



Modified Nanoparticles

Modular Bidentate Hybrid NHC-Thioether Ligands for the Stabilization of Palladium Nanoparticles in Various Solvents

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Dedicated to Professor Hans-Joachim Galla

Abstract: The synthesis of four different bidentate hybrid NHC-thioether ligands is presented. The corresponding palladium nanoparticles are stable in various solvents, depending on the ligand used, and show high chemoselectivity in the hydrogenation of olefins. The solubility of the nanoparticles can be switched multiple times depending on the pH value of the solvent. XPS analysis (which shows a subtle shift in the binding energy) was identified as a convenient tool to establish the binding mode of NHC ligands.

During the last decade, the importance of nanoparticles (NPs) has grown significantly, especially in the fields of organometallic drugs, materials, and catalysis.^[1] However, a common challenge in these research fields is stabilization of the NPs, since agglomeration would render them "inactive" for their designed purpose. NPs are normally stabilized with ligands such as thiols, phosphines, amines, and thioethers.^[2] However, N-heterocyclic carbenes (NHCs),^[3] which are superb ligands in organometallic chemistry, are an emerging class of ligands for NP stabilization.^[4-6] Based on the few existing reports on NHC-stabilized NPs, it can be argued that the long-term stability of these systems is not on a par with those stabilized by thiols. In 2014, we reported a tailor-made NHC, bearing two long alkyl chains in the backbone, which stabilized palladium NPs (PdNPs) for four months, presumably through steric repulsion of the alkyl chains.^[7] The drawback of this system is the difficulty of adapting this design to different polarities (e.g., polyethylene glycol as a polar and water-soluble group), which is needed for solubility and stability in polar media.^[8] Consequently, a broader field of applications could be addressed with a more flexible and modular design in which an alternative stabilizing motif is implemented. We envisioned that the combination of an NHC ligand with a thioether as a hybrid

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bidentate ligand would allow us to exploit the properties of both ligand classes in a synergistic fashion, thereby resulting in enhanced stability of the NPs.^[9] Such a combinatorial approach simplifies the synthesis of the ligand, and in combination with the great variety of thioether motifs, one can quickly adapt the polarity and therefore solubility of the NPs on demand. In terms of stability, the NHC as a stronger donating ligand would bind to the NP through a covalent bond, whereas the thioether would bind through a weaker dative interaction (Scheme 1).



Scheme 1. Hybrid ligand concept: retrosynthetic disconnections and elements of the modular design. PEG3 = triethyleneglycol.

To test our concept of stabilizing NPs with a hybrid NHCthioether bidentate ligand, we synthesized four ligand precursors with different chains attached to the sulfur atom. Since these chains should influence the solubility of the resulting NPs the most, we decided to vary this chain from nonpolar (1a) to polar (1c). The "PEGylated" (1b) and longer-chain carboxylic acid (1d) should have intermediate polarity. The connection between the NHC core and the sulfur atom was set to be a propyl chain. As shown in our related work, small substituents on the nitrogen are beneficial for the stability of the NPs and hence we chose a methyl group in this position.^[7] It should be noted that in principle any other group can be placed there. All ligands could be synthesized in moderate to high yields within a convenient two-step synthesis. The corresponding PdNPs were synthesized through ligand exchange, using a solution of the in situ generated free NHCs and thioether stabilized PdNPs (Scheme 2).^[4f,7] For 1a, we used tetraethyleneglycol thioether stabilized PdNP with a size of 4.5 (± 0.4) nm. In the case of **1b-d** we used **Communications**



Scheme 2. Synthesis of PdNPs by ligand exchange.

a didodecylthioether stabilized PdNP with a size of 4.0(\pm 0.5) nm.

Depending on the polarity of the ligands, the PdNPs could be solubilized in nonpolar solvents like hexane or toluene (2a), polar solvents like acetonitrile or dichloromethane (2b), or water (2c+2d). The PdNPs were analyzed by NMR spectroscopy, which confirmed full exchange of the precursor ligands from the NP surface and stabilization of the PdNPs by the bidentate thioether NHC ligands (see the Supporting Information). The NMR spectra show the expected broad signals, indicating the coordination of the ligands to the NP surface.^[10] Only the alkyl-chain protons located further away from the metal surface show higher intensities (Figure 1A). The absence of the propyl protons suggest a bidentate binding mode, since these signals also suffer from the peak broadening attributed to proximity to the NP core. In order to understand whether the thioether moiety binds only weakly to the surface, which could be attributed to an equilibrium between a mono- and bidentate binding mode, we measured ¹H NMR spectra at different temperatures. Within the temperature range from -40°C to 80°C, no change in the spectra was observed (see Figure 1B), which indicates a strong bidentate binding mode. DLS studies after the variable-temperature (VT)-NMR experiment showed no change in the particle size and the catalytic activity remained the same for the hydrogenation of styrene.

X-ray photoelectron spectroscopy (XPS) was conducted in order to verify whether the NHC is indeed the coordinative species. The N(1s) signals of **2a-d** show binding energies of 400.7-401.2 eV, which is in agreement with reported values.^[4c,6] Compared to the binding energy of the imidazolium salts 1a-d (401.6-401.8 eV), which were used as precursors, a shift to lower binding energies is visible, excluding the presence of the imidazolium salt (see Figure 2A). In order to confirm that the observed shift in binding energy can be attributed to coordination of the NHC to the nanoparticle, three different dicyclohexylimidazole-2-ylidene (ICy) species were analyzed by XPS: the imidazolium salt (ICy·HCl), the free carbene (ICy) and the Pd ICy metal complex (ICy-Pd-Cl; Figure 2B). **ICy**·HCl shows the highest binding energy because the electrons are tightly bound in this cationic molecule (401.5 eV). ICy exhibits two peaks (401.5 and 399.5 eV). The peak at 401.5 eV can be assigned to species that were protonated during sample preparation. The second peak at 399.5 eV derives from the free ICy. The binding energy of the electrons is reduced in this neutral compound. The binding of the free carbene to the metal in complex ICy-Pd-Cl attributed to a loss in electron density, which leads to an increase in binding energy (400.5 eV) compared to the free A - ¹H NMR spectra of 2a = A, 2b = B, 2c = C, 2d = D



Figure 1. A) ¹H NMR spectra of **2a–d. 2a** and **2b** were measured in CDCl₃, **2c** and **2d** were measured in D₂O. All spectra were measured at 300 MHz at 300 K. Note: Since **2c** does not have a long alkyl chain, all protons are located near the NP surface and all signals suffer from broadening. Compared to the other spectra, the signal-to-noise ratio is very low. In the expanded spectrum, broad resonances for the backbone protons and the *N*-CH₂ protons are observed, which are not visible for **2a,b,d**. B) VT experiment with **2a** in [D₈]toluene at 600 MHz. The signal around δ = 2.1 ppm is toluene.

ICy. However, this binding energy is still significantly lower than the binding energy of the imidazolium salt **ICy**·HCl (Δ = 1 eV). Additionally, we performed the same analysis with **ICy**-Au¹-Cl and **ICy**·CO₂ on a silicon wafer in order to observe whether the results fit with our findings (see the Supporting Information), which is indeed the case, with binding energies of 400.8 eV and 401.8 eV, respectively. Based on our data, we suggest that XPS is a convenient method to establish the binding mode of NHCs on metal surfaces. Additionally, the use of non-¹³C-labeled NHC precursors is a major simplification for the analysis of NHCs on nanoparticles or surfaces in comparison to previous methods (mostly liquid-phase and solid-state NMR).

XPS investigation of the S(2p) orbitals of 2a-d showed no specific shifts in the binding energy compared to the imidazolium salts (see the Supporting Information). Therefore, the binding mode of the thioether could not be examined **Communications**



Figure 2. A) X-ray photoelectron spectroscopy (XPS) of the N(1s) signal of the imidazolium salts (**1a–d**) and **2a–d**. B) Comparison of free **ICy**, its HCl salt, and the related Pd allyl complex.

by XPS analysis, which is in accordance with the literature.^[11] Integration of the nitrogen and sulfur signals allowed us to calculate the N/S ratios of 1a-d (1.4–1.7) and 2a-d (1.1–0.9), which should be 2.0 (see the Supporting Information).

The PdNPs were further characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and elemental analysis, which gave a mean size distribution between 3.6 and 5.1 nm and a metal content of 64–79%. The exact values are given in Table 1. Based on the average metal content, the metal-to-ligand ratios could be

Table 1: Analytical data for the NHC-thioether functionalized PdNPs.

Sample	Mean size ^[a]	Mean metal content ^[b]	Metal/ligand ratio
2 a	5.1(±0.7) nm	79%	12.0±2.0:1
2 b	4.4(±0.6) nm	66%	$6.5 \pm 0.7:1$
2c	3.6(±0.5) nm	64%	5.0±1.4:1
2 d	4.5(±0.6) nm	64%	$6.5 \pm 2.3 \!:\! 1$

[a] Measured by TEM. [b] Based on TGA and elemental analysis.

calculated. Since larger NPs have a lower amount of surface atoms, the ratio increases with increasing size of the PdNPs (see Table 1). Exemplary TEM images and size histograms of the PdNPs are shown in Figure 3.

Additional evidence for the bidentate binding of 1a-d on the PdNPs was obtained in control experiments with the ligand 3-methyl-1-octadecylimidazolium bromide (1e), a structural analogue of 1a without the sulfur atom (the



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Figure 3. TEM images and size histograms of the NHC-thioether functionalized PdNPs. A) **2a**. B) **2b**. C) **2c**. D) **2d**.

overall carbon chain is two carbon atoms longer), which successfully, after deprotonation and ligand exchange, stabilized PdNPs (2e; see the Supporting Information). Firstly, we measured the Pd/NHC ratio of 1a and the control ligand by TGA (see the Supporting Information). Since the ratio is the same for both PdNPs (Pd/1a = 2.78:1 and Pd/1e = 2.85:1, a new batch of PdNPs was used for this experiment, which is the cause of the change in metal-to-ligand ratio in comparison to the previous batch), one can conclude that in both cases the surface is densely packed with NHC and the thioether moiety does not prevent the binding of additional NHCs on the surface. Secondly, we performed a competition experiment with 2a and 2e, in which both PdNPs were treated with 2-(2-(2-methoxyethoxy)ethoxy)ethane-1-thiol (TEG-Thiol) to replace 1a/e. If the thioether moiety of 1a actually binds to the surface and enhances the immobilization of the bound ligand, one would expect a slower replacement in comparison to the non-chelating 1e. The PdNPs were treated with TEG-Thiol for 5 minutes in acetonitrile and purified in the same manner as for the standard ligand exchange.^[7] Integration and comparison of the corresponding proton NMR spectra revealed that in both cases, the NHC is partially replaced. The ratios of TEG-thiol to NHC were determined to be 2.2:1 for **1a** and 6.1:1 for **1e** (see the Supporting Information), which indicates an attractive interaction between the thioether and the surface, thus a bidentate binding mode is likely. Overall, we contend that VT experiments, XPS, TGA, and the competition replacement experiment with thiols are all in favor of a bidentate binding mode, but for lack of a suitable analysis method, we cannot prove bidentate binding.

With two ligands with a pH-responsive carboxyl group in hand, we investigated whether we could tune the solubility of the NPs by changing the pH value of the solution (Figure 4). Two samples of 2c and 2d in dist. water (0.5 mgmL⁻¹) were acidified to pH 1 by the addition of aqueous HCl solution (1M). As a result of protonation of the carboxylate function



Figure 4. Dynamic light scattering (DLS) of the carboxylated 2c and 2d at pH 1 and pH 11 in H₂O as a solvent.

and the loss of charge, the PdNPs completely precipitated within 30 minutes. The NPs could be redispersed under basic conditions (pH 11) by using aqueous KOH solution (1M). The stability at extreme pH and the large number of cycles underlines the strong interaction of the thioether-NHC ligand with the NP surface, and therefore the benefit of the bidentate binding mode.^[11] This is in contrast with our previous work on charged NHCs as ligands for nanoparticles, in which irreversible aggregation was observed at pH 1.^[4f] The robustness of our particles can therefore be compared to a gold NHC nanoparticle system reported by Johnson et al., which was stable at pH 2 for several weeks.^[8] With the fully characterized ligand-modified PdNPs in hand, we evaluated their catalytic activity in different solvents, since we envisioned a solvent dependency owing to the influence of the thioether moiety. Knowing of the high activity of PdNPs in hydrogenation reactions, we chose this as a model reaction. Interestingly, our PdNPs (2a-d) showed very high chemoselectivity for terminal double bonds over di- and trisubstituted ones in all of the solvents tested, which was not the case for standard palladium-on-carbon catalysts (for further substrates tested and optimization of the reaction conditions, see the Supporting Information).

The results for the hydrogenation of styrene and isophorone are shown in Table 2. The non-polar PdNP **2a** shows good to excellent conversions for **3** in all of the solvents, with a slight decrease in the case of THF. PdNP **2b** demonstrates an overall excellent performance, but the more polar **2c-d** gave lower conversions of **3** when a non-polar solvent was used. Polar solvents such as methanol produce good to excellent conversions again. These results correlate with the polarity of **2a-d**. The higher the polarity, the better the **Table 2:** Chemoselective hydrogenation of terminal olefins in the presence of di- and trisubstitued olefins.^[a]

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(3 + _	0.1 1 bar 16 h	mg 2a-d H ₂ , 40 °C	5	+	
Catalyst	Substrate	Toluene	CH_2CI_2	THF	MeOH	MeCN
2 a	3	99	99	98	87	99
	4	0	0	0	0	0
2 b	3	99	99	99	99	99
	4	0	0	0	0	0
2c	3	49	43	62	99	99
	4	0	0	0	0	0
2 d	3	61	54	45	99	90
	4	0	0	0	0	0
Pd/C	3	99	99	99	99	99
	4	99	99	99	99	99

[a] All reactions were set up under an argon atmosphere and dry solvents were used. Results show the conversion of **3** and **4** and are given in %. Conversion was determined with GC-FID with mesitylene as an internal standard.

reactivity in polar media and vice versa (see the Supporting Information). This underlines our concept of tuning the reactivity according to the solvent of choice. In contrast to these results stands the conversion of 4, which was essentially 0% in every single tested condition. Looking at the results of palladium on carbon as a catalyst, a quantitative conversion for both substrates was achieved and no chemoselectivity was observed in any tested solvent.

Furthermore, we tested whether the PdNPs could be reused and performed a multiple addition experiment with 2ain toluene. After five consequent additions of **3**, no loss in reactivity was observed (see the Supporting Information). This result underlines the principle of catalyst recycling. To test the heterogeneous nature of the reaction, a mercury droplet test was conducted. The conversion remained at 40% after the addition of mercury, whereas the conversion was quantitative without. This result is an indication of heterogeneous catalysis, but it is not conclusive since mercury could deactivate nanoclusters or homogenous catalysts as well.^[12]

In conclusion, we have developed a bidentate hybrid NHC-thioether ligand for the stabilization of PdNPs in various solvents. The PdNPs were characterized in detail and the NHC binding to metal through a covalent bond was confirmed with XPS. In addition, a chelating/bidentate binding mode was analytically supported for the first time. Hydrogenation experiments showed very high chemoselectivity for terminal over other olefins. Additionally, solubility could be switched by changing the pH value of the solvent. Future work is directed towards different metals for the nanoparticles and the incorporation of chiral motifs into the hybrid ligands.

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