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Synthesis of Water-Soluble Palladium Nanoparticles Stabilized by Sulfonated N-Heterocyclic Carbenes

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Dedication ((optional))

Abstract: A strategy involving the decomposition of palladium(II) organometallic complexes with sulfonated N-heterocyclic carbene ligands (NHC) leads to the formation of stable and water-soluble Pd nanoparticles. Three different methodologies (thermal decomposition, reduction under ¹³CO atmosphere and reduction with H₂) gave particles with different shapes and sizes, ranging from 1.5 to 7 nm. The structures of the organometallic intermediates and organic decomposition products were elucidated by NMR spectroscopy. To check the accessibility of the surface, the nanoparticles were tested as catalysts for the chemoselective hydrogenation of styrene in water. An effect of the particle size on the catalyst activity was observed. The aqueous phase was recycled up to ten times without any precipitation of metallic palladium.

Introduction

Metallic nanoparticles (MNPs) dispersed in aqueous media are interesting for their different applications in catalysis, including green catalysis.^[1] In the case of palladium, for instance, MNPs have been used as catalysts in Suzuki–Miyaura cross-coupling reactions in water.^[2] Surfactants, polymers or dendrimers have been employed to stabilize palladium nanoparticles (PdNPs) avoiding their agglomeration in aqueous solution.^[3] Ligands strongly bond to the surface can also induce interesting reactivity. N-Heterocyclic carbenes (NHC) have shown to form robust transition-metal complexes that have been applied in many homogeneous catalytic processes, some of them in aqueous media.^[4] In recent years, some examples of MNPs stabilized with NHCs directly coordinated to the surface have been reported.^[5,6,7] Some of us have characterized the coordination of such ligands to RuNPs by solid-state NMR

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spectroscopy,^[8] and have explored their application as catalysts in the hydrogenation of arenes.^[9] Additionally, NHCs have been used to synthesize Au,^[6,7,10] Pd,^[7,11] and Ag^[12] NPs as model systems for the formation of conglomerates or 3D networks.

Planellas and co-workers,^[13] and Richter et. al.^[14] have synthesized and characterized PdNPs stabilized with NHCs and have studied their application as catalysts in different processes such as Suzuki couplings or catalytic hydrogenations. However, these MNPs were insoluble in water and required the use of organic solvents. We reported the first example of water-soluble MNPs stabilized with sulfonated NHCs coordinated to the surface of platinum particles.^[15] These MNPs were synthesized by thermal decomposition of water-soluble dimethyl Pt(II) NHC complexes.^[16,17] The PtNPs thus obtained were highly stable in aqueous solution. Concerning PdNPs, Glorius and coworkers have reported the preparation of water-stable Pd nanoparticles stabilized by charged NHC ligands.^[18] In a recent work, we have also communicated the synthesis and characterization of watersoluble NHC-stabilized PdNPs prepared by decomposition of a dimethyl NHC metal complex.^[19] The coordination of the NHC ligand to the metal surface of these nanoparticles was confirmed by the observation of a Knight-shifted signal for the carbenic carbon in solid state ¹³C NMR spectra.

In this work, we report full details regarding the synthesis and characterization of different sulfonated dimethyl palladium(II) NHC complexes and nanoparticles, including liquid and solid-state NMR studies. We also compare different methods for the generation of the PdNPs involving the decomposition of Pd(II) complexes. Particular attention has been paid to the characterization by NMR spectroscopy of the decomposition products and the organometallic intermediates, in order to elucidate the NPs formation mechanism.

Results and Discussion

Synthesis of dimethyl NHC palladium(II) complexes

Ligand exchange from complexes such as $[PdMe_2(tmen)_2]$ or $[PdMe_2(bpy)]$ (tmen = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine; bpy = 2,2'-bipyridine), which are synthetically accessible and display a good thermal stability, is the most general route for the preparation of dimethyl palladium derivatives.^[20] Using these starting materials, several dimethyl NHC Pd complexes have been synthesized up to date, mainly with chelating ligands.^[21,22,23] Following this methodology, we prepared the water-soluble complexes **1a**-**b** in moderate to good yields (58-73%) by treating [PdMe₂(bpy)] with the corresponding carbene obtained in situ by addition of sodium *tert*-butoxide to the 1-mesityl-3-(propyl-3-sulfonate)imidazolium or sodium 1,3-

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bis(propyl-3-sulfonate)imidazolium proligand, in dmso (Scheme 1a). Complexes 1a-b were obtained as cis stereoisomers as shown by the chemical non-equivalence observed in the ¹H NMR spectra between the two halves of the mesityl substituents or the two protons of some methylene groups in the propyl-3sulfonate chains (see Scheme 1b). The same configuration was observed in previously reported [(NHC)₂PdMe₂] complexes.^[23,24] An isotopically substituted analogue of complex 1a, containing carbon-13 in the C² position of the imidazole ring, was also prepared (13C-1a, Scheme 1a). The new complexes were characterized by one- and two-dimensional NMR spectroscopy, FT-IR spectroscopy, mass spectrometry and elemental analysis. Full details are given in the Experimental section and Supporting information (SI, Figures S1-S2). The complexes had to be stored under an inert atmosphere due to the sensitivity of solid samples to atmospheric water, especially in the case of 1b (see below for a discussion of the reactivity of **1a-b** with water). However, the complexes cannot be stored for long periods of time because thermal decomposition is evident after several weeks (especially in the case of 1b), even when stored at low temperature.



Scheme 1. (a) Synthesis of the organometallic precursors **1a-b** and the isotopically modified complex ¹³**C-1a** with the carbenic carbon substituted by carbon-13. (b) Protons Ha and Hb are diastereotopic in the *cis* configuration (assuming a slow rotation of the NHC ligand around the Pd-Carbene bond) while they are related by a symmetry plane in the *trans* configuration.

Synthesis of the Pd nanoparticles 2a-b by thermal decomposition of dimethyl complexes in water

We have recently described that the thermal decomposition of complex 1a in water affords dark-brown solutions containing PdNPs (2a) that remain dispersed in the aqueous solution for indefinite periods of time (Scheme 2).[19] The size of these PdNPs was notably influenced by the heating ramp used to decompose the organometallic precursor while other conditions (temperature, time of heating, or concentration of the metal precursor) had a minor effect. The relative rates of the nucleation and growth steps apparently controlled the nanoparticle sizes. Thus, the largest nanoparticles (4.6 ± 1.7 nm) were generated raising the temperature of the solution slowly (at 1 °C per min) from room temperature to 60 °C (the lowest temperature at which NPs form). The slowest decomposition favored the growth step in this case. The smallest PdNPs (3.0 ± 0.8 nm) were obtained when the metallic precursor was dissolved in water pre-heated to 80 °C, favoring a quick decomposition and, therefore, the nucleation step. The organic products formed in this decomposition were removed from the solution by dialysis. As some coalescence of the nanoparticles was observed during this process, the time of dialysis was optimized after recording TEM images and ¹H NMR spectra at regular intervals to find the best compromise between optimizing the purification (removing as many organic products as possible) and avoiding coalescence of the nanoparticles. TEM and HRTEM images of a sample of purified PdNPs (mean diameter 3.4 ± 0.5 nm) are shown in Figures 1a-b.



Scheme 2. Synthesis of water-soluble PdNPs 2a-b by thermal decomposition of the dimethyl complexes 1a-b.

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Figure 1. (a) TEM image and size distribution, and (b) HRTEM image for PdNPs 2a after dialysis. (c) TEM image and size distribution for 2b after dialysis.

Thermal decomposition of complex 1b also affords stable solutions of PdNPs in water (2b, Scheme 2). These PdNPs are larger than those obtained from 1a under the same conditions (6.6 ± 2.0 nm for 2b compared with 3.6 ± 0.6 nm for 2a under the specific conditions described in the Experimental Section; see Figure S4 in the Supporting Information). A similar tendency (NHC ligands with a stronger steric hindrance led to smaller MNPs) was also observed for Pt nanoparticles prepared recently in our laboratories employing a parallel methodology.^[15] The nanoparticles were purified by dialysis for 12 h (Figure S3) without showing significant coalescence or changes in their size distributions during this process (mean diameters after dialysis: 6.3 ± 1.4 nm; Figure 1c). The hydrodynamic diameter determined by Dynamic Light Scattering (DLS) was 8.1 ± 1.2 nm. The ability to perform DLS measurements is indicative of the good dispersion of the nanoparticles in solution. The hydrodynamic diameter is slightly larger than the TEM diameter because it includes the ligand and solvation layers. The difference between TEM and DLS diameters was similar in the case of 2a (3.4 ± 0.5 nm and 5.2 ± 0.7 nm, respectively), the DLS diameter being coherent with the hydrodynamic diameter determined by diffusion-ordered NMR spectroscopy (6.4 ± 2 nm, Figure S11). After evaporation of the solvent under vacuum, PdNPs 2b were isolated as a black shiny powder in yields of 19% (based on Pd content). As the metal precursor was completely decomposed during the formation of 2b, this low yield is a consequence of metal losses during dialysis. Powder X-Ray Diffractograms (XRD) showed the formation of crystalline nanoparticles with a Pd(0) face-centered cubic packing (fcc, Figure S5). The crystallite size calculated from the XRD data using the Scherrer equation (2.2 nm) was much smaller than the mean size obtained by TEM. A similar divergence between TEM and XRD radii was found in PdNPs 2a, [19] and was ascribed to the polycrystallinity of the nanoparticles observed in the HR-TEM images (Figure 1b).^[25]

The nanoparticles were also characterized by infrared (FT-IR, Figure S6) and ¹H NMR spectroscopy (Figure S3). It is well known that protons close to MNP surfaces typically give broad

or undetectable NMR resonances because of the rigidity induced in the ligands upon coordination to a surface, the inherent heterogeneity of this surface, and the slow tumbling of particles that results in rapid T_2 relaxation times.^[26] However, relatively narrow proton resonances were observed in the ¹H NMR spectrum of the purified PdNPs **2b** in D₂O for the β - and γ methylenes (at 2.15 and 2.85 ppm respectively) of the propylsulfonate chain (and a broader one at 4.3 ppm related to the α position of the chain). The similar effect observed in related NHC-stabilized Pt nanoparticles was rationalized as resulting from the flexibility of the propylsulfonate chains.[15] Their conformation with the sulfonate groups pointing away from the particle was associated with the solubility of the nanoparticles in water. In contrast, the resonances for the same protons were hardly observable in nanoparticles 2a despite their smaller size. The interaction of the mesityl group with the nanoparticle surface possibly reduces the flexibility of the NHC in 2a.^[8,27]

NMR spectroscopy is a very useful technique for the characterization of nanoparticles.^[28] Specifically, solid-state ¹³C NMR spectroscopy has been used in the last years to support the coordination of NHC ligands to the surface of metal nanoparticles.[8,17-19] This characterization is however complicated by the structural and electronic^[29] disorder at the metallic surface and the presence of conduction electrons.^[30] We have recently shown that the ¹³C resonance of the carbenic carbon is shifted to around 600 ppm in NHC ligands coordinated to the surface of PdNPs.[19] This unusual position for the carbenic resonance of an NHC ligand is the result of a Knight shift originated by the presence of conduction electrons in large metal nanoparticles.^[31] We found that this effect was observed for PdNPs exceeding a critical size of around 2 nm. The Knightshifted resonances were so large that they were only observed in ¹³C-enriched samples using ¹³C CPMG or spin-echo MAS NMR experiments (spectra of two samples of ¹³C-2a showing the very broad resonance for the ¹³C-labeled carbenic carbon at -600 ppm are showed in Figure S8). This behavior explains the absence of observable carbenic resonances in the ¹³C Cross-Polarization (CP-MAS) spectra of PdNPs 2b (Figure S7).

A final comment can be done on the composition of these PdNPs. The stoichiometric ratio of imidazole versus palladium can be estimated from the elemental analyses of the samples. The ratios determined in samples of 2a and 2b after purification by dialysis are always close to 1:1 (values ranging from 0.8 to 1.1). Therefore, a part of the imidazolium salts formed in the decomposition of the organometallic precursors was removed by dialysis as the NHC:Pd proportion was originally 2:1 (this is the ratio in the organometallic precursors 1a-b). However, these ratios are yet too high to correspond entirely to NHC ligands coordinated to the metal surface. In our previous communication we estimated by solid-state ¹³C NMR spectroscopy that only a 3 ± 1% of the imidazole species corresponded to NHCs coordinated to the metal surface in a sample of PdNPs ¹³C-2a. The rest of imidazole species are likely in the form of imidazolium salts and presumably play a role in the stabilization of the PdNPs (as commented above, some coalescence was observed when dialysis was prolonged). Indeed, the absence of

resonances ascribable to these organic residues in the ¹H NMR spectra of the PdNPs in solution suggests an interaction between them and the nanoparticle surface. In addition, NOESY experiments performed before purification by dialysis showed a transfer NOE effect between the molecular species and the nanoparticle in the case of 2a (Figure S12). This effect happens when free molecules in solution are in rapid equilibrium with molecules coordinated to the surface of large nano-objects. The negative NOEs of the coordinated molecules are transferred by the fast exchange phenomena to the free ones resulting in negative cross peaks for the latter (same sign as the diagonal peaks).^[32,33] This observation evidences the presence of a weak interaction between the nanoparticles and the decomposition products. The transfer NOE effect disappears after three hours of dialysis, as expected from the slower exchange resulting from the decreased concentration of free imidazolium. Although we cannot determine the nature of the interaction between the organic residues and the PdNP surface, we might propose an organization in multiple layers similar to that observed in ZnO NPs stabilized by alkyamine ligands.^[33]

Mechanism involved in the thermal decomposition of complexes 1a-b

We performed NMR studies to elucidate the intermediates involved in the thermal transformation of complexes 1a-b in water. The dissolution of these complexes in deuterated water was accompanied by immediate formation of the monomethyl species 3a-b (Scheme 3a). Analysis of the gas composition produced during the reaction by ¹H NMR spectroscopy after transfer to a tube containing chloroform- d_1 showed the exclusive formation of methane- d_1 . The selective protonolysis of just one of the two palladium-methyl bonds was not completely unexpected considering the reported reactivity of other dimethyl NHC palladium complexes with Brönsted acids or traces of water.^[22,23] This protonolysis is accompanied by a cis-trans isomerization around the metal center (only one set of NMR resonances was observed for both NHC ligands, Figures S13-S14; the two NHC ligands should be inequivalent in *cis* isomers). The coordination vacancy is probably occupied by a molecule of the deuterated solvent (or deuteroxide anion taking into account the alkalinity of the resulting reaction medium). This uncertainty could not be resolved by ESI mass spectrometry where the heaviest peaks detected corresponded to the tricoordinated fragments [Pd(NHC)₂Me]⁺ (Figures S15-S16). Addition of dmso or cyanide to the above solutions resulted in coordination of the added ligand and clean formation of the expected complexes 4a-b or 5a-b (Scheme 3b) which were characterized by NMR spectroscopy and mass spectrometry (Figures S17-S18). Complex 4b was also prepared directly from [PdMe₂(bpy)] in moderate yields (62%) and fully characterized (see Experimental Section).

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Scheme 3. Decomposition byproducts observed in the formation of the PdNPs 2a-b. The scheme omits the H/D exchanges observed in step c for clarity.

The D₂O solutions were subsequently heated at the temperature used in the preparation of PdNPs 2a-b (80 °C). Under these conditions, the resonances corresponding to the NHC ligand coordinated to palladium(II) in 3a-b disappeared progressively while 2-methylimidazolium (6a-b) and monodeuterated imidazolium ($a-d_1$ or $b-d_1$) were formed (Scheme 3c). No other intermediates were detected in this clean transformation.

Incidentally, deuteration was found not only at the 2-position of **a**-**b** (as reflected in Scheme 3c) but also at other sites of both types of imidazolic products (**a**-**b** and **6a**-**b**). The degree of deuteration was marginal at the 4- and 5-imidazole positions but extensive or complete for the 2-methyl group of **6a**-**b** (see ¹H and ²H NMR spectra in Figures S19-S20 and S23-S24). Handy and Okello have reported H/D exchange between the 2-Me group and the deuterated solvent in a series of 2-methylsubstituted imidazoliums under mildly basic conditions.^[34]

Control experiments revealed that the deuteration of the 2-Me group in **6b** was insignificant after 24 h under neutral conditions, whereas it was fast at pH 13 even in the absence of PdNPs (full deuteration in less than 90 min; Figures S25-S26). This behavior means that the deuteration observed during the decomposition of **1a-b** is promoted by the alkaline medium generated by the hydrolysis of the Pd-C bonds, probably without involvement of Pd species.

In light of the sequence of reactions depicted in Scheme 3, the mechanism of PdNP formation from the dimethyl complexes 1a-b would begin with the hydrolysis of one methyl group leading to the "cationic" monomethyl bis-carbene 3a-b. We propose that the next step is a reductive methyl-NHC coupling to generate a NHC Pd(0) species instead of hydrolysis of a Pd-NHC bond. This proposal is based on the observation that the palladium(II)-carbene bonds of water-soluble NHC complexes are quite stable in alkaline media under conditions similar to those used here.^[35] In addition, seminal work by McGuinness, Cavell, and coworkers showed that alkyl NHC Pd(II) complexes can decompose producing 2-methylimidazolium salts.[36-38] Combined kinetic and DFT studies demonstrated that the mechanism consists in a concerted reductive elimination, and not in carbene insertion into Pd-alkyl bonds.[37] These authors observed that, in coherence with this mechanism, a positive charge on the metal increased the rate of elimination of 2alkylimidalzolium in respect to their neutral counterparts. The decomposition pathway followed by 1a-b contrasts with the one observed in the formation of NHC-protected PtNPs from watersoluble cis-[Pt(NHC)Me2(dmso)] complexes, which mainly involved the elimination of ethane as reducing step.[15,16] It should be noted that reductive alkyl-alkyl coupling has been observed more rarely in Pd(NHC) alkyl complexes than the reductive coupling of the alkyl and NHC ligands.^[24] The preference for this reductive coupling over hydrolysis of the remaining Pd-Me bond in 3a-b should be noted. This behavior is likely to be favored by the cationic nature of the palladium(II) center in 3a-b. In the last step of the nanoparticle formation, the Pd(0) monocarbene species could begin aggregation of the Pd(0) atoms and form nanoparticles, hence liberating a portion of the NHC ligands in the form of imidazolium salt. The amount of imidazolium salts **a-b** measured by ¹H NMR integration during this second step of decomposition was always found significantly lower than that of the coupling product 6a-b found in the first step (the ratio determined by ¹H NMR integration is approximately 40:60% in both cases, Table 1a, Figures S19-S22). This is expected since a fraction of the NHC ligands remains attached to the surface of the nanoparticles or in a second coordination sphere.



(a) Decomposition	under thermal	treatment
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Precursor [conditions]	8a	CH ₃ ¹³ COO [−]	6a or 6b	a or b				
1a			58%	42%				
1b			59%	41%				
(b) Decomposition under ¹³ CO treatment at 1 bar ¹								
1a [room temp, overnight]	79%	~10% ^[b]	4%	17%				
1a [45 °C, 3 days]	69%	~25% ^[b]	4%	27%				
1b [room temp, overnight]		47%	33%	67%				

[a] The composition (in equiv %) was determined by ¹H NMR integration and is referenced to 100% for the total of imidazolium-containing species; 1 mmol = 1 equiv (**6a**, **6b**, **a**, and **b**) or 2 equiv (**8a** and acetate). [b] Overlapped with other resonances; the integral was estimated by deconvolution.

Synthesis of the Pd nanoparticles 7a-b by decomposition of dimethyl complexes under a ¹³CO atmosphere

Besides thermal decomposition, the formation of metal nanoparticles can be achieved by reacting an organometallic precursor with a reductive gas, in general CO and H₂, and using mild reaction conditions. Here, the organometallic complexes 1a-b were stirred overnight under a ¹³CO atmosphere of 1 bar in water at room temperature, leading to dark brown solutions containing the PdNPs 7a-b (Scheme 4). These solutions were again highly stable over time and no aggregation was observed for several months when no purification was performed. The diameters of the nanoparticles measured by TEM before purification were of 1.5 ± 0.3 nm for 7a and 1.9 ± 0.6 nm for 7b (Figures S27 and S28). A clear effect of the decomposition method was observed, as regards to the nanoparticle size. PdNPs obtained by decomposition with CO (7a-b) were significantly smaller than those obtained by thermal decomposition (2a-b). After purification by dialysis against water for 24 h, TEM images showed that the diameters of the small nanoparticles have only slightly increased (to 1.6 ± 0.4 nm for 7a and to 2.4 ± 0.6 nm for 7b; Figure 3) but also that large agglomerates were also formed.

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cis-[(NHC)₂Pd(CH₃)₂]



Scheme 4. Synthesis of water-soluble PdNPs **7a-b** by decomposition of the dimethyl complexes **1a-b** under a ¹³CO atmosphere.



Figure 3. TEM images and size distributions for PdNPs 7a (a) and 7b (b) after dialysis.

After dialysis, the ¹H NMR spectrum of **7a** (Figure S29) still showed several well-defined ¹H resonances that corresponded to the acyl complex Na[trans-Pd(NHC)2(COMe)(OH2)] (8a). This complex is an intermediate generated in the synthesis of the PdNPs (see below) and could not be completely removed during the purification. The resonances of the NHCs on the PdNP surface were too broad to be clearly detected in this spectrum. In the case of 7b, the molecular products were efficiently removed during the dialysis and the ¹H NMR spectrum only showed the broad signals corresponding to the surface NHCs (Figure S30). The resonances for the β and γ positions of the alkyl chain (at 2.15 and 2.85 ppm respectively), and for the positions 4 and 5 of the imidazole ring (around 7.4 ppm) were better defined than those due to the α protons (around 4.3 ppm), which were very broadened, as in 2b, due to their proximity to the particle surface.

The solutions were dried under vacuum to give black shiny powders in yields of 8% for **7a** and 23% for **7b**, based on the metal content. The low yield obtained for nanoparticles **7a** is partly due to the formation of the organometallic complex **8a** as the main reaction product (it represented almost 80% of the ¹H integration of the imidazole-containing species). The NHC:Pd ratios determined by elemental analysis after purification by dialysis (1:1.5 for **7a** and 1:2.5 for **7b**) are lower than in the case of **2a-b**, as it might be expected from the longer dialysis times (24 h) employed for these nanoparticles. However, these ratios are again too high to correspond entirely to NHC ligands coordinated to the metal surface. The partial retention of the imidazole salts in the NP solution might suggest some interaction between them and the PdNP surface. The XRD diffractograms confirmed the *fcc* structure of the Pd(0) nanoparticles (Figure S31). The similarity of the crystallite sizes obtained from the Scherrer equation (1.5 nm for **7a** and 2.3 nm for **7b**) with the TEM diameters proved the monocrystallinity of the objects.

The nanoparticles were further characterized in the solid state by infrared (FT-IR) and ¹H and ¹³C MAS NMR spectroscopy (Figure S32-S35). Coordinated ¹³CO was detected by ¹³C CP-MAS spectroscopy in the form of broad resonances at around 170-180 ppm in 7a. This chemical shift is within the usual range for metal carbonyls in diamagnetic substances (typically between 150 and 250 ppm).^[39] We recently reported that carbonyl resonances are expected to move to high frequencies because of Knight shift, when the PdNP size exceeds the critical threshold of 2-3 nm.[19] Accordingly to this hypothesis, two types of ¹³CO resonances were observed in NPs 7b (2.4 ± 0.6 nm) after treatment of the powder with ¹³CO for 3 days, one centered at around 180 ppm corresponding to the smaller particles composing the sample, and the other expanding up to 800-900 ppm and corresponding to the bigger nanoparticles (Figure S36). The ¹³C resonances of the coordinated NHC ligands appeared in the same regions as in the organometallic precursors, except for the resonances of the carbenic carbons, which were not observable.

Decomposition mechanism under a ¹³CO atmosphere

As already showed above, the dissolution of the organometallic precursors 1a-b in water leads to the monomethyl "cationic" complexes 3a-b, which evolved differently upon treatment with ¹³CO. In the case of 3a (Scheme 5), the aqua ligand was progressively replaced by ¹³CO. The formation of the trans carbonyl complex 9a was demonstrated by the observation of doublets for the PdMe group at -0.12 ppm (¹H) and -3.4 ppm (¹³C) with couplings of 1.6 and 35 Hz, respectively, to the ¹³CO resonance at 176.8 ppm (Figures S38-S39). In a second step, 9a is transformed into the acetyl complex 8a by ¹³CO insertion into the PdMe bond. While the coordination step reverted when the ¹³CO atmosphere was evacuated, this insertion was irreversible. The acyl complex 8a was the main product remaining in the aqueous solution after an overnight treatment of 1a at room temperature, together with smaller amounts of (1-13C)acetate (1H doublet at 1.85 ppm with a coupling constant to ¹³C of 5 Hz), 2-methylimidazolium (6a), and imidazolium (a; Table 1b and Figure S29). Complex 8a was very stable under these conditions (see characterization below). Even when the reaction was extended to three days at 45 °C, the concentration of 8a in the solution showed a modest decrease from 79% to 69% in parallel to the increase from ca. 10% to 25% of the amount of (1-13C)acetate. 2-Methylimidazolium (6a) was formed in comparatively lower amounts (around 4%), irrespective of the reaction time and the temperature (Figure S37). In the case of 3b, the decomposition under ¹³CO occurred without the formation of detectable

amounts of other NHC-metal intermediates. The organometallic species decomposed completely after an overnight ¹³CO treatment at room temperature, giving imidazolium **b**, (1-¹³C)acetate, and 2-methylimidazolium **6b** (Table 1b and Figure S30).



Scheme 5. NHC complexes observed in the formation of PdNPs 7a.

Complex **8a** was characterized by NMR and MS techniques (Figures S40-S44). The methyl protons were observed as a doublet at 1.28 ppm with a coupling of 5 Hz to the (13 C)-carbonyl at 234 ppm. The methyl ¹H resonance was additionally correlated with the methyl ¹³C resonance at 41 ppm by HSQC ¹H-¹³C spectroscopy. These ¹H and ¹³C chemical shifts are characteristic of acetyl Pd^{II} complexes (versus carbonyl-methyl).^[40,41] Thus, for instance, Subramanium and Slaughter reported resonances at 234.5, 44.3 (13 C), and 1.29 ppm (¹H) for the acetyl derivative [Pd(NHC-NHC)(COMe)(CO)]^{*} while the resonances of the carbonyl complex [Pd(NHC-NHC)Me(CO)]⁺ appeared at 183.0, 13.2 (13 C), and -0.29 ppm (¹H).^[40]

The reduction of NHC metal complexes containing alkyl and carbonyl ligands can involve a priori three different processes: (a) alkyl-carbene coupling to give 2-methylimidazolium, [36,37,42] (b) CO insertion into the Pd-alkyl bond followed by OH nucleophilic attack to the acetyl ligand to give acetate, and (c) CO insertion into the Pd-methyl bond followed by acetyl-carbene coupling to give 2-acetylimidazolium.^[36,37,42] We never observed of 2-acetylimidazolium, the formation whereas 2methylimidazolium and acetate elimination were much more favorable in the case of b. The slowing-down of the reductive methyl-carbene elimination with the most sterically demanding NHC ligand a was to be expected from previous studies about the effect of mesityl-substituted NHC ligands on the stability of methyl Pd derivatives.^[40,43] In addition, methyl-carbene coupling occurs essentially after CO coordination considering that 3b produced, under the conditions shown in Table 1b, less than 10% of 6b in the absence of carbon monoxide. On the other hand, the effect of the NHC bulkiness on the formation of (¹³C)acetate is less clear. The stability of the trans acyl complex 8a might be associated to the finding of Van Leeuwen and coworkers that alcoholysis of acylpalladium(II) complexes requires cis coordination between the acyl group and the

alcohol.^[44] *Trans* to *cis* isomerization is more likely in the case of the less sterically demanding ligand **b**. A rate-limiting CO coordination step followed by faster isomerization, insertion and elimination steps would explain the significant amount of (1-¹³C)acetate formed from **3b** and the lack of detection of carbonyl or acyl metal intermediates.

Decomposition of dimethyl complexes under an H₂ atmosphere

Reduction by H₂ is a classical method for the formation of MNPs. As such, it was of interest to determine whether this methodology could also be applied to the preparation of waterstable Pd nanoparticles from complexes 1a-b. When the organometallic precursor 1a was dissolved in water and stirred overnight under 1 bar of H2, a dark-brown solution that was stable over time was obtained (no metallic deposition was observed after 6 months). This solution contained worm-shaped nano-objects (10a) with different sizes (see TEM images in Figures 4 and S45). The ¹H NMR spectrum of the solution showed formation of the imidazolium salt a as the only decomposition product (Figure S46). In the case of the organometallic precursor 1b, we did not obtain any stable nanoobject. Metallic palladium precipitated after stirring for 2 hours under an atmosphere of 1 bar H₂. Hydrido palladium-NHC complexes are often unstable as the attack of the hydride on the carbene results in reductive elimination to give the imidazolium salt.^[45] In both cases, the coalescence of particles or the formation of bulk metallic palladium might be a consequence of the formation of relatively unprotected metal nanoparticles due to the extensive removal of NHC ligands by carbene-hydride coupling. Formation of palladium black has sometimes been observed when NHC complexes are placed under a hydrogen atmosphere.[46] This method of decomposition seems therefore not to be adequate for the preparation of well dispersed isolated Pd nanoparticles.



Figure 4. TEM image of nano-objects 10a obtained by decomposition of complex 1a under an H_2 atmosphere.

Catalytic hydrogenation of styrene

In order to check the activity of the PdNPs as hydrogenation catalysts in water, some of the PdNPs synthesized during this work were tested as catalysts in the chemoselective hydrogenation of styrene at room temperature in water (see complete details in the Supporting Information). Nanoparticles **2a** (0.46 mol%) gave high conversion values (97%) after 3 hours of reaction with no precipitation of metallic Pd. In addition, the

catalyst could be reused under the same reaction conditions after extraction of the organic products. The conversions were almost complete, with yields higher than 80% for at least 10 catalytic cycles (Figure S47) and with no formation of metallic Pd precipitates. The shape of the particles was checked by TEM after hydrogenation (Figure S48) and evidenced extensive coalescence leading to worm-like particles resembling the PdNPs obtained under hydrogen (**10a**).

Conclusions

Herein, we have reported the synthesis of water-soluble PdNPs stabilized with NHC ligands. These particles are highly stable in water, and their sizes are dependent upon the organometallic precursor and the synthetic method employed. The PdNPs are smaller when the most hindered ligand is employed and upon decomposition under a CO atmosphere. For nanoparticles ¹³C-2a, which were obtained by thermal decomposition of Pd(II) NHC complex **1a** labeled in the carbene position, the ¹³C resonance of the carbene carbon coordinated to the nanoparticle surface is shifted to very high frequencies (600 ppm) as a result of the Knight shift effect. As we argued in our previous communication,^[19] the observation of a Knight-shifted signal for the carbene carbon demonstrates the coordination of the NHC ligand to the surface of the particles.

NMR studies in solution helped to elucidate the organometallic intermediates and organic decomposition products involved in the reduction process required for formation of the Pd(0) nanoparticles from their Pd^{II} precursors. Key steps are the reductive coupling between one methyl and one carbene ligand (upon thermal decomposition), the insertion of CO into a Pd-methyl bond followed by elimination of acetate (in the presence of carbon monoxide), or carbene-hydride coupling (under a hydrogen atmosphere). As expected, steric effects can stabilize some intermediates, making the activation steps involved in the reductive couplings or isomerization processes required to reach the adequate stereochemistry less accessible. The decomposition pathways have been studied under conditions that are relevant to many catalytic processes. This knowledge is therefore important for both the high-yield synthesis of PdNPs and for homogeneous processes in which nanoparticle formation must be avoided.

Over the last few years nano-chemistry is tending towards more environmentally friendly conditions in the synthesis and applications of MNPs.^[47] This work constitutes an example of highly stable MNPs synthesized under green conditions that might be of potential interest in different catalytic processes involving palladium in aqueous medium. As an example, we have shown the efficiency of the PdNPs as recyclable catalysts for the chemoselective hydrogenation of styrene.

Experimental Section

General procedures and characterization techniques

General procedures and characterization techniques are given in the Supporting Information.

Synthesis and characterization data for palladium(II) complexes

Synthetic procedures and characterization data is given below for complexes **1a** and **1b**. Characterization data for some representative complexes is also given. Information for other complexes is given in the SI. The imidazolium salts **a**, **b**, and ¹³C-**a** were prepared as reported elsewhere.^[15,48]

cis-Bis[1-mesityl-3-(3-sodium sulfonatopropyl)imidazol-2ylidene]dimethylpalladium(II) (1a): A solution of sodium tert-butoxide (0.072 g, 0.75 mmol) in dry dmso (10 mL) was slowly added to a mixture of [PdMe₂(bpy)] (0.100 g, 0.342 mmol; see SI for preparation details) and imidazolium salt a (0.210 g, 0.683 mmol) under an inert atmosphere. The reaction mixture was stirred at room temperature for 30 minutes, then the solution was poured into dry acetone (60 mL). The precipitate was separated by filtration, washed with dry CH_2CI_2 (2 × 20 mL), and dried under vacuum to afford 1a as a white solid (0.188 g, 58%). Anal. Calcd. (%) for C₃₄H₅₈N₄Na₂O₁₁PdS₃ (**1a**·dmso·4H₂O): C, 43.27; H, 6.15; N, 5.94; S, 10.19. Found: C, 42.94; H, 5.82; N, 5.97; S, 10.33. ¹H NMR (300 MHz, dmso- d_6 , 2.49 ppm): δ 7.26 (d, 1H, Imz-H⁴, ${}^{3}J_{HH}$ = 1.8), 6.98 (s, 1H, Ar), 6.96 (s, 1H, Ar), 6.92 (d, 1H, Imz-H⁵, ${}^{3}J_{HH}$ = 1.8), 3.70 (broad m, 1H, NCH₂), 2.96 (broad m, 1H, NCH₂), 2.31 (s, 3H, Ar-p-Me), 2.18 (m, 2H, CH2SO3), 1.94 (s, 3H, Ar-o-Me), 1.84 (broad m, 2H, CH2CH2CH2), 1.47 (broad s, 3H, Ar-o-Me), -0.89 (s, 3H, PdMe). ¹³C{¹H} NMR (75 MHz, dmso-d₆, 39.0 ppm): δ 193.7 (Imz-C²), 136.8 (Ar-C⁴), 136.5 (Ar-C²), 135.8 (Ar-C¹), 133.9 (Ar-C²), 128.1 (Ar-C³), 128.0 (Ar-C³), 121.1 (Imz-C⁴), 118.5 (Imz-C⁵), 48.3 (NCH₂), 47.5 (CH₂SO₃), 25.4 (CH₂CH₂CH₂), 20.0 (Ar-p-Me), 17.6 (Ar-o-Me), 16.8 (Ar-o-Me), -3.1 (PdMe). ESI-MS (negative ion, MeOH) m/z: 735.2 [M – 2Na – Me]⁻ (calcd. 735.2) 100%.

cis-Bis[1,3-bis(3-sodium

sulfonatopropyl)imidazol-2-

ylidene]dimethylpalladium(II) (1b): Complex 1b (0.249 g, 73%) was prepared as described above for 1a, starting from sodium *tert*-butoxide (0.072 g, 0.75 mmol), [PdMe₂(bpy)] (0.100 g, 0.342 mmol) and b (0.228 g 0.683 mmol). Anal. Calcd. for $C_{22}H_{48}N_4Na_4O_{17}PdS_5$ (1b·dmso·4H₂O): C, 26.44; H, 4.84; N, 5.61; S, 16.04. Found: C, 26.48; H, 4.82; N, 5.60; S, 15.60. ¹H-NMR (300 MHz, dmso-*d*₆, 2.49 ppm): δ 7.09 (s, 2H, Imz-H^{4.5}), 4.27 (m, 2H, NCH₂), 4.03 (m, 2H, NCH₂), 2.45 (m, partially under the solvent resonance, CH₂SO₃), 1.98 (broad m, 4H, CH₂CH₂CH₂), -0.73 (s, 3H, PdMe). ¹³C{¹H} NMR (75 MHz, dmso-*d*₆, 39.0 ppm): δ 192.3 (Imz-C²) 119.4 (Imz-C^{4.5}), 48.5 (NCH₂), 48.4 (CH₂S), 26.5 (CH₂CH₂CH₂), -3.6 (PdMe). ESI-MS (negative ion, MeOH) *m/z*: 787.0 [M – 2Na – Me]⁻ (calcd 787.0) 2%.

Characterization data for 3a: Complex 1a (5.0 mg, 5.3 µmol) was dissolved in deuterium oxide (0.5 mL) into an NMR tube. Methane evolution was immediately observed. The ¹H NMR spectrum was recorded at 45 °C because some resonances appeared broadened at room temperature. ¹H NMR (300 MHz, D₂O, 4.43 ppm, 318 K): δ 7.20 (s, 2H, Imz-H⁴), 6.97 (s, 4H, Ar), 6.92 (s, 2H, Imz-H⁵), 4.17 (broad m, 4H, NCH₂), 2.60 (broad m, partially under the residual dmso resonance, CH₂SO₃), 2.30 (s, 6H, Ar-p-Me), 2.18 (broad m, 4H, CH₂CH₂CH₂), 1,80 (s 12H, Ar-o-Me), -0.46 (s, 3H, PdMe). ¹³C{¹H} NMR (75 MHz, D₂O, 318 K): δ 183.8 (Imz-C²), 141.1 (Ar-*p-Me*), 138.9 (Ar-C¹), 137.9 (Ar-o-Me), 132.3 (Ar-C³), 131.5 and 124.1 (Imz-C^{4,5}), 51.5 (NCH₂), 50.0 (NCH₂), 27.1 (CH₂CH₂CH₂), 23.1 (Ar-p-CH₃), 20.6 (Ar-o-CH₃), -14.5 (PdMe). ESI-MS (positive ion, H₂O/MeOH) m/z: 781.1 [M - OD₂ + Na]⁺ (calcd. 781.1) 52%, 743.1 $[M - OD_2 - CH_3]^+$ (calcd. 743.1) 51%, 345.1 $[6a + Na]^+$ (calcd. 345.1) 100%, 331.1 [a + Na]⁺ (calcd. 331.1) 33%. ESI-MS (negative ion, H₂O/MeOH): 735.1 [M - OD₂- Na]⁻ (calcd. 735.1) 100%.

Trisodium trans-bis[1,3-bis(sulfonatopropyl)imidazol-2-

ylidene](dimethylsulfoxide)methylpalladium(II) (4b): A solution of sodium tert-butoxide (0.072 g, 0.75 mmol) in moist dmso (10 mL) was slowly added to a mixture of [PdMe2(bpy)] (0.100 g, 0.342 mmol) and imidazolium salt b (0.228 g, 0.683 mmol) under an inert atmosphere. The mixture was stirred at room temperature for 30 min. The solution was then poured into dry acetone (60 mL) and filtered. The white solid thus obtained was washed with 2 \times 20 mL of dry CH_2Cl_2 and dried under vacuum (0.213 g, 62%). Anal. Calcd. for $C_{21}H_{46}N_4Na_4O_{18}PdS_5$ (4b·5H₂O): C, 25.17; H, 4.73; N, 5.59; S, 15.99. Found: C, 25.45; H, 4.80; N, 5.71; S, 15.31. ¹H NMR (300 MHz, dmso- d_6 2.49 ppm): δ 7.48 (s, 4H, Imz-H^{4,5}), 4.40 (broad t, 8H, NCH₂), 2.50 (overlapped with the solvent resonance, indirectly observed by HSQC ¹H-¹³C, CH₂SO₃), 2.17 (broad m, 8H, CH₂CH₂CH₂), -0.04 (s, 3H, PdMe). ¹³C{¹H} NMR (75 MHz, dmso d_6 , 39.0 ppm): δ 176.1 (Imz-C²), 121.5 (Imz-C^{4,5}), 48.7 (NCH₂), 47.6 (CH₂SO₃), 26.2 (CH₂CH₂CH₂), -9.3 (PdMe). ESI-MS (positive ion, H₂O/MeOH): 832.0 m/z [M + Na]⁺ (calcd. 832.0) 100%. ESI-MS (negative ion, H₂O/MeOH) m/z: 787.0 [M - dmso - Na]⁻ (calcd. 787.0) 51%, 325.1 [6b - Na]⁻ (calcd. 325.0) 68%.

Characterization data for 8a. ¹H NMR (300 MHz, D₂O, 4.69 ppm): *δ* 7.32 (d, ${}^{3}J_{HH}$ = 2.0, 2H, Imz-H⁴), 7.07 (broad s, 4H, Ar), 7.02 (d, ${}^{3}J_{HH}$ = 2.0, 2H, Imz-H⁵), 4.42 (broad t, 4H, NCH₂), 2.81 (t, ${}^{3}J_{HH}$ = 7.6, 4H, CH₂SO₃), 2.31 (s, 6H, Ar-*p*-*Me*), 2.26 (broad m, 4H, CH₂CH₂CH₂), 1.89 (broad s, 12H, Ar-*o*-*Me*), 1.25 (d, ${}^{3}J_{HC}$ = 5.4, 3H, COMe). ¹³C{¹H} NMR (75 MHz, D₂O): *δ* 233.7 (COMe), 176.6 (Imz-C²), 139.9 (Ar-C⁴), 135.6 (Ar-C²), 130.6 (Ar-C¹), 128.8 (Ar-C³), 123.4 and 121.3 (Imz-C^{4.5}), 49.3 (NCH₂), 48.2 (CH₂SO₃), 41.2 (CO*Me*), 25.8 (CH₂CH₂CH₂), 20.2 (Ar-*p*-*M*), 17.1 (Ar-*o*-*M*). ESI-MS (negative ion, H₂O/MeOH) *m*/*z*: 764.1 [M – H₂O – Na]⁻ (calcd. 764.1) 100%; 735.2 [M – H₂O – ¹³CO – Na]⁻ (calcd. 735.2 m/z) 15%.

Synthesis of and characterization for PdNPs

PdNPs 2: The corresponding palladium complex **1** (0.500 mmol for **1a** and **1b**; 0.200 mmol for 13 **C**-**1a**) was introduced into a 100-mL pressure tube and dissolved in deionized water (50 or 20 mL) under an inert atmosphere. The resulting solution was heated at 80 °C for 15 hours. The dark-brown solutions formed were left to reach room temperature slowly, and were dialyzed against water using a cellulose membrane (MWCO = 14,000 Dalton) for 6 (2a and 13 C-2a) or 12 h (2b). The solution was dried under vacuum to afford the corresponding nanoparticles as a black shiny powder (0.232 g, 59% based on Pd for **2a**; 0.057 g, 19% based on Pd for **2b**; 0.063 g, 39% based on Pd for 3 C-2a). Characterization data is given in the ESI.

PdNPs 7: The corresponding palladium complex 1 (0.500 mmol) was introduced into a 100-mL pressure tube and dissolved in deionized water (50 mL) under an inert atmosphere. The tube was then pressurized at 1 bar of Ar and 1 bar of ¹³CO. The solution was kept under stirring for 15 hours at room temperature. The resulting dark-brown solutions were dialyzed against water using a cellulose membrane (MWCO = 14,000 Dalton) for 24 h. The solution was then dried under vacuum to afford the corresponding nanoparticles as a black shiny powder (0.039 g, 8% based on Pd for **7a**; 0.102 g, 23% based on Pd for **7b**). Characterization data is given in the ESI.

PdNPs 10: The Pd complex **1a** (0.500 mmol) was introduced into a 100mL pressure tube under an inert atmosphere and dissolved in deionized water (50 mL). The tube was then pressurized at 1 bar of Ar and 1 bar of H₂. The solution was kept stirring for 15 hours at room temperature, then dried under vacuum to afford nanoparticles **10a**. Characterization data is given in the ESI.

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