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The Effect of PEGylated Dendrimers on the Catalytic Activity and Stability of Palladium Particles in the Suzuki Reaction

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Abstract Stable dendrimer-coated Pd particles were synthesized using the wet-chemical borohydride reduction method of Pd(II) salts in the presence of low-generation (poly)ethylene glycol-terminated amidoamine-based dendrimers. The identity and structure of the Pd-containing colloids were analyzed by FT-IR spectroscopy, X-ray powder diffraction, thermogravimetric analysis, atom absorption spectroscopy and UV–Vis spectroscopy. Dynamic light scattering experiments have been performed to determine the hydrodynamic diameter of the particles (350–900 nm). The performance of the thus obtained dendrimer-stabilized Pd particles in Suzuki *C,C* cross-coupling reactions of aryl halides and phenyl boronic acid was examined. Turn over numbers of up to 930 could be achieved. The influence of the dendritic stabilizers on the particle size along with the catalytic performance is presented.

Keywords Particles · Palladium · (Amidoamine) dendrimers · (Poly)ethylene glycol

1 Introduction

Nanosized metallic particles exhibiting a large surface-to-volume ratio gained considerable interest in the application as effective catalysts for a variety of chemical transformations [1–4]. Presently, scientific efforts are directed to nanocatalysis, in the field of heterogeneous catalysis, in which the nanoparticles (NPs) are supported on a solid surface (e.g. silica [5, 6], alumina [7, 8]) and in homogeneous catalysis applying colloidal NPs as catalytic active species, respectively [9, 10]. Because metal NPs are thermodynamically unstable with respect to agglomeration and precipitation phenomena, the colloids tend to lose their catalytic reactivity and selectivity [11]. Aggregation of NPs can be avoided by surrounding the appropriate nanoparticle with an electrical double layer of adsorbed ions (e.g. citrate and chloride) or by adsorption of weakly bounded organic surfactant molecules (e.g. long-chain alkyl compounds, tensides, polymers, dendrimers) in the preparation progress, thus providing a protective layer [12]. Common methods to prepare metal colloids involve evaporation/condensation processes of metal–organic and organometallic precursors as well as chemical/electrochemical reduction of metal salts in the presence of surfactants [13, 14].

Since the pioneering work of Crooks and Tomalia [15, 16] the fascinating class of dendrimer molecules has been successfully employed as templates and stabilizing agents, respectively, for a variety of metal NPs, including palladium and platinum [17]. Such particles exhibit a high catalytic activity in hydrogenation reactions of olefins [18] and several *C*,*C* cross-couplings, including Heck [19] and Suzuki reactions [20]. One major advantage of stabilized NPs compared to commonly used palladium phosphine complexes lies in the convenient separation of the catalyst that offers the possibility of recycling.

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Previously, Li and El-Sayed reported on the application of hydroxyl-terminated (poly)amidoamine (PAMAM) dendrimers of second to fourth generation as effective stabilizers for catalytically active Pd NPs in the Suzuki reaction concluding that G4 provides the best protection against Pd black formation [20]. However, these NPs are strongly encapsulated within the dendrimer resulting in a pronounced loss of catalytic activity. For the preparation of effective catalysts, the usage of low generation dendrimers may be advantageous, which in addition are much easier to synthesize. Recently, the synthesis of gold [21] and Fe_3O_4 NPs, [22] stabilized by low-generation PEGylated PAMAM-dendrimers, has been reported by our group. The particle size can be influenced by both the dendrimer and the dendrimer-to-metal ratio.

In continuation of our recent studies in the field of (metallo)dendrimers, [21, 22] the generation of NPs [23–27] and in homogeneous *C,C* cross-coupling, [28–35] we here report on the generation of Pd particles from $Na_2[PdCl_4]$ using the wet-chemical borohydride reduction method. As stabilizer for colloidal Pd particles low-generation (poly)ethylene glycol-terminated amidoamine-based dendrimers are applied. The appropriate Pd particles were used as catalyst in the Suzuki reaction of diverse aryl halides with phenyl boronic acid. The identity and composition of the Pd colloids has been confirmed by X-ray powder diffraction (XRPD), ultraviolet–visible spectroscopy (UV–Vis), thermogravimetric analysis (TGA) along with atom absorption spectrometry (AAS). Dynamic light scattering (DLS) measurements were performed to determine the hydrodynamic diameter of the particles. The influence of the stabilizer used as well as the stabilizer-to-Pd ratio onto the particle size along with the consequences for the catalysts performance will also be discussed.

2 Materials and Methods

2.1 Materials and Instruments

All synthesis procedures were performed under a dry and deoxygenated dinitrogen atmosphere using standard Schlenk techniques. Distilled water was deoxygenated prior to use. All starting materials were obtained from commercial suppliers and were used without further purification. Dendrimers **1** [21] and **2**, [36] 1-bromo-2-methylnaphthalene [37] and 1-bromo-2-methoxynaphthalene [38] were synthesized according to previously published procedures.

The structure of the powder samples was identified by X-ray powder diffraction on a STOE-STAD IP diffractometer with Cu Kα (1.5405 Å) radiation. The surface coating was examined by FT-IR spectroscopy recorded with a FT Nicolet IR 200 instrument. Dynamic light scattering (DLS) measurements were accomplished with a MALVERN Zetasizer Nano Series S 90 and UV–Vis spectroscopy was recorded with a THERMO Genesys 6 spectrometer. Thermogravimetric experiments were performed with a METTLER-TOLEDO TGA/DSC1 1100 system with an UMX1 balance, and atomic absorption spectroscopy was performed on a Thermo Scientific iCE 3000 system.

2.2 Synthesis Procedure for Pd Particles

In a typical experiment, dendrimer stabilized Pd particles were formed in a wet-chemical process, applying stock solutions of the stabilizers **1** or **2**, respectively, in methanol, sodium tetrachloropalladate(II) as palladium source and sodium borohydride in H_2O as reducing agent. An appropriate volume of the respective stabilizer stock solution was mixed with aqueous $Na_2[PdCl_4]$ (molar ratio stabilizer-to-Pd = 1:10, 1:50, 1:100, 1:150, 1:200, 1:250, 1:500, 1:1,000) at ambient temperature, filled up to 3 mL with water and stirred vigorously for 5 min. Subsequent addition of the $Na[BH_4]$ stock solution resulted in the immediate formation of black-colored Pd colloids, which were applied as catalysts in the Suzuki *C,C* cross-coupling reaction after removal of the organic solvent without further purification. (For further information see ESI.)

For characterization purposes the colloids have been isolated. Therefore, the particles were evaporated to dryness and subsequently washed with water and methanol to remove inorganic salts as well as excess surfactant.

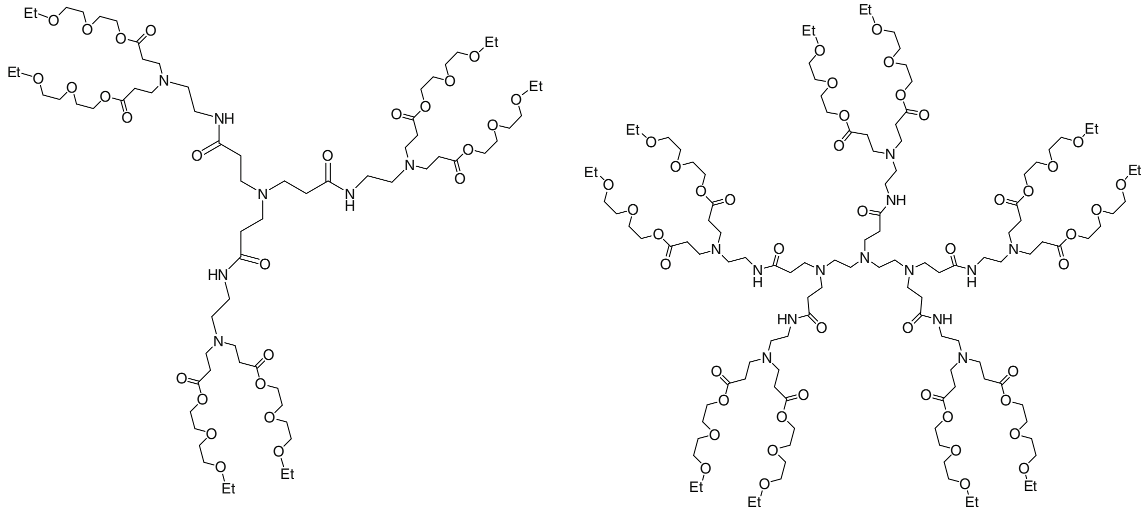
2.3 General Procedure for the Suzuki Reaction

The respective aryl halide (2.0 mmol), phenyl boronic acid (365 mg, 3.0 mmol), acenaphthene (308 mg, 2.0 mmol) as well as the corresponding base K_2CO_3 (830 mg, 6.0 mmol) or K_3PO_4 (1.27 g, 6.0 mmol) were dissolved in 7 mL of a 1,4-dioxane/water mixture (ratio 2:1, v/v) and loaded with the dendrimer-stabilized Pd catalyst **1**:Pd or **2**:Pd (Pd loading = 1.0, 0.25, 0.1 mol%). The colloidal suspensions were stirred at 100 °C for 3 h. The organic phase was filtered through a pad of silica with diethyl ether as eluent. All volatiles were evaporated under reduced pressure. The yields were determined by ^1H NMR spectroscopy applying acenaphthene as internal standard and are an arithmetic average of three independent runs.

3 Results and Discussion

3.1 Preparation and Characterization of Dendrimer-Stabilized Pd Particles

End-grafted ethylene glycol ether-functionalized amidoamine-based low-generation dendrimers **1** [21] and **2** [36]



1 **2**

Scheme 1 Ethylene glycol-functionalized PAMAM dendrimers **1** and **2** [21, 36]

(Scheme 1) were prepared according to published procedures. The obtained PEGylated dendritic molecules of the type $N(CH_2CH_2C(O)NHCH_2CH_2NR_2)_3$ (**1**, R = $CH_2CH_2C(O)O(CH_2CH_2O)_2C_2H_5$), and $(R_2NCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NR_2)_2]_2$ (**2**, R = $CH_2CH_2C(O)O(CH_2CH_2O)_2C_2H_5$) were applied as surfactants for the stabilization of Pd particles generated by the controlled wet-chemical borohydride reduction of $Na_2[PdCl_4]$ (Scheme 2).

Upon addition of the reducing agent, black colored solutions were obtained. The particles do not precipitate in the methanolic/aqueous solution within days and can be maintained upon removal of the solvent and addition of 1,4-dioxane. This indicates that the glycol-functionalized PAMAM-based dendrimers **1** and **2** are efficient stabilizing agents as reported earlier [21, 22].

As an evidence for chemical bonding between Pd and surfactant FT-IR spectroscopy of the organic–inorganic hybrid material was performed. As expected, **1**·Pd (1:Pd = 1:150) revealed no definite absorption, due to the low concentration of the stabilizer. Figure 1 exemplarily shows the FT-IR spectra of **1** and **1**-stabilized Pd colloids at a surfactant-to-palladium ratio of 1:10. The bands of **1** coated on Pd particles attributing to the C–O–C vibrations are bathochromically shifted by 25 cm^{-1} (1,093 and 1,025 cm^{-1}) and 5 cm^{-1} (1,175 cm^{-1}), respectively, when compared to the parent dendrimer **1**. This indicates the dendritic stabilization of the Pd particles.

The formation of Pd particles was investigated by UV–Vis spectroscopy (Fig. 2) with **1**:Pd = 1:150 as representative example. For molecule **1**, absorptions were observed at 213 and 267 nm, respectively, which can be assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions. Upon addition of $Na_2[PdCl_4]$ these transitions are bathochromic shifted by 7 nm. Furthermore, a ligand-to-metal-charge transfer band (LMCT) of the $[PdCl_4]^{2-}$ ions at 235 nm is observed [39]. After wet-chemical reduction with $Na[BH_4]$ this LMCT disappears and the spectrum is dominated by an intensive background absorbance, characteristic for Pd particles (Fig. 2) [40].

To study the composition of the dendrimer-coated Pd particles **1**·Pd (1:150) thermo-gravimetric experiments were performed in a dinitrogen atmosphere (60 mL min^{-1}) in the temperature range of 40–800 °C applying a heating rate of 10 K min^{-1}. Decomposition of the organic stabilizer occurs in various steps between 50 and 630 °C resulting in an overall mass diminution of 7.3 wt% (Fig. 3). After cooling to ambient temperature the sample was heated to 800 °C (10 K min^{-1}) with a gas flow of 40 mL min^{-1} N_2 and 20 mL min^{-1} O_2. As no further mass diminution could be detected, the formation of carbon during the decomposition of the surfactant can be excluded and the residual mass of 92.7 wt% corresponds to the amount of Pd in the colloid.[1] This result could be validated by AAS measurements (93.3 wt% Pd). For a surfactant-to-Pd ratio of 1:150, 91.5 wt% Pd would be expected, the isolated colloids exhibit a **1**:Pd ratio of 1:178.

The phase and crystalline nature of the dendrimer-stabilized Pd particles were confirmed by XRPD experiments on **1**·Pd colloids (molar ratio of **1**:Pd = 1:150) as shown in Fig. 4. The powder diffraction pattern is consistent with standard Pd reflections reported in literature (JCPDS Card No. 46-1043) confirming the formation of Pd

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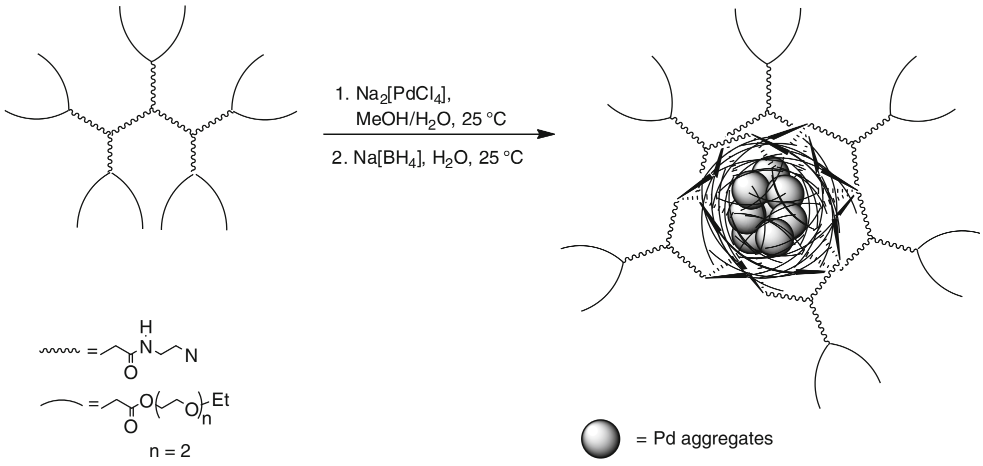
[1] Due to the partial formation of PdO a slight increase in weight of 1.5 wt% was observed.



Scheme 2 Schematic illustration of dendrimer-stabilized Pd particle formation by the wet-chemical borohydride method in methanol as solvent

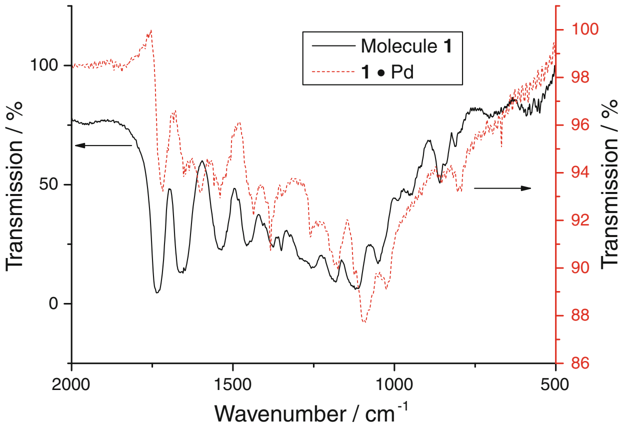


Fig. 1 FT-IR spectra of molecule **1** and **1**·Pd (KBr, 25 °C)

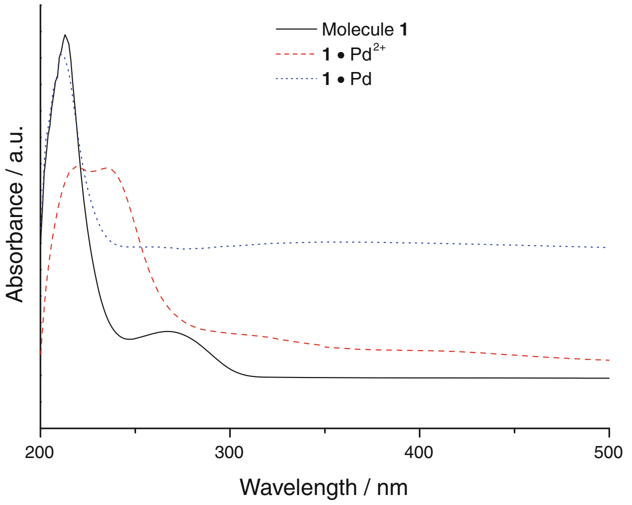


Fig. 2 UV–Vis spectra of **1** ($c = 0.2$ mmol L^{-1}), **1**·Pd^{2+} ($c_{Pd^{2+}} = 1.14$ mmol L^{-1} $c_{\mathbf{1}} = 0.0076$ mmol L^{-1}) and **1**·Pd (**1**:Pd = 1:150, $c_{Pd^{2+}} = 0.285$ mmol L^{-1} $c_{\mathbf{1}} = 0.0019$ mmol L^{-1}) in a mixture of H_2O–MeOH of ratio 1:0.77 (v/v) at 25 °C

with space group *Fd-3m*. The characteristic diffraction peaks could be well indexed. The crystallite size of the colloids as calculated by the Scherrer formula was found to be 6–7 nm [41].

To investigate the effective size of the Pd-containing colloids in solution the hydrodynamic diameter was measured by dynamic light scattering (DLS). The colloids analyzed by DLS were generated following the synthesis protocol as used for the colloids applied in the Suzuki reactions. The smallest particles were observed for a surfactant-to-Pd ratio of 1:150 with 357 (±50) nm (Table 1, entry 4). Both, increase or decrease of the amount of **1** causes the formation of Pd particles with larger hydrodynamic diameters. In case of low surfactant-to-Pd ratios (entries 7 and 8) the increase in particle size can be explained by agglomeration originating from insufficient stabilization of the particles by **1**. For high amounts of surfactant (entries 1 and 2) the formation of larger particles may be due to a decrease in the nucleation rate, which may

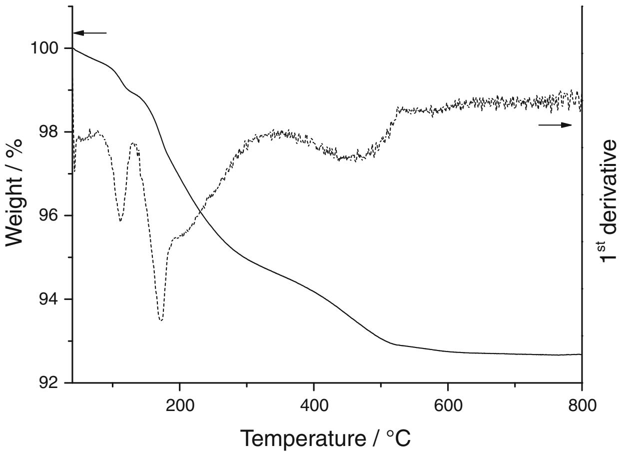


Fig. 3 Thermogravimetric analysis of **1**·Pd (1:150) under dinitrogen (60 mL min^{-1}) using a heating rate of 10 K min^{-1}

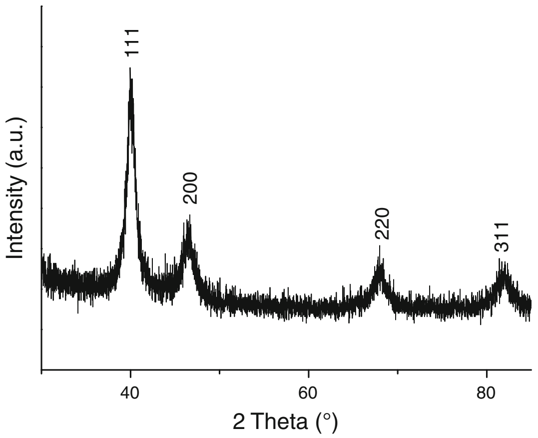


Fig. 4 X-ray powder diffraction pattern derived from **1**·Pd particles (**1**:Pd = 1:150)

be explained by strong interactions between the dendritic molecules and Pd clusters prior to nucleation. It is instructive to note that the hydrodynamic diameter is much higher than the crystallite size measured by XRPD which points to a fast agglomeration process of the particles. [2] Both the use of different reducing agents (polymethylhydrosiloxane, lithium triethylborohydride as thf solution) as well as performing the reducing step at lower temperatures (-20 – 0 °C) did not result in the formation of smaller particles. Noteworthy, the Pd particles discussed here are by far larger than the Au (5.0–60.0 nm) [21] and Fe_3O_4 (5.0–10.0 nm) [22] particles generated in the presence of the same dendritic stabilizer.

3.2 Suzuki *C,C* Cross-Coupling with Dendrimer-Stabilized Pd Particles

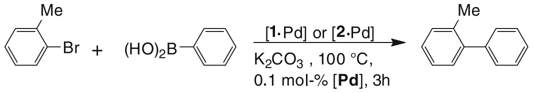
To enrich the family of existing *C,C* cross-coupling catalysts and in order to determine the low-generation dendrimers' impact on the catalytic activity of Pd particles, we applied the appropriate dendrimer-stabilized Pd colloids in Suzuki reactions. In comparative studies the newly synthesized organic–inorganic hybrid materials showed to be efficient catalysts in palladium-mediated transformations of aryl halides with phenyl boronic acid to give biphenyls. The catalytic reactions of the appropriate organic coupling reagents were performed in a 1,4-dioxane-water mixture of ratio 2:1 (v/v) in presence of a base. (Pre)catalyst loadings of 1.0, 0.25 and 0.1 mol% palladium at 100 °C were applied. For the optimization of the reaction conditions the conversion of 2-bromotoluene with phenyl boronic acid was chosen (Table 2).

The applied surfactant impacts the behavior of the Pd colloids in two ways. On the one hand it acts as stabilizing agent that prevents formation of catalytically inactive

Table 1 Hydrodynamic diameters of **1**-stabilized Pd particles with varying molar stabilizer-to-Pd ratios determined by DLS ($c_{Pd^{2+}}$ = 0.2 mmol L^{-1}, 1,4-dioxane:H_2O = 2:1, 20 °C)

Entry	Surfactant-to-palladium ratio	Particle size (nm)
1	1:10	898 (±142)
2	1:50	780 (±55)
3	1:100	370 (±73)
4	1:150	357 (±50)
5	1:200	391 (±18)
6	1:250	418 (±49)
7	1:500	593 (±114)
8	1:1,000	614 (±105)

Table 2 Suzuki *C,C* cross-coupling of 2-bromotoluene and phenyl boronic acid with stabilized Pd colloids generated by **1** and **2** at varying molar surfactant-to-palladium ratios



Entry	Surfactant	Surfactant-to-palladium ratio	Yield (%)
1	–	–	22[a]
2	**1**	1:10	56[b]
3	**1**	1:50	30
4	**1**	1:100	61
5	**1**	1:150	93
6	**1**	1:200	87
7	**1**	1:250	82
8	**1**	1:500	28
9	**1**	1:1,000	21
10	**1**	1:150	14[c]
11	**2**	1:10	9[a]
12	**2**	1:50	16[a]
13	**2**	1:100	58[a]
14	**2**	1:150	22[a]
15	**2**	1:200	32[a]
16	**2**	1:250	40[a]
17	**2**	1:500	35[a]
18	**2**	1:1,000	26[a]

2.0 mmol of 2-bromotoluene, 3.0 mmol of phenyl boronic acid, 6.0 mmol of K_2CO_3, 0.1 mol% Pd, 1,4-dioxane:water (2:1, 7 mL), 100 °C, 3 h

[a] 1.0 mol% Pd

[b] 0.25 mol% Pd

[c] The reaction mixture was extracted with n-hexane and water, after evaporation to dryness the black precipitate obtained was used as the catalyst in a second run

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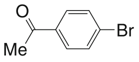
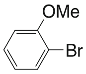
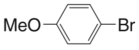
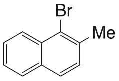
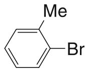
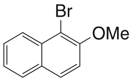
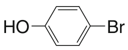
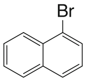
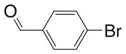
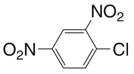
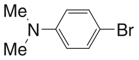
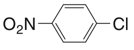
[2] This agglomeration process was complete in the time required for the acquisition of the DLS measurements (approx. 5 minutes).

palladium black (Table 2, entry 1). On the other hand it shields the active catalyst from the substrate molecules [20]. Therefore, the surfactant-to-palladium ratio has to be optimized (Table 2, entries 2–9). A surfactant-to-palladium ratio of 1:150 for surfactant **1** provides the best results (Table 2, entry 5) which corresponds to the particles exhibiting the smallest hydrodynamic diameter (vide supra). Most likely this result is due to the relatively high surface to volume ratio of these particles and consequently the highest number of Pd atoms accessible for substrate molecules. Investigations to reuse the Pd colloids revealed that this is possible in principle (entry 10), however, being associated with a significant diminution of the catalytic productivity. The reason for this behaviour is most probably due to a partial decomposition of the Pd colloid and consequently the formation of catalytically inactive palladium black in course of the catalytic transformation. When changing from surfactant **1 to 2** the catalytic productivity is considerably decreased (Table 2, entry 5 vs. 14) even though a higher Pd loading is applied. Thus, we concentrated on **1** for further investigations.

In order to screen the substrate scope of the dendrimer-stabilized Pd particles different aryl halides were reacted with phenyl boronic acid under the optimized reaction conditions. It can be seen that activated, non-activated and deactivated bromoarenes can be coupled at a catalyst loading of 0.25 mol% Pd, the respective biaryls are formed in good to excellent yields after only 3 h (Table 3, entries 1–7). In comparison with PAMAM dendrimer-stabilized particles synthesized by Diallo et al. [42] significantly higher conversions and excellent yields even with less reactive bromoarenes could be achieved. However, a major drawback of the as-prepared Pd particles is the lower catalytic activity towards the conversion of *ortho*-substituted substrates (Table 3, entries 8–10) and chloroarenes (Table 3, entries 11 and 12).

Table 3 Suzuki *C,C* cross-coupling of various aryl halides with phenyl boronic acid using **1**·Pd as catalyst

Entry	Aryl halide	Yield (%)	Entry	Aryl halide	Yield (%)
1		100	7		74
2		99	8		35
3		98	9		27
4		60	10		10
5		71	11		26
6		70	12		17

2.0 mmol of aryl halide, 3.0 mmol of phenyl boronic acid, 6.0 mmol of K_3PO_4, **1**:Pd = 1:150, 0.25 mol% Pd, 1,4-dioxane:water (2:1, 7 mL), 100 °C, 3 h

Similar results for the transformation of diverse bromoarenes have recently been reported by Mejías et al. [43] applying Pd NPs (2–5 nm) stabilized with PEG-tagged material. In case of deactivated bromo and activated chloroarenes a decrease in catalytic activity is observed even though the reaction temperature is increased up to 130 °C. In contrast Han et al. [44] demonstrated the use of in situ generated PEG-400-stabilized Pd NPs (2–3 nm) in an oxygen-promoted ligand-free Suzuki coupling of activated and non-activated chloroarenes.

4 Conclusion

The preparation and characterization of palladium particles coated with low-generation PEGylated dendritic molecules of the type $N(CH_2CH_2C(O)NHCH_2CH_2NR_2)_3$ (**1**, R = $CH_2CH_2C(O)O(CH_2CH_2O)_2C_2H_5$), and $(R_2NCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NR_2)_2]_2$ (**2**, R = $CH_2CH_2C(O)O(CH_2CH_2O)_2C_2H_5$), respectively, and their application in the Suzuki *C,C* cross-coupling reaction of aryl halides with phenyl boronic acid is reported. The identity and elemental composition of the Pd particles was investigated by XRPD, TGA and AAS demonstrating the presence of surfactant even in case of the isolated particles. The observation of an intensive background absorbance in the UV–Vis spectra indicates the formation of Pd particles. A bathochromic shift of the C–O–C vibrations measured by FT-IR could be observed, due to an interaction between surfactant and Pd particles. Their hydrodynamic diameters, which strongly depend on the surfactant-to-Pd ratio, have been determined by dynamic light scattering to be in the range of 350–900 nm. The smallest Pd colloids were observed for a surfactant-to-Pd ratio of 1:150. Both, increase or decrease of the amount of **1** causes the formation of Pd particles with larger hydrodynamic diameters. Compared to previously reported dendrimer-stabilized Au particles (5.0–60.0 nm) [21] and Fe_3O_4 particles (5.0–10.0 nm) [22] the size of the Pd particles is clearly increased. The dendrimer-coated Pd particles were applied in the palladium-catalyzed Suzuki *C,C* cross-coupling. The reaction of 2-bromotoluene and phenyl boronic acid with potassium carbonate as base was chosen for a pre-screening and to optimize the catalysis conditions. It was found that at a **1**-to-Pd ratio of 1:150 the highest catalytic productivity is observed, which most likely corresponds to the particle size. Diverse activated, non-activated and deactivated bromoarenes have successfully been coupled with phenyl boronic acid at 100 °C and a 0.25 mol% Pd loading (**1**:Pd = 1:150) within 3 h. However, a fairly low activity is observed for the conversion of chloroarenes and *ortho*-substituted substrates.

5 Supporting Information

Detailed information concerning the preparation of the Pd particles and results of further Suzuki reactions are available in electronic supplementary information (ESI).

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