Sulphonated "Click" Dendrimer-Stabilized Palladium Nanoparticles as Highly Efficient Catalysts for Olefin Hydrogenation and Suzuki Coupling Reactions Under Ambient Conditions in Aqueous Media

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Abstract: Water-soluble 1,2,3-triazolyl dendrimers were synthesized by "click chemistry" and used to stabilize palladium nanoparticles (PdNPs). These new "click" dendrimer-stabilized nanoparticles (DSN) are highly stable to air and moisture and are catalytically active for olefin hydrogenation and Suzuki coupling reaction, in aqueous media, under ambient conditions using a low amount of palladium (0.01 mol% Pd). Kinetic studies show high catalytic efficiency and high stability for the new "click" DSN

Introduction

Catalysis in water^[1,2] under ambient conditions is a highly challenging topic in the context of *green chemistry*.^[3] A promising ligandless approach is that using nanoparticle (NP) catalysis,^[4] in particular with dendrimer-stabilized NPs.^[5–7] The catalytic applications of such NPs were pioneered by Crooks using PAMAM dendrimers for hydrogenation and C–C coupling reactions.^[7] Recently, we reported "click"^[8] dendrimers containing triazole ligands^[9a] and showed that they can stabilize PdNPs which efficiently catalyse olefin hydrogenation^[9b] and Suzuki coupling reactions^[9c] in organic media using homeopathic amounts of PdNPs.^[9c,10]

A challenge was then to synthesize water-soluble triazolyl dendrimers to show that PdNPs stabilized by triazolyl dendrimers are also catalytically efficient in aqueous media. We now report the first synthesis of water-soluble dendrimers containing triazole ligands in their structure, (water-soluble triazolyl sulphonate "click" dendrimers) and the corresponding dendrimer-stabilized PdNPs, and we show that they are very in both reactions. The complexation of potassium tetrachloropalladate (K_2PdCl_4) to the triazole ligands present in the dendritic structures was monitored by UV/vis and, after reduction, the nanoparticles were characterized by transmission electron microscopy (TEM).

Keywords: catalysis; dendrimers; nanoparticles; palladium; Suzuki reaction

efficient catalysts in aqueous media even under ambient conditions using only 0.01% mol Pd catalyst. So far, the reported examples of dendrimer-stabilized NP catalysis in aqueous media were performed at high temperatures using relatively high amounts of PdNPs catalyst (> 1%) only with PAMAM or PIP dendrimers.

Results and Discussion

Synthesis of Water-Soluble 1,2,3-Triazolyl Dendrimers

"Click" reactions of the known azido terminated dendrimers^[9b,11] with sodium propargyl sulphonate in water/THF (1:1) yielded the triazolyl sulphonate-terminated dendrimers [Eqs. (1)–(3)]. THF was evaporated, and the dendrimers remained in aqueous solution. They were purified by dialysis against aqueous ammonia solution for three days [in order to remove Cu(I) that remains trapped inside the dendrimer] and against water for one day. The aqueous solution inside the membrane was recovered, water was re-



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moved under vacuum, and the poly-1,2,3-triazolyl sulphonate dendrimers $4-G_0$, $5-G_1$ and $6-G_2$ were obtained as colorless waxy products. Their ¹H NMR spectra, recorded in D₂O, confirmed the structures clearly showing all the expected peaks, especially the triazole protons at 7.8 ppm and the CH_2SO_3Na protons at 4.2 ppm (see Supporting Information, Fig-

ure S1). These dendrimers were characterized by size-exclusion chromatography (SEC) showing monodispersity (polydispersity: 1.00 for 4-G₀ and 1.01 for 5-G₁ and 6-G₂). The infrared spectra confirm the absence of unreacted azido groups. Dynamic light scattering experiments for the poly-1,2,3-triazolyl sulphonate dendrimer 6-G₂ reproducibly give the very large

value of the hydrodynamic diameter of 25.8 ± 0.7 nm in water, which reflects an enormous amount of water solvation in the corona due to the peripheral sulphonate termini.

Complexation of K₂PdCl₄ and Stabilization of PdNPs by the 1,2,3-Triazolylsulphonate Dendrimers

In previous reports,^[9b,c] we showed that 1,2,3-triazolylferrocenyl dendrimers are able to complex Pd(II) in the form of $[Pd(MeCN)_4][BF_4]_2$ and Pd(OAc)_2 by interaction with the triazole ligands, using cyclic voltammetry, UV/vis and ¹H NMR spectroscopy. We now show the interaction of K₂PdCl₄ with the 1,2,3-triazolylsulphonate dendrimers by UV/vis spectroscopy. In Figure 1, we can observe that the spectrum of K₂PdCl₄, that presents two absorption bands at 208 and 235 nm, changes upon addition of dendrimer **4**-G₀ (214 and 227 nm). This change in the UV/vis spectrum can be attributed to the coordination of Pd(II) to the triazole ligands in the dendrimer.

The three generations of 1,2,3-triazolylsulphonate dendrimers (**4**-G₀, **5**-G₁ and **6**-G₂) were used to stabilize PdNPs. Upon addition of the classic reducing agent, NaBH₄, to an aqueous solution of 1,2,3-triazolylsulphonate dendrimers and K₂PdCl₄ (1 equiv. per triazole, 10 equivalents of NaBH₄ as in literature reports^[7]), black homogeneous solutions were obtained and analyzed by TEM.

In our previous studies, it was shown that the type of stabilization of the NPs by the dendrimers mostly depends on the dendrimer size and type of terminal groups (dendrimers with bulky terminal groups encapsulate the NPs forming DENs, and for dendrimers with non-bulky terminal groups the NPs are stabilized



Figure 1. a) UV/vis spectrum obtained for K_2PdCl_4 in water; b) UV/vis spectrum obtained for a mixture of K_2PdCl_4 and dendrimer **4**-G₀ in water (one equiv. of K_2PdCl_4 per triazole).

by several dendrimers, DSNs, Figure 2).^[9b] On the other hand, TEM data now show that, in all cases, the size of the NPs obtained is much larger than the size expected for DENs (G₁: 2.8 ± 0.4 nm instead of 0.9 nm; G₂: 3.0 ± 0.6 nm instead of 1.3 nm) (Figure 4 and Figure 5).^[12] In fact, the sulphonate groups are not bulky enough to encapsulate the NPs by the dendrimers, thus DSNs are obtained for the three generations. The TEM data also show that, in this series of dendrimers, the higher dendrimers forms NPs with larger polydispersity than the smaller dendrimers.

Contrary to dendrimers with bulky termini that usually form relative monodisperse NPs (DENs),^[12] in this series of dendrimers the polydispersity increases with the dendrimer size (Figure 3, Figure 4, and Figure 5). Indeed, in the present case (triazolylsulphonate termini), G_0 is the optimal generation because it forms the smaller NPs with low dispersity (Figure 3).

Use of the New "Click" DSN as Catalysts in Hydrogenation Reactions

The DSNs formed with the new poly-1,2,3-triazolylsulphonate dendrimers are highly stable to air and moisture, and proved to be efficient catalysts for hydrogenation of allyl alcohol at 0.01% mol Pd [Eq. (4)].



Crooks et al. reported the hydrogenation of allylic alcohols in aqueous solutions, presenting catalytic efficiencies around 500 mol H_2 (mol Pd⁻¹)h⁻¹ (TOF, turnover frequency) for monometallic Pd DENs.^[13] The turnover frequencies (TOF) obtained for the hydrogenation of allyl alcohol using the new "click" DSN (0.01% mol Pd) is about sixteen times higher $[DSN-G_0: 8\ 088\ mol\ H_2\ (mol\ Pd)^{-1}h^{-1}]$ than those reported for NPs stabilized by PAMAM.^[13] The stability of the new "click" DSN catalysts was tested by adding the substrate to the catalytic solutions until the catalyst was no longer active. Thus, the new DSNs are highly stable in the catalytic conditions, being reused for more than 10 catalytic cycles at 0.01% mol Pd (TON >100,000). The most efficient catalyst is DSN-G₀, confirming the trend according to which the catalytic activity is a function of the size of the PdNPs, that is, the catalytic reactions are faster for the smaller NPs than for the larger ones (Table 1).



Figure 2. Representation of DSN-G₀.

Use of the New "Click" DSN as Catalysts in Suzuki Coupling Reactions

There are a few reports of the use of PdNPs stabilized by dendrimers to catalyze the Suzuki coupling reaction,^[14] but in all cases the reactions were performed at high temperatures using relative large amounts of PdNP catalyst. The PdNPs stabilized by poly-1,2,3-triazolylferrocenyl dendrimers, recently reported by our group, were shown to be catalytically active in the Suzuki coupling reaction, in organic solvents, at room temperature using low catalyst amounts (between 0.1% and 1 ppm), although these NPs are air-sensitive and the yields were never quantitative (<70%).^[9b,c] These studies showed evidence for the atom-leaching mechanism in Suzuki coupling reaction catalyzed by PdNPs at room temperature, a mechanism analogous to that proposed earlier by de Vries for the high-temperature Heck reaction.^[10]

The DSNs formed with the new poly-1,2,3-triazolylsulphonate dendrimers were tested as catalysts in the Suzuki coupling reaction at 25 °C, in aqueous media [Eq. (5)].

In order to compare the catalytic efficiencies of the new "click" DSNs using different amounts of catalyst, the reactions were carried out using 0.1% mol Pd and 0.01% mol Pd. Thus, in aqueous media, the Suzuki coupling reaction appears to follow the atom-leaching





Figure 4. DSN-G₁: a) TEM image and b) size distribution.



Figure 5. DSN-G₂: a) TEM image and b) size distribution.

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Table 1. Catalytic efficiency (TOF values) and stability (TON values) of the new "click" DSNs in the hydrogenation of allyl alcohol using 0.01% mol Pd.

PdNPs	Diameter ^[a] [nm]	$TOF^{[b]}$ [mol H ₂ (mol Pd) ⁻¹ h ⁻¹]	TON
DSN-G ₀	2.3 ± 0.2	8 088	123 500
DSN-G ₁	2.8 ± 0.4	7 742	100 000
DSN-G ₂	3.0 ± 0.6	5 173	86 000

^[a] Diameter of the DSNs, obtained by TEM.

^[b] The catalytic activity of the DSNs was investigated for the hydrogenation of allyl alcohol at 0.01% mol Pd, in H₂O, 25°C and 1 atm H₂. Reactions were followed by GPC and TOF values were determined on the basis of the yield of formation of propanol.

Table 2. Catalytic efficiency (TOF) and stability (TON) of the water-soluble "click" DSNs in Suzuki coupling reactions of iodobenzene, at 25 °C, using 0.1 and 0.01% mol Pd.

%Pd	PdNPs	<i>t</i> [h]	Yield [%]	TOF ^[a]	TON
0.1%	DSN-G ₀	6 h	96%	167	960
	DSN-G ₁	6 h	95%	158	950
	DSN-G ₂	6 h	70%	117	700
0.01%	$DSN-G_0$	6 h	92%	1 533	9 200
	DSN-G ₁	6 h	94%	1 567	9 400
	DSN-G ₂	6 h	70%	1 167	7 000

^[a] TOFs are expressed in mol PhI (mol Pd)⁻¹h⁻¹. The catalytic activity of the DSNs was investigated for iodobenzene, at 25 °C, in H₂O/ethanol (1:1). Reactions were followed by GPC and TOF values were determinated on the basis of the yield of biphenyl.

mechanism, because there is no significant difference between the TOFs obtained for NPs of different sizes (comparing DSN-G₀ with DSN-G₁ and DSN-G₂) and the catalytic efficiency is higher for lower concentration of catalyst (Table 2).

Bromobenzene was also used as the substrate to test our new "click" DSN catalysts in aqueous conditions. A quantitative yield was obtained for the reaction carried out at 100 °C, using the DSN-G₀ (0.01% mol Pd) which showed an impressive catalytic efficiency [TOF: 8,700 mol H₂ (mol Pd)⁻¹h⁻¹] and high stability (TON: 10,000).

Conclusions

In conclusion, we have synthesized the first-water soluble "click" dendrimers, and shown that they can form PdNPs that are stable DSNs with three dendrimer generations. These new "click" DSNs are very efficient catalysts down to 0.01% mol Pd in aqueous media for allylic alcohol hydrogenation and Suzuki reactions between $PhB(OH)_2$ and PhX (X = I or Br). For the later reaction, they show impressive TOFs and TONs in aqueous media at room temperature for iodobenzene and at 100°C for bromobenzene. Finally, the Pd-atom leaching mechanism^[9c,10] disclosed with triazolylferrocenyl click-DSNs in organic solvent is also operating in aqueous media with the new DSNs, but the yields in Suzuki heterocoupling are quantitative at 0.01% mol Pd with these water-soluble DSNs whereas they were never so with the organic DSNs whatever the DSN catalyst loading. In our previous study with analogous "click" dendrimers containing ferrocenyl and other hydrophobic termal groups, intra- vs. inter-dendritic PdNP stabilization was shown to depend on the dendrimer generation. On the other hand, the stablilization of the PdNPs is always interdendritic with sulphonate-terminated dendrimers in the present study. It is remarkable that, although the stabilization of the PdNPs is not intradendritic but outside the dendrimers, the catalysis is so efficient. It is probable that the environment of the PdNP surface by several dendrimers is optimal concerning the PdNP stabilization without inhibition of the surface Pd atoms. The PdNP is a reservoir of catalytically active Pd atoms, and this combination of outer-dendritic stabilization and lack of surface inhibition appears to be essential for the efficient delivery of catalytically active Pd atoms. It is this very situation that affords the invaluable ligandless approach for the use of Pd catalysis. This efficient ligandless catalysis under ambient conditions in an aqueous solvent compares favourably with other more classic approaches of dendritic palladium catalysis.^[16]

Experimental Section

General Data

The chloromethylsilyl dendrimers were prepared according to ref.^[11] and sodium propargyl sulphonate was prepared according to ref.^[15] Dialysis membranes were purchased from Aldrich.

Transmission Electron Microscopy (TEM)

The samples were prepared by setting a drop of a 4.41×10^{-4} M water solution of PdNPs (concentration in mol Pd) on a holey-carbon-coated Cu TEM grid. The size of the nanoparticles was measured using the software *sigmascan***pro** (for each sample, about 100 nanoparticles were measured).

Gas Chromatography

GPC data were recorded on a Hewlett Packard 5890 Series II gas chromatograph, equipped with a Stabilwax® (Crossband® Carbowax®-PEG) column and a flame ionization

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detector. Helium was used as the carrier gas for all the substratres. The injector and detector temperatures were 240 °C.

General Synthesis of Azido-Dendrimers

The chloroalkyl-dendrimer and sodium azide (2 equiv. per branch) were heated at 80 °C for 16 h in dry DMF. The solvent was removed under vacuum, the crude product was dissolved in dichloromethane, washed twice with water, dried with sodium sulphate, filtered under paper, and the solvent was removed under vacuum. The dendrimer was precipitated using dichloromethane/methanol.

General Procedure for the "Click" Reactions

The azido-dendrimer (1 equiv.) was dissolved in 10 mL of tetrahydrofuran (THF), and 5 mL of an aqueous solution of sodium propargyl sulphonate (1.5 equiv. per branch) was added. CuSO₄ was added (1 equiv. per branch, 1M aqueous solution) at 0°C, followed by dropwise addition of a freshly prepared solution of sodium ascorbate (2 equiv. per branch, 1 M aqueous solution). Water was added, giving a 1:1 THF/ H₂O solution that was allowed to stir for 1 hour at room temperature. After removing THF under vacuum, the dendrimers remained dissolved in the aqueous solution. The dendrimers were purified by dialysis against 1 L of aqueous ammonia solution for three days [in order to remove Cu(I) that remains trapped inside the dendrimer] and against 1 L of water for one day (the dialysis solutions were changed twice a day). After removing water, the poly-1,2,3-sulphonate dendrimers were obtained as colorless waxy products.

Synthesis of 1

The 9-azido-dendrimer 1 was synthesized from the 9-chloromethylsilyl-dendrimer^[11] (0.190 g, 0.130 mmol) using the general procedure for azido-dendrimers. The product 1 was obtained as a colorless waxy product; yield: 0.196 g (0.129 mmol, 99%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 6.94$ (s, 3H, arom. CH), 2.72 (s, 18H, CH₂N₃), 1.62 (s, 18H, SiCH₂CH₂CH₂), 1.07 (s, 18H, SiCH₂CH₂CH₂), 0.58 (s, 18H, $SiCH_2CH_2CH_2)$, 0.042 [Si(CH_3)_2]; ¹³C NMR (CDCl_3, 75.0 MHz): $\delta = 145.7$ (arom. C_q), 121.5 (arom. CH), 43.9 $(SiCH_2CH_2CH_2),$ 41.9 (Cq),41.1 $(CH_2N_3),$ 17.7 (SiCH₂CH₂CH₂), 15.0 (SiCH₂CH₂CH₂), -4.04 [Si(CH₃)₂]; ²⁹Si NMR (CDCl₃, 59.62 MHz): $\delta = 3.33$ (*Si*(CH₃)₂CH₂N₃); IR: $v_{N_3} = 2093 \text{ cm}^{-1}$; anal. calcd. for $C_{63}H_{129}N_{27}Si_9$: C 49.86, H 8.57; found: C 49.31, H 8.30.

Synthesis of 2

The 27-azido-dendrimer **2** was synthesized from the 27chloromethylsilyl-dendrimer^[11] (0.100 g, 0.0163 mmol) using the general procedure for azido dendrimers. The product was obtained as a colorless waxy product; yield: 0.101 g (0.0161 mmol, 99%). ¹H NMR (CDCl₃, 300 MHz): δ =7.16 and 6.89 (double d, 36H, p. C₆H₄ of dendron), 3.53 (s, 18H, SiCH₂O), 2.71 (d, 54H, CH₂N₃), 1.62 (s, 72H, CH₂CH₂CH₂Si), 1.09 (s, 72H, CH₂CH₂CH₂Si), 0.55 (s, 72H, CH₂CH₂CH₂Si), 0.0061 [s, 54H, Si(CH₃)₂CH₂O], 0.043 [s, 162 H, Si(CH₃)₂CH₂N₃]; ¹³C NMR (CDCl₃, 75.0 MHz): $\delta = 159.2$ (OC_{Ar}), 139.1 (arom. C_q of the dendron), 127.2 and 113.6 (arom. CH of the dendron), 60.3 (SiCH₂O), 43.1 (ben-zylic C_q of the core and dendron), 41.1 (CH₂CH₂CH₂Si), 29.8 (SiCH₂N₃), 17.6 (CH₂CH₂CH₂Si), 15.0 (CH₂CH₂CH₂Si), 0.0023 [Si(CH₃)₂CH₂O], -3.99 [Si(CH₃)₂CH₂N₃]; ²⁹Si NMR (CDCl₃, 59.6 MHz): d = 3.33 (SiCH₂N₃), 0.52 (SiCH₂O); IR: v_{N₃} = 2093 cm⁻¹; anal. calcd. for C₂₈₈H₅₄₃O₉N₈₁Si₃₆: C 54.94, H 8.69; found: C 54.16, H 8.54.

Synthesis of 3

The 81-azido-dendrimer 3 was synthesized from the 81chloromethylsilyl-dendrimer^[11] (0.100 g, 0.0050 mmol) using the general procedure for azido-dendrimers. The product was obtained as a colorless waxy product; yield: 0.102 g (0.0049 mmol, 99%). ¹H NMR (CDCl₃, 300 MHz): $\delta = 7.16$ and 6.86 (double d, 144 H, *p*-C₆*H*₄), 3.53 (s, 72 H, SiC*H*₂O), 2.71 (d, 162 H, CH₂N₃), 1.62 (s, 234 H, CH₂CH₂CH₂Si), 1.09 (s, 234H, CH₂CH₂CH₂Si), 0.55 (s, 234H, CH₂CH₂CH₂Si), 0.0062 [s, 216H, Si(CH₃)₂CH₂O], 0.039 [s, 486H, Si-(CH₃)₂CH₂N₃]; ¹³C NMR (CDCl₃, 75.0 MHz): $\delta = 159.5$ (OC_{Ar}) , 139.0 (arom. C_q of the dendron), 127.4 and 113.9 (arom. CH of the dendron), 60.6 (SiCH₂O), 43.4 (benzylic C_q of the core and dendron), 41.4 (CH₂CH₂CH₂Si), 30.1 $(SiCH_2N_3)$, 17.9 $(CH_2CH_2CH_2Si)$, 15.6 $(CH_2CH_2CH_2Si)$, 0.0027 [Si(CH₃)₂CH₂O], -3.74 [Si(CH₃)₂CH₂N₃]; ²⁹Si NMR $(CDCl_3, 59.6 \text{ MHz}): \delta = 3.32 (SiCH_2N_3), 0.51 (SiCH_2O); IR:$ $v_{N_3} = 2093 \text{ cm}^{-1}$; anal. calcd. for $C_{963}H_{1785}O_{36}N_{243}Si_{117}$: C 56.06, H 8.72; found: C 55.31, H 8.62.

Synthesis of 4

The 9-SO₃Na-dendrimer 4 was synthesized from 9-azidodendrimer 1 (0.100 g, 0.066 mmol) and sodium propargyl sulphonate (0.126 g, 0.89 mmol) using the general procedure for "click" reactions. The product was obtained as a colorless waxy product; yield: 0.133 g (72%). ¹H NMR (D_2O_2 , 300 MHz): $\delta = 7.83$ (s, 9H, CH of triazole), 6.96 (s, 3H, CH of arom. core), 4.19 (s, 18H, CH₂SO₃Na), 3.98 (s, 18H, SiCH₂-triazole), 1.61 (s, 18H, CH₂CH₂CH₂Si), 1.07 (s, 18H, CH₂CH₂CH₂Si), 0.56 (s, 18H, CH₂CH₂CH₂Si), -0.013 [s, 54 H, Si(CH₃)₂]; ¹³C NMR (D₂O/MeOD, 75.0 MHz): $\delta =$ 145.5 (C_g of triazole), 127.9 (CH of arom. core), 122.1 (CH of triazole), 51.2 (CH₂SO₃Na), 43.9 (SiCH₂CH₂CH₂), 41.9 (benzylic Cq), 35.2 (SiCH₂-triazole), 22.1 (SiCH₂CH₂CH₂), 17.3 $(SiCH_2CH_2CH_2)$, -4.0 $[Si(CH_3)_2]$; anal. calcd. for C₉₀H₁₅₆O₂₇S₉N₂₇Si₉Na₉: C 38.65, H 5.62; found: C 37.62, H 5.41. Polydispersity index obtained by SEC: 1.00.

Synthesis of 5

The 27-SO₃Na-dendrimer **5** was synthesized from the 27azido-dendrimer **2** (0.070 g, 0.011 mmol) and sodium propargyl sulphonate (0.064 g, 0.45 mmol) using the general procedure for "click" reactions. The product was obtained as a colorless waxy product; yield: 0.075 g (66%). ¹H NMR (D₂O/MeOD, 300 MHz): δ =7.82 (s, CH of triazole), 7.12 and 6.76 (s, arom. CH of dendron), 4.19 (s, CH₂SO₃Na), 3.94 (s, SiCH₂-triazole), 3.59 (s, SiCH₂O), 1.52 (s, CH₂CH₂CH₂Si), 1.02 (s, CH₂CH₂CH₂Si), 0.49 (s, CH₂CH₂CH₂Si), -0.074 [s, Si(CH₃)₂]; ¹³C NMR (D₂O/MeOD, 75.0 MHz): δ =145.5 (C_q of triazole), 128.2 and 114.6 (arom. CH of the dendron), 122.1 (CH of triazole), 60.3 (SiCH₂O), 50.5 (CH₂SO₃Na), 43.9 (SiCH₂CH₂CH₂), 41.9 (benzylic Cq), 34.2 (SiCH₂-triazole), 21.1 (SiCH₂CH₂CH₂), 17.3 (SiCH₂CH₂CH₂), -4.0 [Si-(CH₃)₂]. Polydispersity index obtained by SEC: 1.01.

Synthesis of 6

The 81-SO₃Na-dendrimer 6 was synthesized from the 81azido-dendrimer 3 (0.050 g, 0.0024 mmol) and sodium propargyl sulphonate (0.042 g, 0.29 mmol) using the general procedure for "click" reactions. The product was obtained as a colorless waxy product; yield: 0.041 g (53%). ¹H NMR $(D_2O/MeOD, 300 \text{ MHz}): \delta = 7.89 \text{ (s, CH of triazole)}, 7.09$ and 6.83 (s, arom. CH of dendron), 4.10 (s, CH₂SO₃Na), 3.94 (s, SiCH₂-triazole), 3.58 (s, SiCH₂O), 1.51 (s, CH₂CH₂CH₂Si), 1.01 (s, CH₂CH₂CH₂Si), 0.52 (s, CH₂CH₂CH₂Si), -0.068 [s, Si(CH_3)₂]; ¹³C NMR (D₂O/MeOD, 75.0 MHz): $\delta = 145.8$ (C_q of triazole), 127.9 and 114.8 (arom. CH of the dendron), 122.5 (CH of triazole), 60.3 (SiCH₂O), 50.8 (CH₂SO₃Na), 43.9 (SiCH₂CH₂CH₂), 41.9 (benzylic Cq), 34.8 (SiCH₂-triazole), 21.8 (SiCH₂CH₂CH₂), 17.3 (SiCH₂CH₂CH₂), -4.0 [Si-(CH₃)₂]. Polydispersity index obtained by SEC: 1.01. Hydrodynamic diameter obtained by dynamic light scattering in water: 25.8 ± 0.7 nm.

General Procedure for the Preparation of the PdNP's

The procedure is described using the preparation of DSN-G₀ as an example: 1 mL of a 3.6×10^{-4} M water solution of dendrimer 4-G₀ (1.0 mg, 3.6×10^{-4} mmol) was introduced in a Schlenk flask. 1.1 mL of a 2.9×10^{-3} M water solution of K₂PdCl₄ (1.1 mg, 3.2×10^{-3} mmol, 1 equiv *per* triazole) was added. Water was added, providing a 8.82×10^{-4} M (in Pd) solution that was stirred for 5 min, then NaBH₄ (1 mg, 3.2×10^{-2} mmol, 10 equiv. per Pd) was added, and the light yellow solution turned to black indicating the nanoparticle formation.

Hydrogenation Reactions

The nanoparticles were freshly prepared in a Schlenk flask in an aqueous solution $(8.82 \times 10^{-4} \text{ M} \text{ in Pd})$, and 10,000 equiv. of the substrate was added. The Schlenk flask was filled with H₂ (1 atm), and the solution was allowed to stir at 25 °C. For re-use of the catalyst, the substrate was added to the reaction solution until the catalyst was no longer active. Calculation of the turnover frequency (TOF) was carried out using several samples of the solution that were extracted at different reaction times and analyzed. Calculation of the turnover number (TON) was carried out using the sum of substrate that reacted in all the catalytic cycles, after analyzing the final reaction solution.

Suzuki Reactions with DSNs

In a Schlenk flask, the nanoparticles were freshly prepared in aqueous solution (8.82×10^{-4} M in Pd), then ethanol was added, providing a 1:1 water/ethanol solution. K₃PO₄, phenylboronic acid and iodobenzene or bromobenzene were successively added. The solution was allowed to stir under N₂ at 25°C for iodobenzene and at 100°C for bromobenzene.

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References

- Aqueous-Phase Organometallic Catalysis. Concepts and Applications, 2nd edn., (Eds.: B. C. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, 2004; F. Joo, Acc. Chem. Res. 2002, 35, 738.
- [2] For aqueous-biphasically catalyzed Suzuki reactions using organometallic catalysts, see: M. Beller, J. G. E. Krauter, A. Zapf, Angew. Chem. Int. Ed. Engl. 1997, 36, 772; E. Paetzold, G. Oehme, J. Mol. Cat. A 2000, 152, 69; C. Dupuy, K. Adiey, L. Charruault, V. Michelet, M. Savignac, J.-P. Genêt, Tetrahedron Lett. 2001, 42, 6523.
- [3] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory* and *Practice*, Oxford University Press, New York, **1998**.
- [4] H. Bönnemann, W. Brijoux, in: Active Metals, (Ed.: A. Fürstner), VCH, Weinheim, 1996, p 339; M. T. Reetz, W. Helbig, S. A. Quaiser, in: Active Metals, (Ed.: A. Fürstner), VCH, Weinheim, 1996, p 279; N. Toshima, Y. Yonezawa, New J. Chem. 1998, 22, 1179; B. F. G. Johnson, Coord. Chem. Rev. 1999, 190, 1269; A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 2002, 102, 3757; S. Mandal, P. R. Selvakannan, D. Roy, R. V. Chaudhari, M. Sastry, Chem. Commun. 2002, 3002; J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichner, J. Am. Chem. Soc. 2002, 124, 4228; H. Ohde, C. M. Wai, J. Kim, M. Ohde, J. Am. Chem. Soc. 2002, 124, 4540; A. Roucoux, J. Schulz, H. Patin, Adv. Syn. Catal. 2003, 345, 222; H. Bönnemann, K. S. Nagabushana, in: Encyclopedia of Nanoscience and Nanotechnology, (Ed.: H. S. Nalwa), ASP, Stevenson Ranch, 2004, Vol. 1, p 777; M. Bronstein, in: Encyclopedia of Nanoscience and Nanotechnology, Vol 7, (Ed.: H.S. Nalwa), ASP, Stevenson Ranch, 2004, p 193; M. Bronstein, in: Dekker Encyclopedia of Nanoscience and Nanotechnology, (Eds.: J. A. Schwarz, C. I. Contescu, K. Putyera), Marcel Dekker, New York, 2004, p 2903; F. Lu, J. R. Aranzaes, D. Astruc, Angew. Chem. Int. Ed. 2005, 44, 7852; D. Astruc, Inorg. Chem. 2007, 46, 1884; Nanoparticles and Catalysis, (Ed.: D. Astruc), Wiley-VCH, Weinheim, 2007.
- [5] For metallodendrimer catalysis, see: G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* 1999, 99, 1689; D. Astruc, F. Chardac, *Chem. Rev.* 2001, 101, 2991; G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* 2001, 40, 1828; R. Kreiter, A. W. Kleij, R. J. M. K. Gebbink, G. van Koten, in: *Dendrimers IV: Metal Coordination, Self Assembly, Catalysis*, (Eds.: F. Vögtle, C. A. Schalley), *Top. Curr. Chem.* Springer Verlag, Berlin, 2001, Vol. 217, p 163; R. van Heerbeeck, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* 2002, 102, 3717; D. Astruc, D. Méry, *Coord. Chem. Rev.* 2005, 250, 1965.

- [6] M. Zhao, L. Sun, R. M. Crooks, J. Am. Chem. Soc. 1998, 120, 4877; L. Balogh, D. A. Tomalia, J. Am. Chem. Soc. 1998, 120, 7355; K. Esumi, A. Suzuki, N. Aihara, K. Usui, K. Torigoe, Langmuir 1998, 14, 3157.
- [7] Reviews: R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, Acc. Chem. Res. 2001, 34, 181; R. W. J. Scott, O. M. Wilson, R. M. J. Crooks, Phys. Chem. B 2005, 109, 692.
- [8] For click chemistry, see: H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004; V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51.
- [9] a) C. Ornelas, J. R. Aranzaes, E. Cloutet, S. Alves, D. Astruc, Angew. Chem. Int. Ed. Engl. 2007, 46, 872;
 b) C. Ornelas, L. Salmon, J. Ruiz, D. Astruc, Chem. Commun. 2007, 4946;
 c) A. Diallo, C. Ornelas, J. R. Aranzaes, L. Salmon, D. Astruc, Angew. Chem. Int. Ed. 2007, 46, 8644;
 C. Ornelas, L. Salmon, J. Ruiz, D. Astruc, Chem. Eur. J. 2008, 14, 50.
- [10] A. H. M. de Vries, F. J. Parlevliet, L. Schmeder-van de Vondervoort, J. H. M. Mommers, H. J. W. Hender-ickx, M. A. N. Walet, J. G. de Vries, *Adv. Synth. Catal.* 2002, 344, 996; A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Hendericks, J. G. de Vries, *Org. Lett.* 2003, 5, 3285; J. G. de Vries, *Dalton Trans.* 2006, 421; N. T. S. Phan, M. Van der Sluys, C. J. Jones, *Adv. Synth. Catal.* 2006, 348, 609.
- [11] a) F. Moulines, D. Astruc, Angew. Chem. Int. Ed. Engl. 1988, 27, 1347; F. Moulines, L. Djakovitch, R. Boese, B. Gloaguen, W. Thiel, J.-L. Fillaut, M.-H. Delville, D. Astruc, Angew. Chem. Int. Ed. Engl. 1993, 32, 1075; V. Sartor.; L. Djakovitch, J.-L. Fillaut, F. Moulines, F. Neveu, V. Marvaud, J. Guittard, J.-C. Blais, D. Astruc, J. Am. Chem. Soc. 1999, 121, 2929; b) J. Ruiz, G. La-

fuente, S. Marcen, C. Ornelas, S. Lazare, J.-C. Blais, E. Cloutet, D. Astruc, J. Am. Chem. Soc. 2003, 125, 7250.

- [12] The size of the PdNPs was calculated using the equation n=4π r³/3V_g, where n is the number of Pd atoms, r is the radius of the Pd nanoparticle and V_g is the volume of one Pd atom (15 Å³): D. V. Leff, P. C. Ohara, J. R. Heath, W. M. Gelbart, J. Phys. Chem. 1995, 99, 7036; A. Labande, J. Ruiz, J. , D. Astruc, J. Am. Chem. Soc. 2002, 124, 1782; M.-C. Daniel, J. Ruiz, S. Nlate, J.-C. Blais, D. Astruc J. Am. Chem. Soc. 2003, 125, 2617; R. W. J. Scott, O. M. Wilson, S.-K. Oh, E. A. Kenik, R. M. Crooks, J. Am. Chem. Soc. 2004, 126, 15583.
- [13] Y. Niu, L. K. Yeung, R. M. Crooks, J. Am. Chem. Soc. 2001, 123, 6840; S.-K. Oh, Y. Niu, R. M. Crooks, Langmuir 2005, 21, 10209; O. M. Wilson, M. R. Knecht, J. C. Garcia-Martinez, R. M. Crooks, J. Am. Chem. Soc. 2006, 128, 4510.
- [14] E. H. Rahim, F. S. Kamounah, J. Frederiksen, J. B. Christensen, *Nano Letters* 2001, 9, 499; L. K. Yeung, R. M. Crooks, *Nano Letters* 2001, 1, 14; M. Pittelkow, K. Moth-Poulsen, U Boas, J. B. Christensen, *Langmuir* 2003, 19, 7682; R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* 2004, 108, 8572.
- [15] E.-H. Ryu, Y. Zhao, Org. Lett. 2005, 6, 1035.
- [16] K. Heuze, D. Mery, D. Gauss, D. Astruc Chem. Commun. 2003, 2274; K. Heuzé, D. Méry, D. Gauss, J.-C. Blais, D. Astruc, Chem. Eur. J. 2004, 10, 3936; J. Lemo, K. Heuzé, D. Astruc Org. Lett. 2005, 7, 2253; Y. F. Lu, J. Ruiz, D. Astruc Tetrahedron Lett. 2004, 9443; D. Astruc, K. Heuze, S. Gatard, D. Méry, S. Nlate, L. Plault Adv. Synth. Catal. 2005, 347, 329; J. Lemo, K. Heuze, D. Astruc Inorg. Chim. Acta 2006, 359, 4909; J. Lemo, K. Heuze, D. Astruc Chem. Commun. 2007, 4351.