Pd-Nanoparticles Stabilized by Pyridine-Functionalized Poly(ethylene glycol) as Catalyst for the Aerobic Oxidation of α,β -Unsaturated Alcohols in Water

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INTRODUCTION The selective oxidation of alcohols to carbonyl compounds or acids is a reaction of long standing academic and industrial research interest.^{1,2} Because of the increasing demand for environmentally compatible oxidation protocols, which avoid the generation of a large amount of heavy-metal waste and usage of organic solvents as reaction medium, a great deal of research activity is been focusing on alternative "greener" synthetic protocols using supercritical carbon dioxide³⁻⁷ or water⁸ as reaction medium and oxygen as the final hvdrogen acceptor.⁸ Efficient homogeneous catalysts applied in water-phase aerobic alcohol oxidation reactions are Ru9- and Pd-based¹⁰⁻¹³ with acetate,⁹ water soluble phenanthrolines^{11,12} or biquinolines¹³ as stabilizing ligands. Conversely, well established heterogeneous catalysts employed for the same catalytic process are based on metal nanoparticles (NPs) which are either incarcerated in organic cross linked polymers,^{14,15} anchored onto carbon,¹⁶ alumina¹⁷ and hydroxyapatite¹⁸ or stabilized by end-functionalized poly(ethylene glycol) (PEG).¹⁹⁻²² The latter polymer, which is cheap, biocompatible and watersoluble, decreases the polarity of water by reducing hydrogen bond interactions among water molecules.²³ As a consequence, PEG is a co-solvent increasing the solubility of organic compounds in water which is mandatory for an efficient catalytic substrate conversion. Furthermore, the easy end-functionalization of PEG with metal coordinating units brings about the formation of water-soluble macroligands which stabilize well-defined molecular metal complexes or metal NPs.^{24,25} Moreover, oxygen atoms of the poly(ether)

structure of PEG are suitable to stabilize metal cations of different atom size and metal $\mbox{NPs.}^{26,27}$

Herein, we present the synthesis and coordination chemistry of 4-pyridinemethylene end-capped MeO-PEG (\mathbf{L}^{Py}) to Pd(II). The obtained Pd(II) macrocomplexes gave, upon reduction with dihydrogen pressure \mathbf{L}^{Py} -stabilized Pd-NPs. The Pd(II)- and Pd(0)-based catalysts were applied to convert α,β -unsaturated alcohols into the corresponding carbonyl compounds in water under aerobic oxidative reaction conditions.

RESULTS AND DISCUSSION

The macroligands of the formula MeO-(CH₂CH₂O)₁₁₆CH₂CH₂OR with R = 4-pyridinemethylene (L^{Py}) and benzyl (L^{Bn}) were straightforwardly obtained by a reported mesylation reaction of MeO-(CH₂CH₂O)₁₁₆CH₂CH₂OH (L^{OH}),²⁸ followed by the reaction of the isolated mesylate with NaH in dry DMF in the presence of the corresponding alcohol (i.e., 4-hydroxymethyl pyridine and benzylalcohol) [Scheme 1(a)]. L^{Py} and L^{Bn} were obtained as white solids in 86 and 71% yield, respectively.

The successful end-functionalization of \mathbf{L}^{OH} was proved by ¹H NMR spectroscopy. As a result, the ¹H NMR spectra of \mathbf{L}^{Py} and \mathbf{L}^{Bn} , acquired in CD₂Cl₂, showed for the benzylic hydrogen atoms a singlet at 4.59 and 4.55 ppm, respectively, which is slightly shifted to lower frequency compared to the analogous ¹H NMR signal of PyCH₂OH (4.73 ppm) and PhCH₂OH (4.66 ppm, J = 6.7 Hz). Moreover, ¹H NMR spectra of \mathbf{L}^{Py} and \mathbf{L}^{Bn} , acquired in DMSO-d₆, confirmed the absence

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a) Synthesis of macroligands



b) Synthesis of Pd(II) macrocomplexes bearing L^{Py}

$$Pd(OAc)_{2} + 2L^{Py} \xrightarrow{CH_{2}Cl_{2}} trans-[Pd(OAc)_{2}(L^{Py})_{2}] (1a) \xrightarrow{2L^{Py}/p-TsOH} [Pd(L^{Py})_{4}](OTs)_{2} (2a)$$

c) Synthesis of Pd-NPs

 $Pd(0)@[2HL^{Py}(OAc)] (1b) \leftarrow \frac{H_2 (15 \text{ bar})}{CH_2Cl_2} 1a \xrightarrow{2) H_2 (15 \text{ bar})} Pd(0)@[2L^{Py}+2(HL^{Py})(OAc)] (2b')$ $2a \xrightarrow{H_2 (15 \text{ bar})} Pd(0)@[2L^{Py}+2(HL^{Py})(OTs)] (2b)$ $Pl(OAc) \rightarrow 44 Bn \xrightarrow{H_2 (15 \text{ bar})} Pl(O)@[2L^{Py}+2(HL^{Py})(OTs)] (2b)$

$$Pd(OAc)_{2} + 4L^{Bn} \xrightarrow{H_{2} (15 \text{ bar})}{CH_{2}Cl_{2}} Pd(0)@4L^{Bn} (3b)$$

SCHEME 1 Syntheses of PEG-based macroligands, Pd(II)-macrocomplexes and Pd-NPs.

of a triplet centered at 4.56 ppm (J = 5.2 Hz), which was assigned to the terminal hydroxyl group of $\mathbf{L}^{OH,29}$ The number-averaged molar mass (M_n) of \mathbf{L}^{Py} and \mathbf{L}^{Bn} was determined by ¹H NMR spectroscopy ($M_n = 5200$ g/mol) [i.e., by integration of the singlets assigned to (CH_2CH_2O)_n (3.60 ppm) and to the terminal CH_3O unit (3.36 ppm)]. In addition, (GPC)-analyses carried out on the isolated macroligands in THF showed a M_n of 7750 g/mol and a polydispersity index (PDI) of 1.05. The molar mass values determined by ¹H NMR integration and GPC-analysis are significantly different. This experimental fact is related to the use of polystyrene to calibrate GPC columns.³⁰

The isolated macroligand L^{Py} was used to coordinate Pd(OAc)₂ (OAc = acetate) in CH₂Cl₂, yielding the neutral Pd(II) macrocomplex of the formula *trans*-[Pd(OAc)₂(L^{Py})₂] (**1a**) [Scheme 1(b)]. The addition of two molequivalents of L^{Py} to a CH₂Cl₂ solution of **1a** in the presence of *p*-toluene-sulfonic acid (*p*-TsOH) gave the bis-cationic Pd(II) macrocomplex of the formula [Pd(L^{Py})₄](OTs)₂ (**2a**). Both latter macrocomplexes were isolated in ca. 80% yield, as yellowish (**1a**) and beige (**2a**) powders. The occurred coordination of L^{Py} to Pd(II) in **1a** and **2a** has been proved by ¹H NMR and UV-vis spectroscopy. As a result, the ¹H NMR spectrum of **1a** showed a doublet at 7.38 ppm (i.e., *m*-H atoms of the pyridine unit) which is shifted to higher frequency compared to

that of $\mathbf{L}^{\mathbf{Py}}$ (7.29 ppm), while the *o*-pyridine hydrogen atoms of **2a** showed a chemical shift at 9.64 ppm, which is diagnostic for their interaction with the oxygen atoms of *p*-toluenesulfonate, as proved for related Pd(II) compounds.^{31,32} UVvis spectra, acquired in water, showed for **1a** an adsorption shoulder centered at 225 nm due to the Pd-pyridine interaction, which is lacking in the spectrum of $\mathbf{L}^{\mathbf{Py}}$ [Fig. 1(a)], while in **2a** the UV-vis contribution originating from MLCT is masked by the absorption peak of the tosylate anion at 228 nm, as confirmed by the comparison of the UV-vis spectra of **2a** and (HL^{Py})(OTs) [Fig. 1(b)].

The macrocomplexes **1a** and **2a** were reduced with dihydrogen (15 bar) in solution (i.e., CH_2Cl_2) at room temperature, yielding Pd-NPs stabilized by $(HL^{Py})(OAc)$ (**1b**) or by L^{Py} and $(HL^{Py})(OTs)$ present in a 1:1 molar ratio in **2b**. Both latter pyridinium salts are obtained upon the protonation reaction of the corresponding free acid (i.e., HOAc and *p*-TsOH, generated by the reduction of Pd(OAc)₂ and Pd(OTs)₂) with L^{Py} . In contrast, Pd-NPs in **2b**' and **3b** were obtained by in situ reductions of **1a** in the presence of $2L^{Py}$ and of Pd(OAc)₂ in the presence of L^{Bn} , respectively [Scheme 1(c)].

UV-vis spectra of 1b and 2b, acquired in water, showed a significantly lower UV-absorption in the region from 200 to 245 nm, due to the absence of the MLCT contribution,





FIGURE 1 UV-vis spectra acquired in H₂O: (a) L^{Py}, 1a and 1b; (b) L^{Py}, (HL^{Py})(OTs), 2a and 2b.

instead a featureless broad plasmon resonance, typically found for spherical Pd-NPs, was shown.³³ In this context, it is interesting to note that **1b** showed a significantly more intense plasmon resonance in the range of 280 to 360 nm compared to **2b**, which is due to the higher Pd(0) content in **1b** (1.1 wt %) than in **2b** (0.51 wt %).

The Pd-NPs size and their degree of aggregation has been revealed by (TEM)-analysis. Representative (TEM)-images of **1b** and **2b**, shown in Figure 2, clearly proved for **2b** the occurrence of spherical and well-separated Pd-NPs with an average size of 6.33 ± 1.40 nm [Fig. 2(b)], whereas **1b** showed non-defined worm-like NP aggregates [Fig. 2(a)].

The degree of Pd-NP aggregation found in 2b' [Fig. 2(c)] was comparable to that of 1b [Fig. 2(a)], while the highest degree of particle aggregation was encountered in 3b [Fig. 2(d)]

which contains the benzyl-functionalized macroligand L^{Bn} . Since **2b** and **3b** were the two extreme cases concerning the tendency of Pd-NP aggregation, we tested the Pd-NP-stabilizing ability of the corresponding macroligands. To this purpose, we carried out centrifugation experiments with water solutions of 2b and 3b under identical experimental conditions. As a result, only from the water solution of 3b separated a black solid, which was identified by means of X-ray powder diffraction (XRPD) analysis as polymer free Pd-NPs with a mean diameter of 6.0 nm (i.e., determined by the Debye-Scherrer method³⁴ using the Pd(111) Bragg reflex of the XRPD pattern of Fig. 3, trace b). (TEM)-analyses combined with the result of the centrifugation experiments corroborate the importance of $\mathbf{L}^{\mathbf{Py}}$ to control the aggregation process of NPs and hence their homogeneous distribution within the polymer matrix.



FIGURE 2 (TEM)-images of: (a) 1b, (b) 2b, (c) 2b' and (d) 3b.



FIGURE 3 XRPD spectra of: (a) 3b and (b) Pd-NPs isolated from 3b after the centrifugation experiment.

To compare the oxidative thermal degradation behavior of L^{Py} and L^{Bn} with that of **1b**, **2b** and **3b** in the solid state, thermogravimetric analyses (TGA) were carried out in a temperature range from 30 to 700 °C and in the presence of an air flux.³⁵ The results of these analyses are shown in Figure 4, which presents the weight loss of all compounds in an interval from 5% (onset) to 50%.³⁶

From an analysis of the TGA data emerged that: (a) the thermal behavior of $\mathbf{L}^{\mathbf{Py}}$ and $\mathbf{L}^{\mathbf{Bn}}$ is comparable to that of commercial $\mathbf{L}^{\mathbf{OH}}$, which is in accordance with a random scission of the poly(ether) chain and not with an unzipping process of the polymer chain which starts from the polymer chain ends;³⁷ (b) the presence of Pd-NPs in the polymer matrix exerts a stabilizing effect on the macroligands against oxidative thermal degradation (Fig. 4), which is superior to that observed for Fe-NPs present in poly(ether)-based polymers;³⁸ (c) the degree of Pd-NP aggregation, which determines the contact surface area between the polymer phase and the NPs, is crucial for the thermal stability of the PEGbased macroligands. As a consequence, the stability of the



FIGURE 4 TGA of L^{OH}, L^{Py}, L^{Bn}, 1b, 2b and 3b carried out in air atmosphere.

polymer ether chains against oxidative thermal degradation increases in the order 3b < 1b < 2b as does the distribution of the Pd-NPs within the polymer matrix (Fig. 4).

The stability of $\mathbf{L}^{\mathbf{Py}}$ in solution against oxidative degradation has been tested by applying real oxidative catalytic conditions (i.e. water solution of $\mathbf{L}^{\mathbf{Py}}$ was heated at 60 °C in the presence of K_2CO_3 and 30 bar of air for 14 h) and by analyzing afterwards the isolated polymers by GPC.³⁶ As a result, $\mathbf{L}^{\mathbf{Py}}$ proved not to degrade significantly under the chosen experimental conditions (i.e., $\mathbf{L}^{\mathbf{Py}}$: $M_n = 7750$ g/mol, PDI: 1.05; after treatment under oxidative experimental conditions: $M_n = 8300$ g/ mol, PDI: 1.08), since the variation of M_n and of the PDI are within the error range of a typical (GPC)-analysis.

The Pd(II) macrocomplexes **1a** and **2a** and the macroligandstabilized Pd-NPs **1b**, **2b** and **3b** were applied to catalyze the aerobic oxidation (i.e., 30 bar of air) of selected α , β -unsaturated alcohols [i.e., cinnamyl alcohol (A), *trans*-2-



SCHEME 2 Syntheses of PEG-based macroligands, Pd(II)-macrocomplexes and Pd-NPs.

Materials Views

TABLE 1 Aerobic Oxidation of α , β -Unsaturtaed Alcohols in Water Catalyzed by **1a**, **1b**, **2a**, **2b**, **2b'**, **3b** and **4**^a

Entries	Catalyst	Substrate	Conv (%)/TOF ^b			Sel (%) ^c		
			2 h	4 h	14 h	2 h	4 h	14 h
Pd(II) ^d								
1	1a	А	57/29	78/20		98	99	
2 ^e	1a	А	83/41			99		
3	2a	А	52/26	78/20		96	95	
4 ^e	2a	А	87/43			99		
5	4	А	71/36	85/21		85	85	
Pd(0) ^f								
6	1b	А		30/200	76/145		93	91
7	2b	А		29/193	99/189		90	89
8 ^g	2b	А		30/200	98/187		77	75
9 ^e	2b	А		27/180	88/177		98	98
10 ^h	2b	А	98/127			95		
11 ^{h,i}	2b	А	97126			94		
12	2b	В		27/180	88/168		100	100
13	2b	С		4/27	14/27		100	100
14	2b	D		29/193	90/171		99	98
15	2b′	А		40/267	79/150		91	93
16	3b	А		30/200	70/133		94	88
17 ^e	3b	А		21/140	61/116		99	99

^a Catalytic conditions: T (60 °C), water (5.0 mL), p(air) (30 bar).

 $^{\rm b}$ TOF expressed in mmol product \times (mmol precatalyst \times h) $^{-1}$

 $^{\rm c}$ Chemoselectivity referred to the $\alpha,\beta\text{-unsaturated carbonyl compound.}$

^d Pd amount (0.01 mmol), substrate (1.00 mmol).

 $^{\rm e}$ Addition of $K_2 CO_3$ (0.25 mmol).

methylcinnamyl alcohol (B), geraniol (C) and 2-cyclohexen-1ol (D)] in water, giving the corresponding α , β -unsaturated carbonyl compound as major product (Scheme 2). Aromatic and aliphatic alcohols showed under identical catalytic conditions a low conversion to the corresponding carbonyl compound of around 10–20% after a reaction time of 14 h.

The performance of the catalysts was screened by using cinnamyl alcohol as substrate. The amount of catalyst used for the oxidative reactions was based on its Pd content which was determined by ICP-OES.

As far as the catalytic activity is concerned, the Pd-NPs-based catalysts showed an almost ten times higher activity compared to the Pd(II)-based macrocomplexes. As a consequence, a substrate to Pd molar ratio of 2600 was applied in **1b**, **2b**, **2b'** and **3b**-catalyzed reactions, while **1a** and **2a** gave acceptable substrate conversions only with a substrate to Pd molar ratio of 100 (Table 1, entries 6,7, 15 and 16 vs. entries 1 and 3). The performance of the latter Pd(II)-catalysts in terms of activity is comparable to that of Pd(OAc)₂-(bathoneocuproine-disulfonate-disodium) **(4)**, which is known to be one of the most efficient Pd(II) catalysts for the aerobic alcohol oxidation in water.¹² The activity of all Pd(II)-based catalysts decreased with time, which is in

^f Pd amount (0.003 mmol), substrate (8.00 mmol).

^g p(air) (1 bar).

^h Substrate (0.778 mmol).

ⁱ Fourth catalytic cycle.

accordance with the formation of Pd-black in the course of the catalytic reaction (Table 1, entries 1–5).

The Pd-NPs-based catalysts showed a cinnamyl alcohol conversion which is comparable for a reaction time of 4 h (Table 1, entries 6, 7, 15, and 16) and in the range of activity found for a Pt/Bi-catalyst supported on alumina (i.e., TOF 144 h^{-1}), which is one of the most active and chemoselective heterogeneous catalyst for the oxidation of the latter substrate in water in the presence of a detergent.^{18,39}

By carrying out analogous catalytic reactions lasting 14 h, catalysts suffered from deactivation, except **2b**, which showed the highest longevity, regardless of the substrate employed (Table 1, entries 7, 12, 13, and 14). (TEM)-images, acquired on recovered **2b** after catalytic reactions lasting 4 h [Fig. 5(a)] and 14 h [Fig. 5(b)], showed a size distribution for the Pd-NPs which is comparable to that of as-synthesized **2b** (i.e., 6.33 ± 1.40 nm (as-synthesized), 6.11 ± 0.93 nm (after 4 h catalysis) and 5.65 ± 1.38 nm (after 14 h catalysis)), corroborating hence the catalyst longevity of **2b**.

The rather low conversion of geraniol (substrate C) by **2b** is due to the weak interaction of the aliphatic carbon backbone with the surface of the Pd-NPs, which is a prerequisite for the oxidative addition of the alcohol functionality (i.e., JOURNAL OF POLYMER SCIENCE Chemistry



FIGURE 5 (TEM)-images of 2b: (a) after 4 h, (b) after 14 h of catalysis and (c) after 4 h catalysis in the presence of K₂CO₃.

formation of the Pd-alcoholate as the key step in the alcohol oxidation reaction) at a low coordinated Pd atom located at the edge or corner of the Pd-NPs. 40

As far as the chemoselectivity of the catalytic oxidation reactions is concerned, substrates B and C were converted into the corresponding α , β -unsaturated carbonyl compound with a chemoselectivity of 100%. Conversely, the oxidation of substrates A and D gave the corresponding α , β -unsaturated carbonyl compound as major product (Scheme 2). The formation of the corresponding saturated alcohols and carbonyl compounds as minor products is the result of a competition reaction between either substrate or product and oxygen to accept dihydrogen from Pd-NPs. The higher the adsorption probability of substrate and product on the Pd-NP surface, the lower the chemoselectivity for the unsaturated carbonyl compound.^{39,41}

As a consequence, catalytic reactions carried out in the presence of only 1bar of air gave a very low chemoslectivity (i.e., 77%) for the α , β -unsaturated carbonyl compound, while the substrate conversion remained comparable to that obtained in the presence of 30 bar of air (Table 1, entry 8 vs. 7). This latter experimental result is in accordance with the role of oxygen in these catalytic reactions as dihydrogen acceptor and not as scavenger of strongly Pd-NP-adsorbing compounds, such as CO, which may be formed by decarbonylation reactions.⁴¹

The chemoselectivity of the oxidation reactions with substrate A was positively altered in the presence of a Broensted base such as K_2CO_3 , regardless of the catalyst employed (Table 1). As a result, the associated catalysts' activity increased with 1a and 2a, and decreased with 2b and 3b compared to catalytic reactions carried out in the absence of base. These catalytic results may be rationalized with the role of K₂CO₃ as an external base, which stabilizes the Pd(II) catalyst in case of **1a** and **2a**. The negative effect of K_2CO_3 on the catalytic activity of 2b (Table 1, entry 9 vs. 7) and 3b (Table 1, entry 17 vs. 16) might be ascribed to the coverage of the Pd-NP surface with (OH)-groups which hamper the access of substrate and product to the reactive metal atoms. As a consequence, the chemoselectivity of the oxidation reaction is increased on the expense of catalytic activity.⁴¹ It is important to mention at this point, that the mean size of the Pd-NPs of 2b did not change significantly during catalysis carried out in the presence of K_2CO_3 for 4 h (i.e., 6.26 ± 1.51 nm) as shown by the corresponding (TEM)-image [Fig. 5(c)].

Recycling experiments were carried out with **2b** in the presence of cinnamyl alcohol at a substrate to Pd molar ratio of 260, showing a constant substrate conversion (i.e., 98%) and chemoselectivity (i.e., 95%) for four consecutive catalytic runs (Table 1, entries 10 and 11). Importantly, the organic phase containing product, not converted substrate and diethyl ether (i.e., extraction medium) exhibited a Pd content of ca. 25 ppb (i.e., determined by ICP-OES) for each catalytic cycle.

EXPERIMENTAL

Materials

 \mathbf{L}^{OH} ($M_n = 5,200$ g/mol), 4-hydroxymethyl pyridine, benzyl alcohol, *n*-trioctyl amine; Pd(OAc)₂, NaH, mesyl chloride, Na₂CO₃ and *p*-TsOH monohydrate were purchased from Sigma-Aldrich. Compound **4** was prepared as described by a literature procedure.¹² 4-Hydroxymethyl pyridine and NaH were utilized and stored under dry N₂ atmosphere. \mathbf{L}^{OH} was dried under vacuum at 70 °C for 1 h before use. CH₂Cl₂, stabilized with amylene, was purchased from Panreac; DMF (anhydrous) and THF (HPLC-grade and BHT-stabilized) were purchased from Fluka Chemika; *n*-hexane (puriss.) and Et₂O (puriss. p.a. and stabilized with BHT) were purchased from Sigma-Aldrich. All solvents were used without further purification and anhydrous DMF was handled under a dry N₂ flux.

Synthesis

Synthesis of L^{Py}

Mesylated L^{OH} (9.10 g, 1.750 mmol), which was synthesized by following a reported procedure,²⁹ 4-hydroxymethyl pyridine (384.0 mg, 3.500 mmol) and NaH (84.0 mg, 3.500 mmol) were weighted in a round-bottom flask (250.0 mL) and dissolved in anhydrous DMF (80.0 mL) with vigorous stirring at 60 °C under a N₂ atmosphere. After a reaction time of 4 h, the orange reaction mixture was cooled to room temperature and filtered through a sand path and then through a paper filter to obtain a clear orange solution. After cooling the latter solution to 0 °C, cold 2-propanol (100.0 mL) was added, obtaining a pale-yellow precipitate which was separated from solution by filtration on a Buchner filter and successively washed with cold 2-propanol (50.0 mL) and *n*-hexane (20.0 mL). The white solid obtained was dried under vacuum to constant weight. Yield: 7.96 g (86%). $M_{\rm n} = 5200$ g/mol. $M_{\rm n}$, determined by ¹H NMR spectroscopy, refers to the polymer chain.

Synthesis of (HL^{Py})(OTs)

In a round-bottom flask L^{Py} (500.0 mg, 0.100 mmol) and *p*-TsOH monohydrate (37.0 mg, 0.200 mmol) were dissolved in water (5.0 mL) and stirred at room temperature for 3 h. Then 2-propanol (20.0 mL) and cold Et₂O (40.0 mL) were added to the clear colorless reaction mixtures, causing the precipitation of the polymer product as a colorless viscous liquid, which solidified after treating it with cold Et₂O (20.0 mL). The obtained solid was dried by vacuum at room temperature giving a waxy product. Yield: 451.0 mg (88%).

Synthesis of L^{Bn}

Mesylated $\dot{\mathbf{L}}^{OH}$ (1.14 g, 0.220 mmol), benzyl alcohol (45.5 μ L, 0.440 mmol) and NaH (11.0 mg, 0.440 mmol) were placed in a round-bottom flask and dissolved in anhydrous DMF (10.0 mL) under vigorous stirring at 60 °C under a N₂ atmosphere. After a reaction time of 4 h, the pale-yellow reaction mixture was cooled to room temperature and filtered successively through a sand path and filter paper to give a clear colorless solution. After cooling the latter solution to 0 °C, cold 2-propanol (50.0 mL) was added and the obtained white precipitate was separated from solution by filtration with a Buchner filter and washed with cold 2-propanol (20.0 mL) and *n*-hexane (10.0 mL). The obtained white waxy solid was dried by vacuum at room temperature to constant weight. Yield: 771.0mg (71%). M_n (¹H NMR) = 5200 g/mol, refers to the polymer chain.

Synthesis of 1a

 L^{Py} (4.00 g, 0.750 mmol) and Pd(OAc)₂ (87.0 mg, 0.390 mmol) were dissolved in CH₂Cl₂ (40.0 mL) and the resulting turbid solution was stirred in air for 24 h. Afterwards, the obtained solution was filtered through a paper filter and to the clear yellow solution was added *n*-hexane (50.0 mL), which caused the precipitation of a brown viscous oil. The supernatant was decanted off and the obtained brown oil was washed twice with *n*-hexane (30.0 mL) to give a brown waxy product which was dried by vacuum to constant weight yielding a beige solid: Yield: 3.33 g (82%). Pd content (ICP-OES): 0.96 wt %.

Synthesis of 2a

1a (910.5 mg, 0.084 mmol) and L^{Py} (891.7 mg, 0.168 mmol) were dissolved in CH_2Cl_2 (20.0 mL) under stirring by means of a magnetic stirring bar. To the obtained clear amber colored solution was added *p*-TsOH monohydrate (32.0 mg,

0.168 mmol). After a reaction time of 24 h the solution was successively filtered through a HPLC cartridge (0.2 μ m PTFE membrane) and cooled to 0 °C. Then cold 2-propanol (100.0 mL) was added to the latter solution and an off-white slurry was formed which was kept at 0 °C for 1 h. Afterwards, the obtained solid was successively filtered, washed with cold 2-propanol (20.0 mL) and *n*-hexane (20.0 mL) and dried by vacuum at room temperature. Yield: 1.47 g (81%). Pd content (ICP-OES): 0.47 wt %.

Synthesis of 1b, 2b, 2b', and 3b

1a and **2a** (400.0 mg) were dissolved in deareated CH_2Cl_2 (30.0 mL) at room temperature. Afterwards the clear solutions were transferred under nitrogen into a stainless steel autoclave (80.0 mL). The autoclave was charged with dihydrogen (15 bar) at room temperature and stirring started. After a reaction time of 1 h, the autoclave was successively depressurized, the black solutions transferred into a round bottom flask and concentrated to dryness, giving **1b** and **2b** as black solids. Pd content (ICP-OES): 1.1 wt % (**1b**) and 0.51 wt % (**2b**).

The *in situ* syntheses of $\mathbf{2b'}$ and $\mathbf{3b}$ were carried out as follows:

2b': **1a** (400.0 mg, 0.037 mmol) was dissolved in deareated CH_2Cl_2 (30.0 mL) at room temperature. Afterwards L^{Py} (392.8 mg, 0.074 mmol) was added to the latter solution, which was transferred into a stainless steel autoclave (80.0 mL) under nitrogen and pressurized with dihydrogen (15 bar). The synthesis proceeded as described above for **1b** and **2b**. Pd content (ICP-OES): 1.2 wt %.

3b: L^{Bn} (400.0 mg, 0.075 mmol) and Pd(OAc)₂ (4.3 mg, 0.019 mmol) were dissolved in deareated CH₂Cl₂ (30.0 mL) at room temperature. The obtained yellow solution was stirred for half an hour and then transferred into a stainless steel autoclave (80 mL), which was pressurized with dihydrogen (15 bar). The synthesis proceeded as describe above for **1b** and **2b**. Pd content (ICP-OES): 1.1 wt %.

Aerobic Alcohol Oxidation Reactions Catalyzed by 1a, 2a, 1b, 2b, 2b', and 3b

A stainless steel autoclave (80.0 mL) was successively charged with water (5.0 mL), the desired amount of catalyst, substrate and where used with K_2CO_3 . Then, the autoclave was sealed and heated to 60 °C by means of an oil bath. Once the latter reaction temperature was reached the autoclave was charged with air (30 bar) and magnetic stirring was started. After the desired reaction time, the autoclave was cooled to room temperature by means of an ice-water bath and the air pressure released. The crude reaction mixture was transferred into a separation funnel and the water suspension was extracted with diethyl ether (3 \times 8.0 mL). The combined organic phases were subjected to (GC)- and (GC-MS)-analyses.

Recycling Experiments with 2b

A stainless steel autoclave (80.0 mL) was charged with 2b (65.0 mg, 0.003 mmol), cinnamyl alcohol (100.0 μL , 0.778

mmol) and water (5.0 mL) at room temperature. The autoclave was then sealed, heated to 60 °C by means of an oil bath and charged with air (30 bar). After a reaction time of 2 h the autoclave was cooled to room temperature, the air pressure released, and the suspension transferred into a separation funnel. The water phase was extracted with diethyl ether (3 × 8.0 mL). Afterwards, the recovered water phase was placed again in the autoclave and cinnamyl alcohol (100.0 μ L, 0.778 mmol) added. The second, third, and fourth catalytic cycle were carried out as described above.

Centrifugation Experiments with Water Solutions of 2b and 3b

Water solutions of **2b** and **3b** with a concentration of 10 mg/mL were subjected to centrifugation at 6000 rpm for 6 h. During this time period only in the case of **3b** a black powder separated from the corresponding water solution. The black solid was successively separated from solution, washed with deionized water, dried by vacuum at room temperature and analyzed by XRPD. Even after doubling the centrifugation time (i.e., 12 h at 6000 rpm) no precipitate separated from water solution of **2b**.

Instruments and Characterization

UV-vis spectra were recorded on a Varian-Cary 4000 UV-vis spectrophotometer using a quartz cuvette with an optical path length of 10 mm. The measurements were carried out on deionized water solutions of the polymer compounds using a concentration of 0.3 mg/mL.

(TEM)-analyses were carried out on a TEM PHILIPS CM 12, equipped with an OLYMPUS Megaview G2 camera and using an accelerating voltage of 80 keV. Samples for (TEM)-analyses were prepared by depositing a drop of the water solution of the corresponding sample on a holey film of a 300 mesh Cu grid, followed by the evaporation of the solvent.

TGA were performed under an air flux of 200 mL/min by using a SEIKO TG/DTA 7200 instrument calibrated within as reference sample. Measurements were carried out in the temperature interval from 30 to 700 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min.

XRPD spectra were acquired on a X'Pert PRO (PANalytical) powder diffractometer using Cu K_{α} radiation ($\lambda = 1.541874$ Å) and a parabolic MPD mirror for Cu radiation. Spectra were acquired in a 2 Θ range from 10 to 60° with a step size of 0.1050°.

(GC)-analyses were performed with a Shimadzu 2010 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μ m film thickness) VF-WAXms capillary column. (GC-MS)-analyses were performed with a Shimadzu QP 5000 apparatus, equipped with a 30 m (0.32 mm i.d., 0.50 μ m film thickness) CP-WAX 52 CB WCOT-fused silica column.

(ICP-OES)-analyses were carried out on an ICP apparatus of the type Perkin Elmer Optima 2000 OES DV.



CONCLUSIONS

The PEG-based macroligand L^{Py} was straightforwardly synthesized by pyridine end-functionalization of PEG monomethyl ether and employed to stabilize Pd(II) in a neutral (1a) and bis-cationic (2a) macrocomplex, characterized by a L^{Py} to Pd molar ratio of 2 and 4, respectively. Unlike 1a, 2a revealed to be a suitable molecular precursor for the generation of spherical and well-dispersed Pd-NPs (2b) with a mean diameter of 6.33 ± 1.40 nm. The homogeneous distribution of the Pd-NPs in 2b exerted a significant stabilizing effect on the poly(ether) chain of \boldsymbol{L}^{Py} against its oxidative thermal degradation. From a screening of the Pd(II)- and Pd-NP-based catalysts in the aerobic oxidation of α,β unsaturated alcohols in water emerged 2b as the most stable catalyst, showing TOF-values up to 200^{-h} and high chemoselectivity even for prolonged reaction times. Consequently, 2b proved to be an efficient recyclable catalyst releasing a low amount of Pd (ca. 25 ppb per catalytic cycle) into the organic phase.

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