Negatively Charged N-Heterocyclic Carbene-Stabilized Pd and Au Nanoparticles and Efficient Catalysis in Water

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ABSTRACT. Herein we describe the synthesis of negatively charged N-heterocyclic carbene (NHC)-functionalized palladium and gold nanoparticles (NPs), which are stable in water for over three months. The formation of these NHC−NPs proceeds via an efficient ligand exchange procedure. This method was successfully applied to different negatively charged NHCs bearing sulfonate and carboxylate groups. The obtained PdNPs were investigated as catalysts in hydrogenation reactions and showed high catalytic activity (TON up to 2500 and TOF up to 2000 h^{-1}).

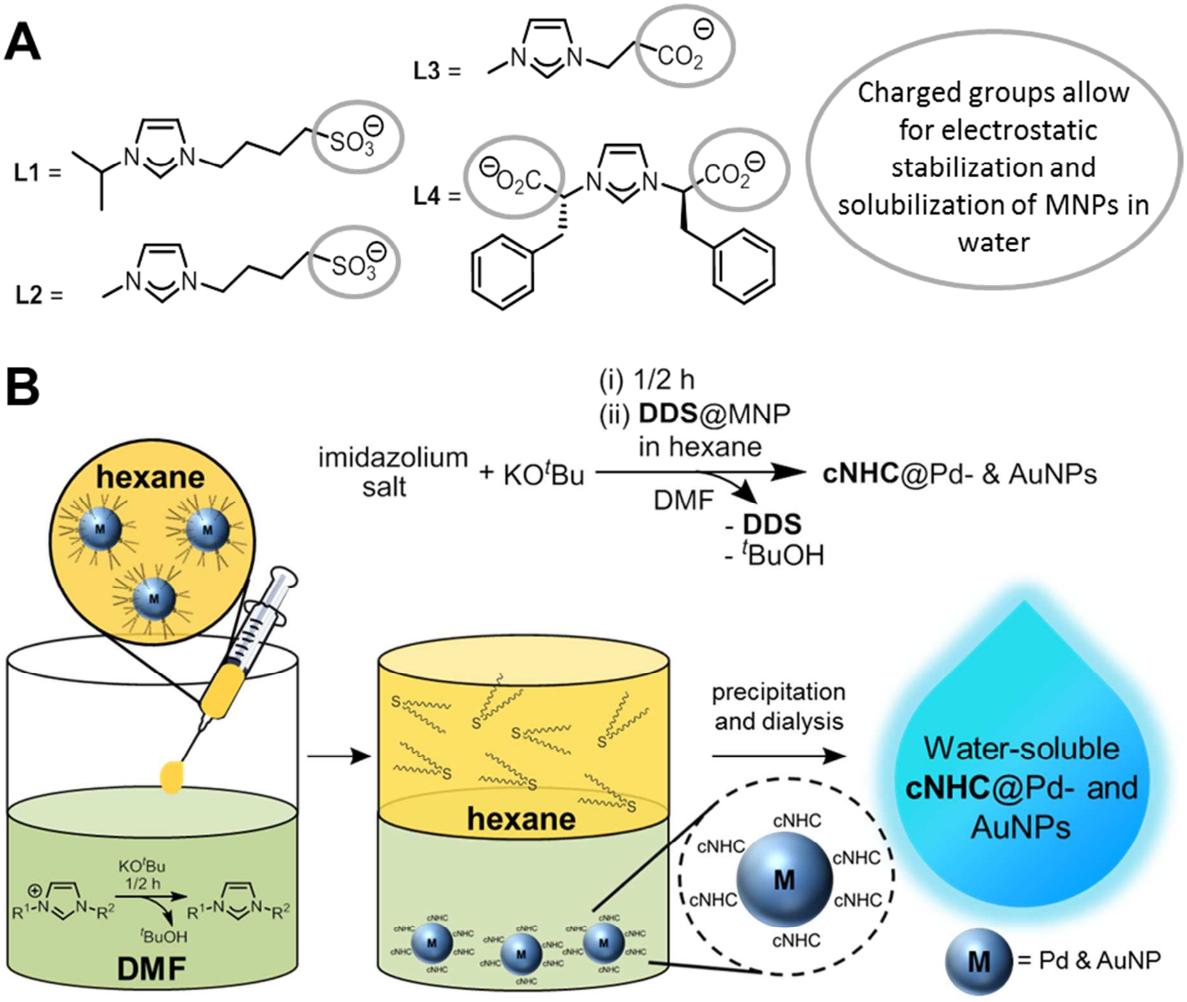
KEYWORDS. metallic nanoparticles, N-heterocyclic carbene, ligand exchange, catalysis, anionic nanoparticles

INTRODUCTION

In the last decades, interest in nanoparticles (NPs) has significantly increased due to their numerous applications in material science, medicine and catalysis.[1] The large surface area of metal NPs (MNPs) compared to bulk material allows for efficient metal-substrate interactions to take place, rendering MNPs attractive candidates for catalysis. Furthermore, the novel physical and chemical properties of the nanoscale dimension can lead to unprecedented activities and reaction pathways.[2] However, due to their high surface energy, MNPs tend to aggregate which leads to a decrease in their surface area and thus a loss in activity. Stabilization of MNPs is generally achieved with the use of ligands such as thiols, amines, disulfides, thioethers, phosphines[3] or, more recently, N-heterocyclic carbenes (NHCs).[4,5] The neutral, electron-rich NHCs form a strong covalent bond with the metallic surface which is key to their stabilization of NPs and allows the NPs to maintain their size-dependent properties. An advantage of using NHCs as ligands is the feasible modification of the N-heterocycle with different functional groups which can give rise to a tunable surface. To date, only a few examples of NHC-functionalized NPs are described in the literature with limited applications.[4,5] Among them, two different approaches have been used to form the NHC-stabilized NP systems: (1) the metal complex decomposition route, largely exploited for the formation of Ru,[4a,d] Pt,[4b,f] Au[4c,e,g] and PdNPs[4g] and (2) the ligand exchange strategy for the synthesis of Pd and AuNPs.[5] The ligand exchange approach is desirable because it uses preformed NPs with defined sizes and shapes. Several protocols have been established for the synthesis of these NPs.[5,6] Very recently, we presented a new NHC bearing two long alkyl chains in its backbone which is capable of stabilizing Pd and AuNPs.[5b] These sterically-stabilized NPs showed good solubility in apolar solvents with interesting chemoselectivity in hydrogenation reactions. In the continuation of this work, we were interested in synthesizing NPs suitable for catalysis in aqueous media. We considered employing negatively charged NHC ligands in electrostatic stabilization of MNPs. The electrostatic stabilization of NPs has been previously demonstrated by addition of ionic liquids[7] or salts,[8] such as an ammonium halide, citrate, polyacrylate or polyoxometallate during NP formation. It is known that the stabilization of the NPs relies on repulsive electrostatic interactions generated from a diffuse double layer at the surface of NPs coated with charged ligands.[8f,g,h] However, it has been shown that NHCs bind very strongly to the metal surface,[4l] thus giving an interesting platform to tune the reactivity of the metal NP. To date, only one example of employing charged NHCs for the stabilization of PtNPs has been reported. This work by Chaudret et al. featured NHCs bearing a negatively charged sulfonate group and the corresponding NHC-MNPs were made by the decomposition protocol.[4j] However, the catalytic activity of these nanostructures was not investigated in depth. Herein we present the first example of Pd and AuNPs stabilized by charged NHCs. We installed various negatively charged NHCs possessing different functional groups (sulfonates or carboxylates) following the ligand exchange method. All of these NPs showed long-term stability in water. These PdNPs showed high activity in hydrogenation reactions conducted in aqueous media (TON up to 2500 and TOF up to 2000 h^{-1}).

SYNTHESIS

In order to obtain stable MNPs in water, we synthesized a library of NHCs bearing negatively charged sulfonate (**L1** & **L2**) and carboxylate groups (**L3** & **L4**, see Scheme 1 A). The use of ligands **L1**-**L4** for Pd or for MNPs has not been previously reported and there is only one example of an **L4**-Au complex.[9]



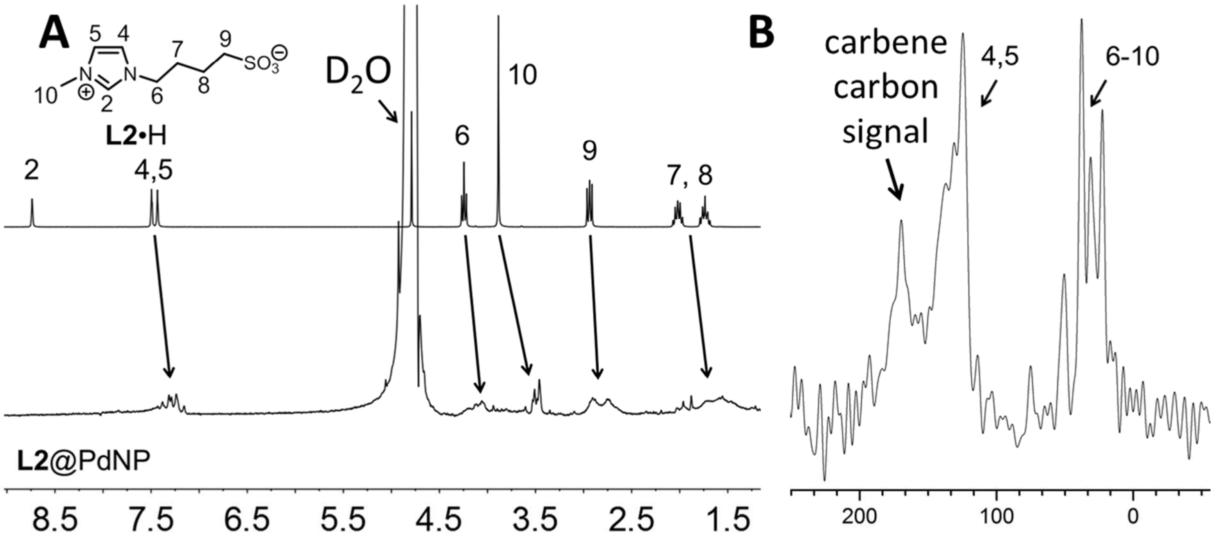
Scheme 1: A. Negatively charged NHCs (**L1**-**L4**) for the stabilization of Pd and AuNPs in aqueous media. **B**. Schematic representation of the ligand exchange procedure using **DDS**@MNPs as precursor.

The subsequent synthesis of NHC functionalized Pd and AuNPs was realized by use of the ligand exchange method. As was previously demonstrated,[5b] displacement of weakly binding thioethers from the NP surface by stronger binding NHCs is a general procedure to attach a variety of NHC ligands to MNPs. The ligand exchange was performed by mixing didodecylsulfide (**DDS**) stabilized Pd- and AuNPs with the desired charged NHCs (cNHCs) in a biphasic hexane/DMF system (see Scheme 1B). The NHCs were generated *in situ* by deprotonation of the corresponding imidazolium salts with KO^{t}Bu. After the addition of

DDS@MNPs, a phase transfer of the MNPs from hexane into the more polar DMF phase could be observed, indicating the successful ligand exchange on the NP surface. The NPs were then purified by repeated washing and dialysis against water. Using this approach, we were able to synthesize the first water-soluble Pd and AuNPs using cNHCs ligands. These NPs were stable for more than three months.

RESULTS AND DISCUSSION

Characterization of the cNHC@MNPs by NMR spectroscopy showed that the thioether **DDS** was completely displaced from the NP surface. The ^{1}H NMR spectra, measured in D_2O, showed broad peaks corresponding to the protons of the NHCs (Scheme 2A). This peak broadening is caused by the coordination of the NHCs to the NP surface and has also been observed for comparable PtNP systems.[5j] MAS ^{13}C NMR spectroscopy performed for **L2**@PdNPs confirmed the successful coordination of the NHC to the NP surface (see Scheme 2 B). In addition, a ^{13}C labeled derivate of **L3** was synthesized and attached to PdNPs. The ^{13}C NMR spectra obtained from **^{13}C-L3**@PdNP, measured in D_2O, showed a broad peak of high intensity in the typical region for a metal coordinated carbene (166.7 ppm). The signals corresponding to the other carbon atoms had lower intensities (~0.06%).[11] This data indicates that a carbene species is stabilizing the MNPs.



Scheme 2: **A**. ^1H NMR spectra, measured in D_2O, of imidazolium salt **L2** (top) and **L2**@PdNP (bottom) showing the successful coordination of the NHC to the NPs as indicated by a broadening of the proton signals. **B**. ^{13}C MAS-NMR spectra of **L2**@PdNPs showing a peak at ~170 ppm corresponding to the carbene carbon atom.

The composition of the purified MNPs was further investigated by thermogravimetric analysis (TGA) and elemental analysis giving a metal content in the range of 61 – 67% for the PdNPs and 82-93% for the AuNPs. Based on the average metal content, detected by TGA and elemental analysis, a metal:ligand (M:Lig) ratio could be calculated. The results are given in Tables 1 and 2 together with a summary of the main characteristics for the cNHC@Pd- and AuNPs. Due to the steric demand of the substituents, **L4**@PdNPs have a higher M:Lig ratio compared to the other cNHC@PdNPs. The cNHC@AuNPs show a higher M:Lig ratio because their larger size distribution decreases the relative amount of surface atoms.

Table 1. Main Analytics for the **cNHC**@PdNPs.

	Size / nm	**^{13}C NMR shift**	**Ø Metal content**[a]	**M:Lig ratio**	**Solubility at pH 4**
L1@PdNP	4.1 (± 0.6)	n. d.	63%	4.5 : 1	dissolved
L2@PdNP	4.1 (± 0.6)	170 ppm[b]	63%	4.0 : 1	dissolved
L3@PdNP	4.1 (± 0.6)	166.7 ppm[c]	65%	3.5 : 1	precipitated
L4@PdNP	4.0 (± 0.6)	n. d.	70%	7.0 : 1	precipitated

[a] Measured by TGA and elemental analysis. [b] ^{13}C MAS-NMR. [c] Measured in D_2O.

Table 2. Main analytics for the **cNHC**@AuNPs.

	Size / nm	**Ø Metal content**[a]	**M:Lig ratio**	**Solubility at pH 4**
L1@AuNP	4.1 (± 1.6)	92%	10 : 1	dissolved
L2@AuNP	4.7 (± 1.5)	90%	14 : 1	dissolved
L3@AuNP	4.9 (± 1.7)	88%	12 : 1	precipitated

[a] Measured by TGA and elemental analysis.

The size of the cNHC@MNPs was then investigated by TEM. The PdNPs showed a narrow size distribution with a mean size of 4.1 (±0.6) nm for **L1-L3**@PdNP and 4.0 (±0.6) nm for **L4**@PdNP (see Figure 1 for TEM images of **L1**@PdNP). Thus, no changes in size or size distribution during the ligand exchange were detected (**DDS**@PdNP (4.0 (±0.6) nm)). On the other hand, if **DDS**@AuNPs were applied in the ligand exchange procedure, a significant decrease in the mean size from 8.5 (±1.7) nm (**DDS**@AuNP) to 4.1 (±1.5) nm (**L1**@AuNP), 4.7 (±1.6) nm (**L2**@AuNP) and 4.9 (±1.7) nm (**L3**@AuNP) was observed. Due to the restructuring of the AuNPs, the size distributions increased from 20% to 34-36%, yielding polydisperse cNHC@AuNPs. The decrease in size of AuNPs during a ligand exchange with

NHCs[5c] seems to be attributed to dissociation of NHC-Au^{I} complexes from the NP surface, leading to a shrinking of the AuNPs. NMR spectroscopic analysis of the cNHC@AuNPs before and after dialysis provided further insight into this phenomenon. Before dialysis, the NMR spectra of cNHC@AuNPs showed sharp signals that could be attributed to a molecular NHC-Au^{I} species in solution. This was validated by ESI-MS analysis confirming the presence of NHC-Au^{I} complexes. After dialysis of the cNHC@AuNPs, no NHC-Au^{I} complexes were detected by NMR or ESI-MS. As mentioned above, the NMR spectra of the purified cNHC@AuNP only show the expected broad signals of NHC ligands coordinated to the NP surface.[10] Also, AuNPs showed no further size changes or aggregation after purification. The long-term stability of the cNHC@MNPs was investigated by DLS and UV/vis measurements and no change in the mean size or the maximum of the SPR band was observed after three months.[10] An aqueous solution of the cNHC@MNPs could even be exposed to liquid nitrogen without aggregation occurring (e.g. for lyophilisation).[10]

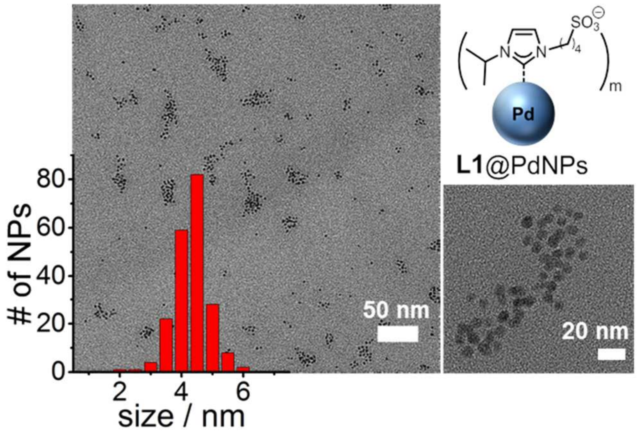
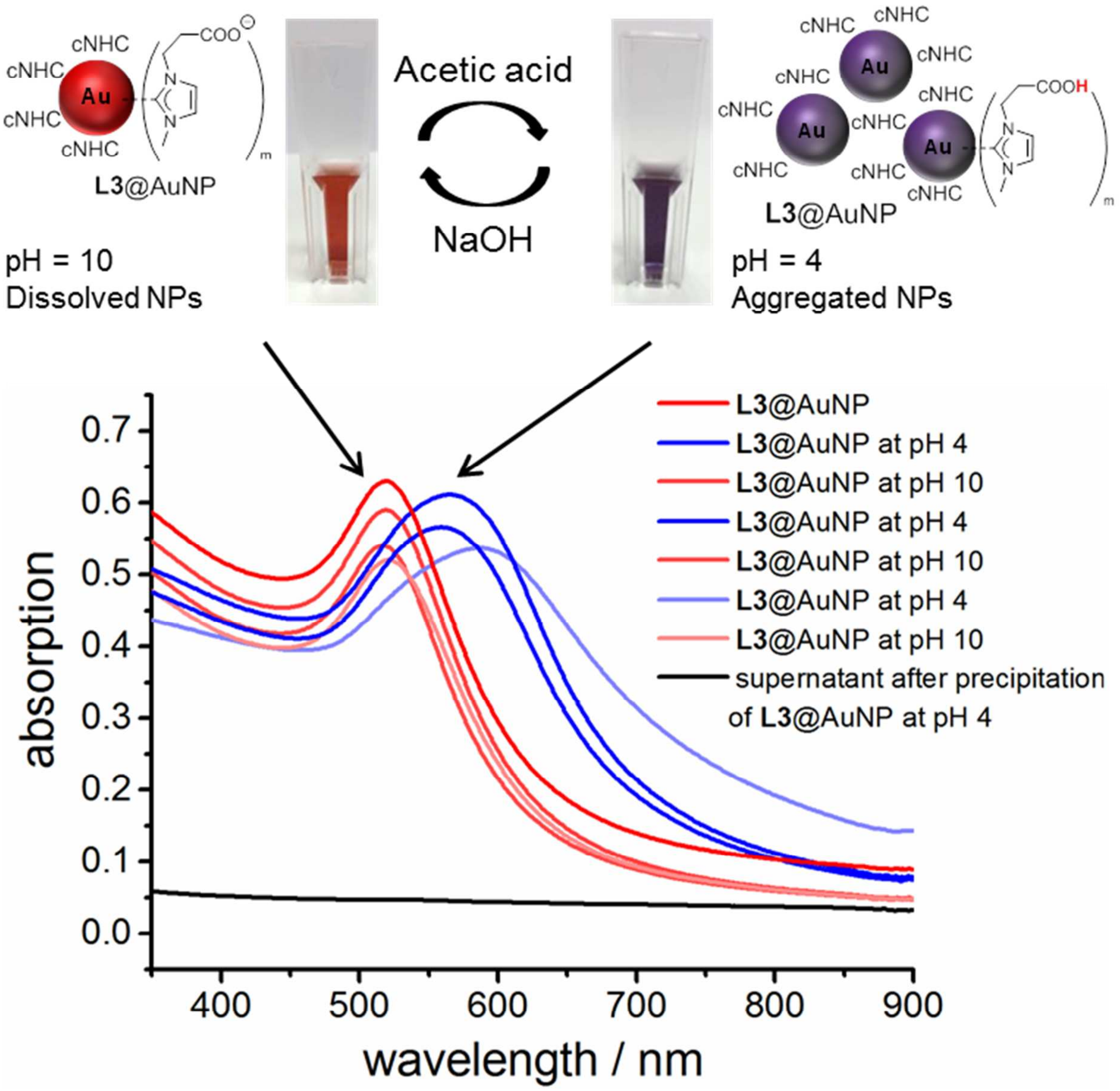


Figure 1: TEM images and size histogram of **L1**@PdNP showing a narrow size distribution of 4.1 (±0.6) nm.

Concerning the electrostatic stabilization of the NPs, zeta potential measurements were performed giving values between –30 to –50 mV. As NPs with a zeta potential under –30 mV or over +30 mV are considered to be stable in aqueous media, these results confirmed the stabilization of the MNPs by the cNHCs.[4b,10] The stability against acidic conditions was tested by exposing the samples of cNHC@MNPs to pH 4 and pH 1. Pd and AuNPs stabilized by the sulfonated ligands **L1** and **L2** were stable in aqueous solution at pH 4 whereas MNPs functionalized with the carboxylate ligands **L3** and **L4** aggregated under these conditions.[10] This observation is attributed to the partial protonation of the carboxylate function and the loss in electrostatic repulsion between the NPs, thus leading to a clustering. When **L3**@AuNP was used, this behavior could be monitored with UV/vis spectroscopy by observing changes in the characteristic SPR band of AuNPs. **L3**@AuNPs show an absorption maximum at 518 nm, which is shifted to 560 nm at pH 4 (when the solution was acidified by the addition of 1M acetic acid). This shift to higher wavelengths is characteristic for aggregated AuNPs. The aggregates of **L3**@AuNPs could be redispersed by adjusting the pH to 10 (by addition of 1M sodium hydroxide). This behavior is reversible for at least three cycles (see Scheme 3). If the NPs were exposed to pH 4 for ~30 minutes, the NPs completely precipitated out of the solution (Scheme 3, black curve). The decrease in signal intensity is attributed to the dilution of the sample upon the addition of acid and base.



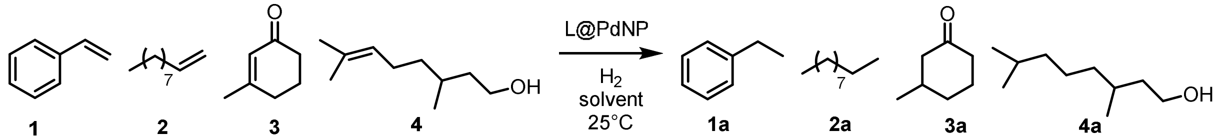
Scheme 3: UV/vis measurements of **L3**@AuNPs in aqueous solution showing the reversible aggregation and redispersion of the NPs depending on the pH.

L3@PdNPs showed the same reversible aggregation/redispersion behavior over 3 cycles as confirmed by DLS measurements. However, **L4**@PdNP showed the formation of larger aggregates after the second cycle. This can be explained by the sterically demanding substituents leading to a weaker metal-ligand bond and lowering the stabilization of the **L4**@PdNP in the aggregated state.[10]

When kept under basic conditions, the NPs could repeatedly be dried and redispersed in aqueous media without changes to their size (monitored by DLS measurements).

These water-stable NPs are particularly interesting as catalysts, especially the PdNPs, since they can catalyze the chemical transformations in aqueous media. The catalytic activity and selectivity of these new PdNPs was investigated in the hydrogenation of olefins with different degrees of substitution (namely styrene (**1**), 1-decene (**2**), 3-methyl-2-cyclohexenone (**3**) and citronellol (**4**)).[5b] Competition experiments with these substrates were conducted. We were mainly interested in evaluating the influence of the nature of the ligand on the catalytic activity. The first trials were conducted using 0.25 mg of **L1**@PdNP (~0.16 mg of "Pd"/ 0.2 mmol of substrate) in different water-miscible solvents under 10 bar of H_2 for 16 h. In various solvents (toluene/MeOH, CH_3CN, THF and DMF), styrene (**1**) and 3-methyl-2-cyclohexenone (**3**) were successfully hydrogenated whereas the hydrogenation of 1-decene (**2**) and citronellol (**4**) resulted in moderate or poor yields (Table 3, entries 1-4). The non-quantitative conversion of 1-decene (**2**) is explained by the competitive isomerization of the double bond to internal positions as we have previously observed with NHC-MNP mediated hydrogenations.[5b] In acetonitrile (Table 3, entry 2), an interesting chemoselectivity for the α,β-unsaturated carbonyl compound **3** compared to the trisubstituted alkene **4** was observed. This selectivity in acetonitrile was further exploited in the hydrogenation of citral (**6**) bearing both an α,β-unsaturated carbonyl and a trisubstituted alkene function, leading to citronellal (**6a**) as the sole product (Table 4, entry 1). Interestingly, the use of water as solvent led to reduction of all the four compounds (**1-4**) with very good yields (Table 3, entry 5) even at low pressure of H_2 (2 bar) (Table 3, entry 6), after a shorter reaction time (1 h) (Table 3, entry 10) and with a small amount of **L1**@PdNP (Table 3, entry 9), leading to TON values up to 2500.[10] The use of dimethyl sulfoxide poisoned the catalyst and resulted in a dramatic decrease in the catalytic activity with a total chemoselectivity for styrene (**1**) (Table 3, entry 11). Using ligand **L4**@PdNP gave similar results to **L1**@PdNP (Table 3, entry 7), whereas the use of **L3**@PdNP led to a slight decrease in the catalytic activity (Table 3, entry 8). In order to investigate the potential difference in activity induced by the different ligands, the reaction was performed with a very small amount of PdNP (0.063 mg (~ 0.041 mg of "Pd")/0.2 mmol of substrate) and short reaction time (1 h). Under these conditions, significant differences were observed. While **L4**@PdNP hydrogenated three of the four compounds (**1**, **2** and **3**) in a quantitative manner (Table 3, entry 13), **L1**@PdNP and **L3**@PdNP gave good yields for only two substrates (**1** and **2**) (Table 3, entries 12 and 15), and **L2**@PdNP only reduced styrene (**2**) (Table 3, entry 14). The latter finding was further exploited in the chemoselective reduction of sorbinaldehyde (**7**) which resulted in the completely selective reduction of the **•**,**•**-double bond (Table 4, entry 2). Among the four ligands tested, **L4**@PdNPs showed the best catalytic activity giving TOFs of ~2000 h^{-1}.[10] The catalytic activity of these water-soluble NPs was compared with a commercial Pd/C 5% catalyst (Evonik). At high catalyst loadings (0.16 mg of Pd/ 0.2 mmol of substrate), Pd/C gave slightly higher yields compared to **L4**@PdNP (Table 3, entry 16). However, at low catalyst loadings (0.041 mg of Pd/ 0.2 mmol of substrate), **L4**@PdNP remained active whereas the reactivity of Pd/C was greatly diminished, hydrogenating only styrene (**1**) with poor conversion (Table 3, entry 17). The possibility of recycling these PdNPs was also investigated with **L3**@PdNPs. After a first catalytic cycle of 16h (Table 3, entry 8), the NPs were analyzed by TEM measurements and showed nearly the same size distribution (4.0 (±0.7) nm) as they did prior to catalysis (4.1 (±0.6) nm). The NPs were separated from the reaction mixture by precipitation at pH 4. After washing, the NPs were redispersed in water by adjusting the pH to slightly basic conditions and then subjected to a second catalytic cycle. The recycled NPs remained active in the hydrogenation of all substrates (**1**-**3**) except substrate **4** (Table 3, entry 18). In order to eliminate the possibility that these hydrogenations were catalyzed by a homogeneous NHC-Pd complex (formed by leaching of the Pd-NPs) rather than by the cNHC-MNP itself,[12] a PEPPSI-type Pd complex bearing **L1** as ligand (Figure 2) was synthesized and tested in hydrogenation. Complex **5** as was found to be inactive in this reaction (Table 3, entry 19), showing that the active catalytic species is most likely heterogeneous in nature.[13]

Table 3. Competition experiments.



Entry	Solvent	P (bar)	Time (h)	Amount of NP (mg/0.2 mmol)	L	Yield (%)[a]			
						1a	2a	3a	4a
1	Toluene/MeOH (70 : 30)	10	16	0.25 (~ 0.16 mg “Pd”)	**L1**	100	97	90	46
2	CH_3CN	10	16	0.25	**L1**	100	63	91	6
3	THF	10	16	0.25	**L1**	97	16	79	4
4	DMF	10	16	0.25	**L1**	100	67	100	60
5	H_2O	10	16	0.25	**L1**	100	100	100	88
6	H_2O	2	16	0.25	**L1**	100	100	90	75
7	H_2O	2	16	0.25	**L4**	88	94	100	71
8	H_2O	2	16	0.25	**L3**	97	100	82	54
9	H_2O	2	16	0.05	**L1**	98	100	95	66
10	H_2O	2	1	0.25	**L1**	94	74	92	65
11	DMSO	2	16	0.25	**L1**	100	6	Trace	0
12	H_2O	2	1	0.063 (~ 0.041 mg “Pd”)	**L1**	100	89	45	12

13	H_2O	2	1	0.063	**L4**	98	96	92	18
14	H_2O	2	1	0.063	**L2**	58	Trace	0	0
15	H_2O	2	1	0.063	**L3**	99	88	37	0
16	H_2O	2	1	3.2 mg Pd/C (5%) (= 0.16 mg “Pd”)	-	100	100	100	98
17	H_2O	2	1	0.8 mg Pd/C (5%) (= 0.041 mg “Pd”)	-	16	0	0	0
18	H_2O	2	16	0.25 (recycled NPs)	**L3**	98	91	65	0
19	H_2O	2	1	0.89 mg **5** (= 0.16 mg “Pd”)	**L1**	trace	0	0	0

[a] GC yield.

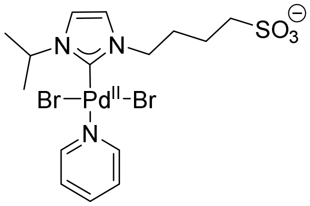


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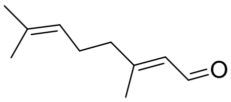
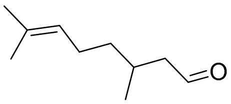
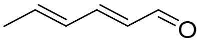
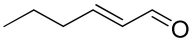
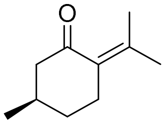
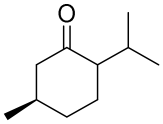
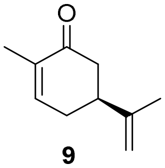
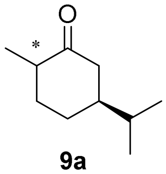
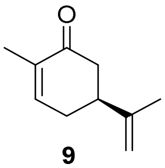
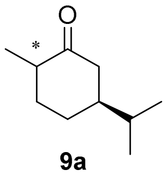
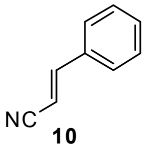
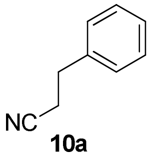
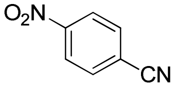
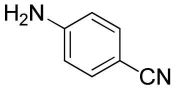
Figure 2: Structure of the NHC-Pd^{II}-complex **5.**

After establishing the high catalytic activity of these cNHC-PdNPs in water, more complex substrates were tested. The tetrasubstituted alkene pulegone (**8**) was completely reduced after 16 hours under 2 bar of H_2, albeit as a 1:1 mixture of two diastereoisomers (Table 4, entry 3). We were also interested in testing the influence of the *N*-alkyl substituents of **L4**@PdNP on the stereochemical outcome of the reaction. We found that **L4**@PdNP only slightly improved the diastereoselectivity in the hydrogenation of (+)-carvone (**9**) (55:45 d.r. with **L1**@PdNP (Table 4, entry 4) vs. 65:35 d.r. with **L4**@PdNP (Table 4, entry 5)). Next, the reducible functional group was varied. While cyano groups were inert under the reaction conditions (Table 4, entries 6 and 7), nitroarene **11** was fully converted into the corresponding amine (**11a**) (Table 4, entry 7).

Table 4. Investigation of the Reactivity of PdNPs.

Entry	**Substrate**	**L**	**Amount of NP (mg/0.2 mmol)**	**Conditions**	**Product**	**Conv (%) Selectivity^a**
1	 **6**	**L4**	0.25	H_2 (5 bar) CH_3CN, 24 h, 50°C	 **6a**	100 >99:1
2	 **7**	**L2**	0.063	H_2 (2 bar) H_2O, 1 h, 25°C	 **7a**	100 >99:1
3	 **8**	**L1**	0.25	H_2 (2 bar) H_2O, 16 h, 25°C	 **8a**	100 d.r. 50:50
4	 **9**	**L1**	0.25	H_2 (2 bar) H_2O, 1 h, 25°C	 **9a**	63 d.r. 55:45
5	 **9**	**L4**	0.25	H_2 (2 bar) H_2O, 1 h, 25°C	 **9a**	60 d.r. 65:35

6	 **10**	**L1**	0.25	H_2 (2 bar) H_2O/DMF (1:1), 16 h, 25°C	 **10a**	100 >99:1
7	 **11**	**L1**	0.25	H_2 (2 bar) H_2O, 2 h, 25°C	 **11a**	100 >95:5

[a] Conversions and selectivities determined by GC-FID.

CONCLUSION

In summary, novel negatively-charged NHC-stabilized Pd- and AuNPs were synthesized by the ligand exchange method. Four structurally distinct NHCs bearing either sulfonate or carboxylate moieties were applied. The resulting cNHC-MNPs showed long-term stability in water. Upon variation of the pH, **L3**@PdNPs showed a reversibility between the aggregated and soluble form in water, demonstrating the underlying concept of electrostatic stabilization. Finally, cNHC-PdNPs were tested in catalytic hydrogenation reactions and were found to be highly active and chemoselective in hydrogenation reactions in aqueous media. Our Pd-nanosystems outperformed commercial Pd/C at low catalyst loadings. A recycling study showed that recycled cNHC-PdNPs are catalytically active. The lack of catalytic activity of a homogeneous Pd-complex bearing **L1** as ligand indicated that the catalytic species is most likely heterogeneous in nature.

ASSOCIATED CONTENT

Supporting Information.

Experimental procedures, characterization data, TEM images and ^{1}H and ^{13}C NMR spectra are available free of charge via the Internet at http://pubs.acs.org.

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