the water phase and the red-brown color of the organic phase. The water phase was removed by syringe, and a freshly prepared NaBH₄ aqueous solution (6.1 mL, 0.1 M, 11.6 mg, 0.306 mmol, 2.5 equiv.) was added dropwise over 1 h with vigorous stirring. The reaction mixture quickly darkened, and after stirring for 2 h at RT the colorless water phase was discarded and the organic phase recovered, washed with HCI solution (10 mL, 0.1 м), NaOH solution (10 mL, 0.1 м), and deionized water (3×10 mL). The organosol was dried over anhydrous Na_2SO_4 and stored at $4\,^\circ C.$ The formation of Pd@TOAB NPs was confirmed by TEM analysis. The molar concentration of Pd in the colloidal toluene solution was measured by ICP-AES.

Preparation of PTA-capped Pd NPs, Pd@PTA (1:1) (2)

The same procedure (Method A) described above for **1** was followed for the preparation of **2**, except for the use of a colloidal suspension of Pd@TOAB (1:2) instead of Pd@TOAB (1:4). An aqueous solution of PTA (3.9 mg, 2.48×10^{-2} mmol, 4.98×10^{-3} M) was added to a toluene solution of Pd@TOAB (1:2) (4 mL, 2.48×10^{-2} mmol, 6.23×10^{-3} M) at RT to have a final Pd/PTA ratio of 1:1. Yield: 40% based on Pd (ICP-AES analysis). NMR data were coincident with those obtained for **1**. Average NP diameter: 2.8 ± 0.4 nm (TEM analysis).

Preparation of mPTA-capped Pd NPs, Pd@(mPTA)I (3)

The same procedure described above the preparation of **2** was followed, although in this case a longer reaction time (1 h) was required to obtain efficient ligand exchange and a higher excess of ligand (8 equiv. instead of 4 equiv. used for PTA) was needed to transfer all the Pd from the organic to the aqueous phase. Alternatively, these NPs could be prepared by following the so-called organometallic approach described in the literature for related systems, that is, by decomposition of an organometallic precursor under a H₂ atmosphere.^[12] Thus, Pd(dba)₂ (75.0 mg, 0.13 mmol) was dissolved in dry THF (5 mL), and the solution was cooled to -30 °C in a liquid nitrogen/ethanol bath. Then, a solution of (mPTA)I (7.8 mg, 2.6×10^{-2} mmol, 0.2 equiv.) in dry THF (30 mL) was added to the cooled solution of Pd precursor. The resulting mixture was

transferred by suction into a Parr autoclave and pressurized at RT with H₂ (3 bar). The solution was stirred at RT for 18 h. The Pd NPs precipitated from THF as a dark brown–black powder. The colorless supernatant phase was eliminated by filtration through a cannula, the NPs were recovered and washed with pentane to eliminate the excess dba. PXRD analysis of the dry powder and TEM analysis of a colloidal solution in water confirmed the formation of Pd NPs protected by (mPTA)I. Yield: 30% based on Pd (ICP-AES analysis); Average NP diameter: 3.5 ± 0.4 nm (TEM analysis); ¹H NMR (300.13 MHz, D₂O, 20 °C): $\delta = 2.71$ (s, 3H, CH₃), 3.64–3.91 (m, 4H, PCH₂N), 4.25–4.61 (m, 4H, $2 \times PCH_2N^++2 \times NCH_2N)$, 4.72–5.23 ppm (m, 4H, NCH₂N); ³¹P{¹H} NMR (121.49 MHz, D₂O, 20 °C): $\delta = -1.5$ ppm (s); ¹³C{¹H} NMR (100.61 MHz, D₂O, 20 °C): $\delta = 45.6$ (d, ¹J_{PC}=21.3 Hz, PCH₂N), 50.1 (s, N⁺-CH₃), 56.4 (d, ¹J_{PC}=32.8 Hz, PCH₂N), 69.1 (s, NCH₂N). 80.0 ppm (s, NCH₂N).

Catalytic hydrogenation

In a typical experiment, a 100 mL stainless-steel autoclave (ICCOM) was equipped with a carousel containing seven glass vials each of 3 mL capacity. Each vial, which contained a magnetic stirrer, was charged with an aqueous suspension of Pd@PTA NPs under an inert atmosphere. The chosen unsaturated substrate was added to each vial, then the autoclave was sealed and purged with H₂ (twice), finally it was pressurized with H₂ (10 bar). The reaction mixtures in the autoclave was depressurized, dichloromethane was added to extract the organic compounds (unreacted substrate and products), and the organic phase was analyzed by GC. Each test was repeated twice to check reproducibility.

Acknowledgements

The authors thank MIUR for partial funding under the PRIN 2009 project, the EC for additional funding under COST Action CM0802 (PhoSciNet). Dr. Alexander M. Kalsin (INEOS-RAS Moscow, Russia) is thanked for fruitful discussions, Dr. G. Ghini (University of Florence) for running UV/Vis spectra, and CEME for providing access to TEM instruments.

Keywords: biphasic catalysis · hydrogenation · nanoparticles · palladium · cage compounds

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Received: January 29, 2013 Revised: April 22, 2013 Published online on

FULL PAPERS

The Cat in the Cap: Water-soluble Pd nanoparticles with mean diameters in the range 2.8–3.5 nm are obtained by using 1,3,5-triaza-7-phosphaadamantane and its *N*-methyl derivative as capping agents. These nanoparticles are used in catalytic C=C and C=C bond hydrogenations under mild conditions and show moderate to good conversions and recyclability for up to nine consecutive runs for selected examples. Scale bar = 100 nm.



R, R' = H, Ph, alkyl

M. Caporali,* A. Guerriero, A. lenco, S. Caporali, M. Peruzzini, L. Gonsalvi*



Water-Soluble, 1,3,5-Triaza-7phosphaadamantane-Stabilized Palladium Nanoparticles and their Application in Biphasic Catalytic Hydrogenations at Room Temperature