CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200701410

"Click" Dendrimers: Synthesis, Redox Sensing of $Pd(OAc)_2$, and Remarkable Catalytic Hydrogenation Activity of Precise Pd Nanoparticles Stabilized by 1,2,3-Triazole-Containing Dendrimers

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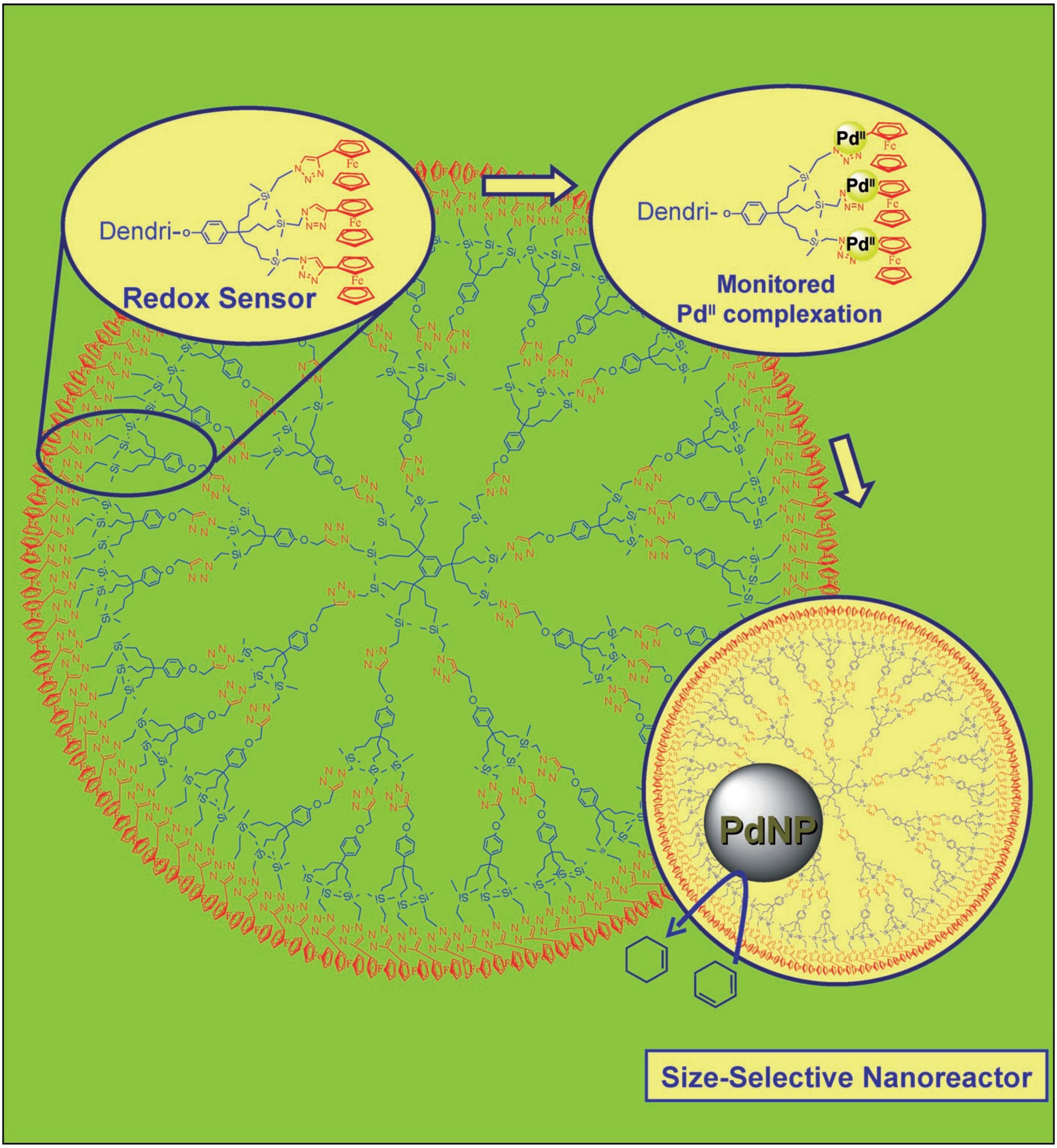

Abstract: “Click” dendrimers containing 1,2,3-triazolyl ligands that coordinate to $Pd^{II}(OAc)_2$ have been synthesized in view of catalytic applications. Five of these dendrimers contain ferrocenyl termini directly attached to the triazole ligand in order to monitor the number of Pd^{II} that are introduced into the dendrimers by cyclic voltammetry. Reduction of the Pd^{II}–triazole dendrimers by using $NaBH_4$ or methanol yields Pd nanoparticles (PdNPs) that are stabilized either by several dendrimers (G_0, DSN) or by encapsulation inside a dendrimer (G_1 and G_2: DEN), as confirmed by TEM. Relative to PAMAM–DENs (PAMAM = poly(amidoamine)), the “click” DSNs and DENs show a remarkable efficiency and stability for olefin hydrogenation under ambient conditions of various substrates. The influence of the reductant of Pd^{II} bound to the dendrimers is dramatic, reduction with methanol leading to much higher catalytic activity than reduction with $NaBH_4$. The most active NPs are shown to be those derived from dendrimer G_1, and variation of its termini groups (ferrocenyl, alkyl, phenyl) allowed us to clearly delineate, optimize, and rationalize the role of the dendrimer frameworks on the catalytic efficiencies. Finally, hydrogenation of various substrates catalyzed by these PdNPs shows remarkable selectivity features.

Keywords: dendrimers • ferrocene • heterogeneous catalysis • hydrogenation • nanoparticles • palladium

Introduction

Dendrimers[1] occupy a privileged place among branched macromolecules,[2] because they are multifacet monodisperse macromolecular compounds, the supramolecular properties of which[3] have potential applications in medicinal chemistry[4] and others fields of nanosciences, such as sensors[5] and green catalysts.[6] Dendrimers have indeed been shown to encapsulate a variety of substrates of interest,[3] as exemplified by the concept of “molecular box”.[3a] The incorporation of metals into the dendrimer backbone brought a variety of novel properties in dendrimer chemistry and was in particular applied to catalysis.[7] Since the turn of the millennium, the interest in nanoparticle (NP) catalysts has considerably increased, because this class of catalysts appears as one of the most promising solutions towards efficient reactions under mild, environmentally benign conditions in the context of green chemistry.[8] The stabilization of NPs for further catalytic use has been achieved by a variety of means including polymers, ligands, surfactants, ionic liquids, and supercritical micro-emulsions.[9] While all these stabilization media provide small, catalytically efficient NPs, one of the very best ways to control particle sizes and morphologies in order to understand and optimize the NP catalytic activity is that using dendrimers.[7]

The synthesis of NPs stabilized by dendrimers was first reported in 1998[10] either by encapsulation of the NP within a single dendrimer (dendrimer-encapsulated NPs, DENs) or by surrounding the NPs by several dendrimers (dendrimer-stabilized NPs, DSN). PAMAM-OH or PPI-modified dendrimers (PAMAM-OH = poly(amidoamine)-OH, PPI = poly(propyleneimine)) are the most common dendrimers used to encapsulate the NPs; the interior amido or amino groups first bind the transition-metal cations followed by its reduction to metal atoms forming NPs that remain inside the dendrimer.[7,11] The dendrimer structure is thus used as template to prepare monodispersed NPs. Depending on the encapsulated metal NPs, DENs showed unusual properties as catalysts for hydrogenation[7,12–14] and C–C coupling reactions.[15] Hydrogenation reactions in organic synthesis and industrial applications are an essential research field devoted to the design of more selective catalysts, such as transition-metal NP-based catalysts.[16]

Palladium is one of the most efficient metals in catalysis, and Pd–DENs have been widely investigated.[7] The catalytic activity of the Pd–DENs evidently depends on their nature (PAMAM, PPI, or other), generation, size, and the kind of functional group at the dendrimer periphery.

Crooks et al. pioneered[7] the use of DENs as catalysts and reported the hydrogenation of allylic alcohols in aqueous solutions, presenting catalytic efficiencies around $500\,mol\,H_2(mol\,Pd)^{-1}\,h^{-1}$; TOF, turn over frequency) for monometallic Pd DENs.[13] Bimetallic DENs have also been tested in catalysis, in aqueous conditions, giving TOF values of $1300\,mol\,H_2(mol\,Pd)^{-1}\,h^{-1}$ both with Au/Pd-DENs for hydrogenation of allyl alcohol[17] and Pd/Rh-DENs for partial hydrogenation of 1,3-cyclooctadiene.[18] Esumi et al.[19] modified PAMAM dendrimers with hydrophobic groups in order to study the formation of DENs in organic solvents (M = Au, Pt). Crooks et al. used this synthetic approach to synthesize hydrophobic Pd–DENs, using modified–PPI dendrimers and tested them as catalysts in organic solvents.[14] These Pd–DENs gave initial TOFs, for hydrogenation of 1-hexene, of $120\,mol\,H_2(mol\,Pd)^{-1}\,h^{-1}$ in $CHCl_3$/MeOH (2:1) and were

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being quite instable under hydrogenation conditions (precipitation after 20 min).[14] However, all these studies have been carried out exclusively with PAMAM or PPI dendrimers. Therefore, it is essential to design specific ligand-containing dendrimers with several generations to examine and optimize the key parameters governing the catalytic properties, that is, efficiency, selectivity, and stability.

Our group has recently reported, in a preliminary form, the synthesis of some poly-1,2,3-triazolylferrocenyl[20] dendrimers assembled by "click" chemistry;[21] these dendrimers contain triazole units and are able to complex metal cations. One of our goals is to investigate the NP encapsulation properties of these new hydrophobic, heterocyclic-ligand-containing dendrimers, in order to examine the influence of the structural and functional dendritic features on the catalytic efficiency and stability. Another goal is for these dendrimers to serve as sensors inter alia of metal ions so as to control the stoichiometry and number of Pd^{II} that can be introduced into each dendrimer. Successful sensing of cationic transition-metal ions could indeed so far be achieved.

In the present article, we report new poly-1,2,3-triazolyl dendrimers including dendrimers that contain ferrocenyl termini.[20] These dendrimers were assembled and functionalized by click chemistry[21] and thus all contain 1,2,3-triazole units. They are able to 1) complex Pd^{II}, 2) stabilize and encapsulate PdNPs, and 3) produce highly active and size-selective DENs catalysts for hydrogenation. The variation of the dendritic structure in the interior backbone and periphery of the dendrimers allows to investigate the influence of these structural variations on the catalytic properties of the new DENs. The dramatic effect of the nature of the reducing agent ($NaBH_4$ vs. methanol) opposite to that known in polymer-stabilized PdNP catalysis and the remarkably size-selective properties of the catalysts with various olefin substrates are also reported and discussed in this article.

Results and Discussion

Synthesis and functionalization of the triazolyl dendrimers: To efficiently complex palladium(II) and improve the stabilization of PdNPs, dendrimers containing triazole ligands were designed by "click chemistry".[20]

The dendritic construction starts with the known nona-allylation of [FeCp(η^6-mesitylene)][PF_6], quantitatively yielding the nona-allyl dendritic core **1** on a large scale subsequent to visible-light photolysis that removes the metal moiety.[22] Hydrosilylation of terminal olefinic bonds of the nona-allyl core, with $HSiMe_2(CH_2Cl)$ and Karsted catalyst, regioselectively gives the nonachloromethyl(dimethyl)silyl (dendri-$(CH_2Cl)_9$) intermediate, **3**,which upon reaction with NaN_3 provides the nona-azide **4**.

The known phenoltriallyl dendronic brick p-$HOC_4H_4C(CH_2CH{=}CH_2)_3$ (**2**), obtained by one-pot reaction of [FeCp(η^6-*p*-chlorotoluene][PF_6] with allyl bromide and *t*BuOK,[22] is functionalized using propargyl bromide at the phenol focal point, giving the new dendron **5** suitable for click chemistry. Then, the Cu^I-induced click reaction between **4** and **5** in water/THF yielded the first-generation 27-allyl dendrimer **6**, assembled with nine 1,2,3-triazole links; it is characterized by its molecular peak at 3937.42 ($[M+Na]^+$) in the MALDI TOF mass spectrum (calcd for $C_{234}H_{327}N_{27}O_9Si_9Na$: 3938.04). Repetition of this sequence of reactions yield the 27-azido intermediate **8**, then the 81-allyl second-generation dendrimer **9**, containing 36 triazole links in two layers (9 + 27) (see Scheme 1). Note, that whereas this "click" reaction is usually catalytic in Cu^I (5% Cu^I is used by most authors), the present click dendrimer synthesis requires a *stoichiometric amount* of Cu^I, because Cu^I remains trapped inside the dendrimer and is only removed as $Cu^I(NH_3)_6^+$ by washing with an aqueous ammonia solution. This feature is further confirmed by the recognition and titration studies of the click dendrimers with Cu^I.[20] On the other hand, an advantage of this procedure variation is that the click reaction is much faster here than in the standard procedure (0.5 h at 20 °C instead of 16 h).

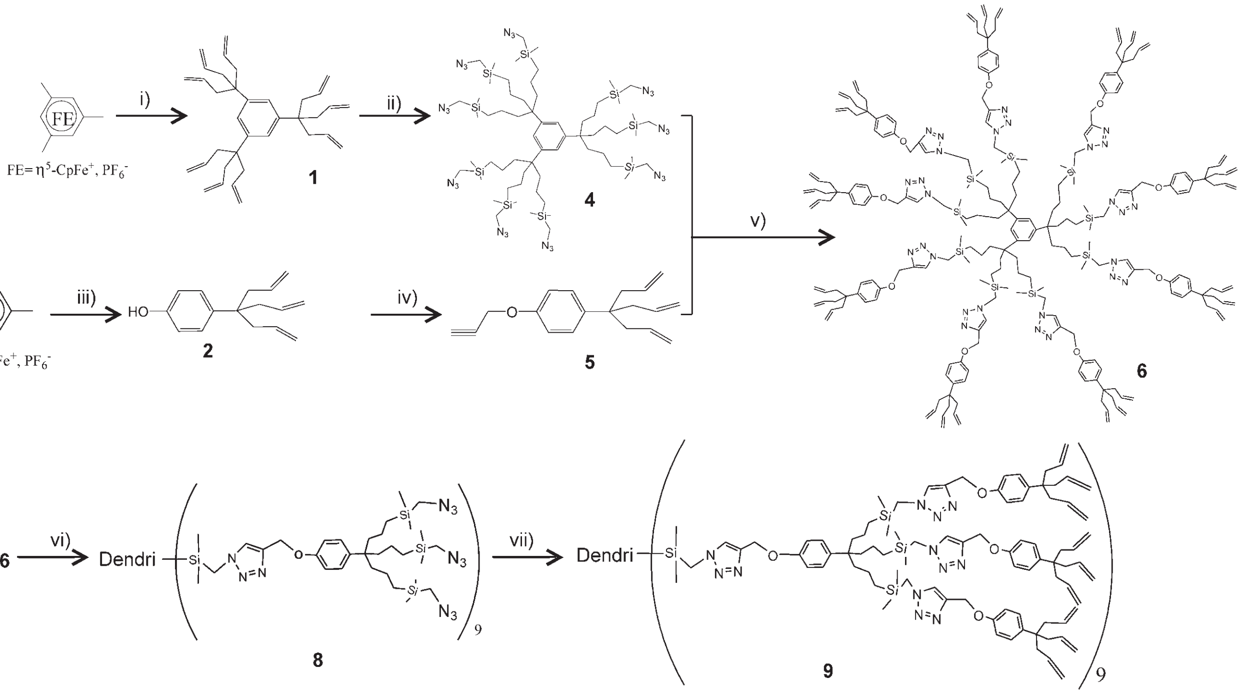
Reactivity studies carried out at different temperatures, to study the regioselectivity of the click reaction in the dendritic construction, show that the formation of the undesired 1,5-disusbtituted 1,2,3-triazole isomer is favored by an increase in temperature. For example, at 50 °C, both 1,4- and 1,5-isomers are obtained in a 7:3 ratio and can be easily identified by their different NMR signals for the triazole proton ($\delta=7.49$ ppm for the 1,4-isomer and $\delta=7.62$ ppm for the 1,5-isomer, see the Supporting Information p. 44). The click dendrimers reported here do not present any trace of 1,5-disubstituted 1,2,3-triazole isomer. This selectivity is achieved by adding the sodium ascorbate dropwise at 0 °C, this procedure minimizes the heating caused by the exothermic click reaction and therefore avoids the formation of the 1,5-isomer.

These dendrimers can be further functionalized with ethynylferrocene, also by "click chemistry", generating triazolylferrocenyl dendrimers.[20]

To study the dendritic effects on the type of NP stabilization and on the catalysts performance, three different generations of poly-1,2,3-triazolylferrocenyl dendrimers were synthesized: G_0 with nine terminal ferrocenyl-triazole units (**12**-G_0), G_1a with 36 triazole units (9 interior + 27 terminal) (**13**-G_1a) and G_2a with 117 triazole units (9+27 interior + 81 terminal) (**14**-G_2a) (see Scheme 2). The nona-triazolylferrocenyl dendrimer **12**-G_0 is characterized by its molecular peak at 3408.18 ($[M]^+$) in the MALDI TOF mass spectrum (calcd for $C_{171}H_{219}N_{27}Si_9Fe_9$: 3408.12); all the rest of dendrimer series was further characterized by size-exclusion chromatography (SEC), showing the size progression and polydispersity lower than 1.02.

The role of the interior triazole units on the encapsulation and catalytic efficiency of the PdNPs was also studied with poly-1,2,3-triazolylferrocenyl dendrimers that do not contain interior triazole units, and that only have triazolylferrocenyl units at the periphery.

Dendrimers assembled by the Williamson coupling reaction[22] (dendri-$(CH_2Cl)_{27}$ and dendri-$(CH_2Cl)_{81}$) provide,



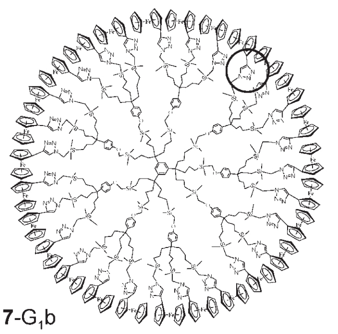
Scheme 1. "Click" assembly of dendrimers.i) 1. CH_2=$CHCH_2Br$, KOH, THF, RT, 3 d; 2. *hν*vis, MeCN; ii) 1. $HSiCH_2(CH_3)_2Cl$, Kartsted catalyst, diethyl ether, RT, 13 h; 2. NaN_3, DMF, 16 h, 80 °C; iii) CH_2=$CHCH_2Br$, *t*BuOK, THF, RT, 5 d; iv) propargyl bromide, acetone, reflux, 16 h; v) $CuSO_4$, sodium ascorbate, THF/H_2O, RT, 30 min; vi) 1. $HSiCH_2(CH_3)_2Cl$, Kartsted catalyst, dietehyl ether, RT, 13 h; 2. NaN_3, DMF, 16 h, 80 °C; vii) $CuSO_4$, sodium ascorbate, **5**, THF/H_2O, RT, 30 min.

upon reaction with NaN_3, the azido dendrimers dendri-$(CH_2N_3)_{27}$ (**15**) and dendri-$(CH_2N_3)_{81}$ (**16**) that further react with ethynylferrocene by "click" chemistry yielding G_1b (**17**-G_1b) with 27 triazolyl-ferrocenyl termini and G_2b (**18**-G_2b) with 81 triazolyl-ferrocenyl termini, respectively (full drawings of the structures of **15** and **16** are available in the Supporting Information).

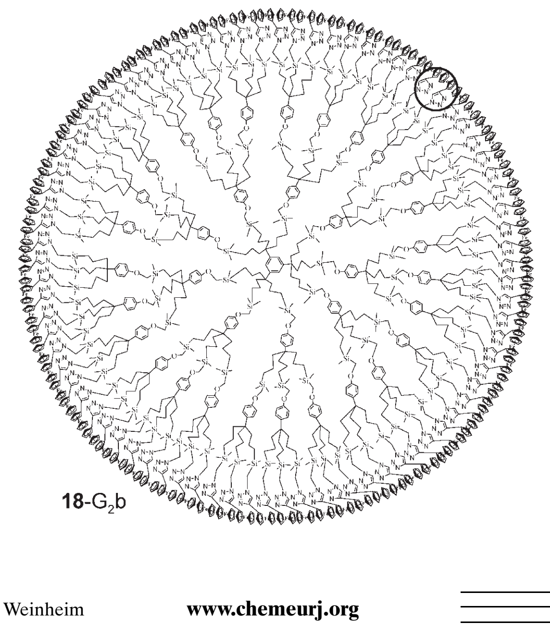
Both 81-triazolylferrocenyl dendrimers (**14**-G_2a and **18**-G_2b) are also characterized by dynamic light scattering (DLS) that provide the diameters of these dendrimers in dichloromethane: **14**-G_2a: 12 ± 0.5 nm, **18**-G_2b: 9 ± 0.5 nm.

The poly-1,2,3-triazolylferrocenyl dendrimers present a bulky periphery due to the ferrocenyl group located at the termini of the dendritic tethers. To confirm the crucial role of the bulky periphery and to understand the influence of the ferrocenyl group on the stabilization of the PdNP and catalyst performances, the 27 ferrocenyl terminal units of **17**-G_1b were replaced by 27 dendronic-9-propyl units (**21**-G_1c) (bulky) and by 27 phenyl units (**22**-G_1d) (not bulky). The synthesis of these dendrimers was also carried out by "click chemistry" between the dendri-$(CH_2N_3)_{27}$ (**16**) and the ethynyl-dendronic-9-propyl (**20**) and phenylacetylene (see Scheme 3).

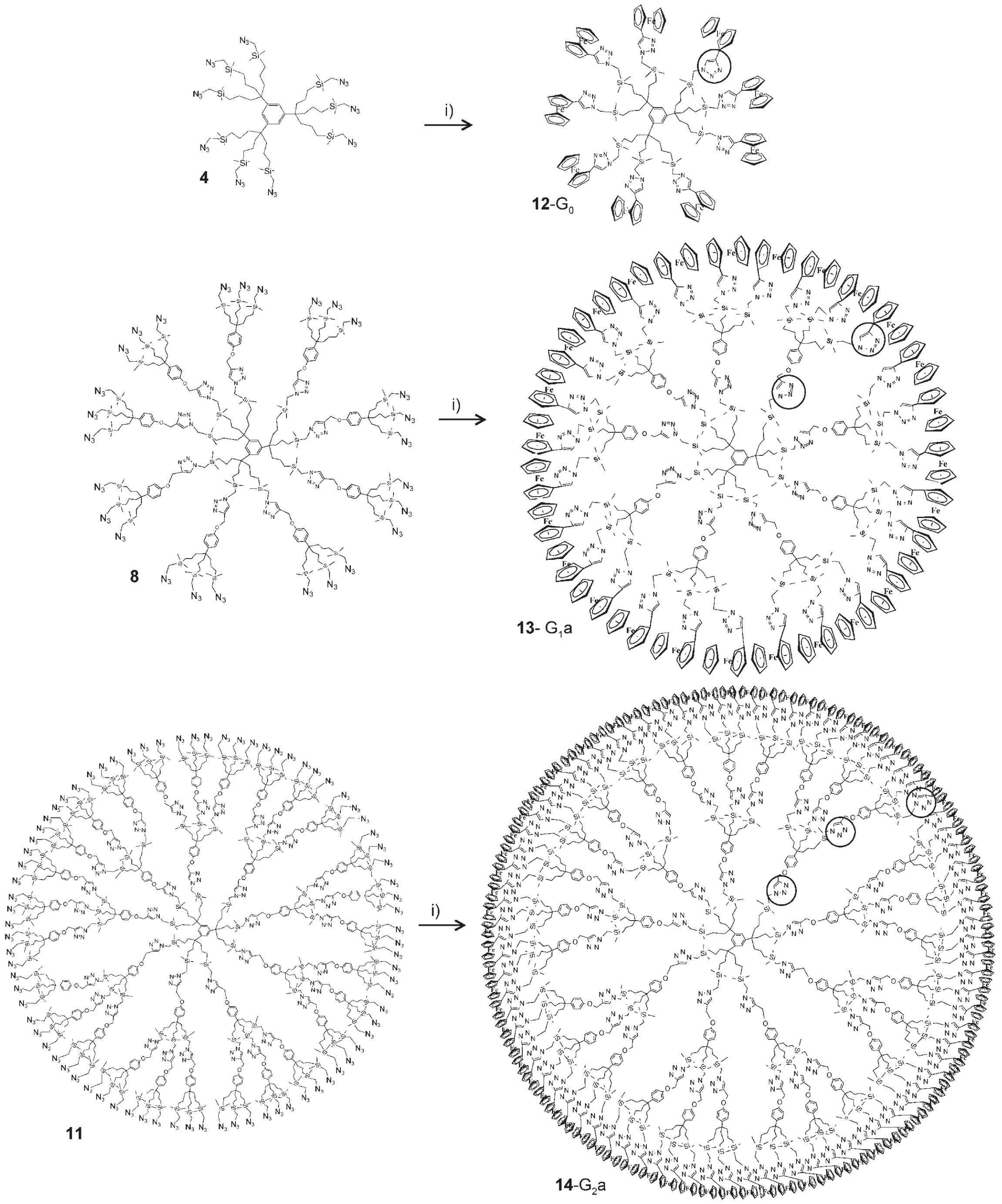
All the seven poly-1,2,3-triazolyl dendrimers reported here were used to stabilize PdNPs (characterized by transmition electron microscopy, TEM) and tested as catalysts in hydrogenation of styrene at 0.1 % mol Pd. Different types of PdNP stabilization caused by the variation of dendrimer



17-G_1b



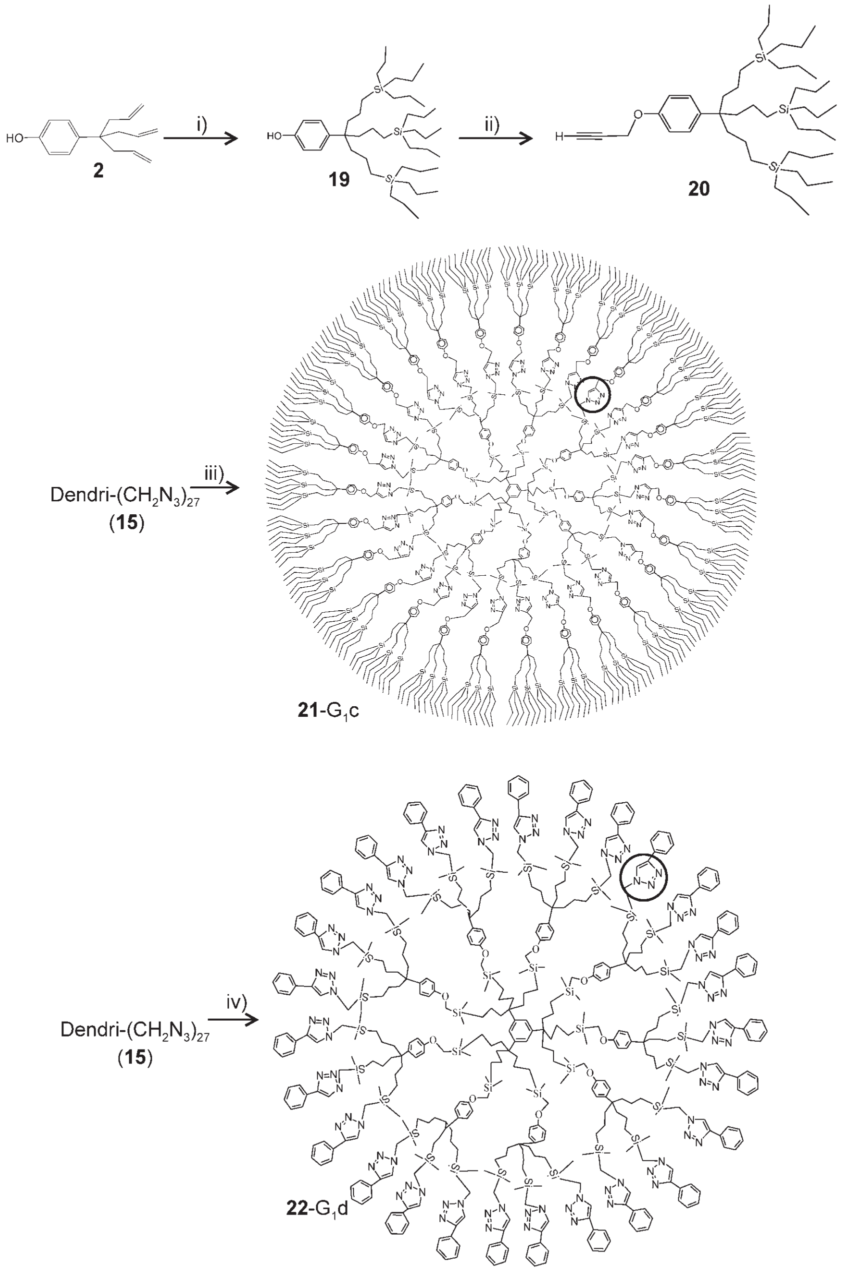
18-G_2b



Scheme 2. Synthesis of the 1,2,3-triazolylferrocenyl dendrimers by "click Chemistry". i) $CuSO_4$, sodium ascorbate, THF/H_2O, RT, 30 min, ethynylferrocene.

structures and the influence of the dendritic structure on the catalytic performances are discussed further in this article.

Complexation of $Pd(OAc)_2$ to the triazole ligands inside the dendrimer: The complexation of $Pd(OAc)_2$ to the triazole groups of the poly 1,2,3-triazolylferrocenyl dendrimers was monitored by cyclic voltammetry,[23] and UV/Vis and ^{1}H NMR spectroscopy. In the cyclic voltammetry studies, the ferrocenyl group, directly attached to the triazole fragment, was used as a redox monitor. The poly-1,2,3-triazolylferrocenyl dendrimers show a single, fully reversible cyclic voltammetry (CV) wave for all the equivalent (but distant) ferrocenyl groups, the potentials of which are similar and the electrostatic factor being very weak.[24] Complexation of $Pd(OAc)_2$ to the poly-1,2,3-triazolylferrocenyl dendrimers in $CHCl_3$/MeOH (2:1) gives a new reversible CV wave that appears at a potential more positive than that of the initial wave, showing that the Pd–dendrimer assembly is more dif-



Scheme 3. Synthesis of the dendron **20** and dendrimers **21**-G_1c and **22**-G_1d. i) $HSi(CH_2CH_2CH_3)_3$, Karsted catalyst, diethyl ether, RT, 15 d; ii) propargyl bromide, acetone, reflux, 16 h; iii) $CuSO_4$, sodium ascorbate, **20**, THF/H_2O, RT, 5 h; iv) $CuSO_4$, sodium ascorbate, phenylacetylene, THF/H_2O, RT, 30 min.

ficult to oxidize than the dendrimer alone. Titrations of $Pd(OAc)_2$ with poly-1,2,3-triazolylferrocenyl dendrimers indicates that each triazole unit binds one $Pd(OAc)_2$ (see Table 1 and Figure 1 for CV data). Moreover, the titration graphs show that, for **13**-G_1a, which possesses two triazole layers, the intensity of the ferrocenyl wave does not vary before 25 % (i.e., 9 out of 36) of the Pd^{II} species is added to the dendrimer solution. This means that the inner triazole layer (nine triazoles) binds Pd^{II} first, and the ferrocenyltriazoles only bind Pd^{II} when the inner triazole ligands are already saturated with Pd^{II}. For **14**-G_2a, the initial ferrocenyl wave does not decrease before 20 Pd^{II} fragments are added per dendrimer. This amount is lower than the two first-generations (36 triazoles), indicating that Pd^{II} starts binding to the ferrocenyltriazole at the periphery before the second triazole layer is saturated. This means that complexation of the inner layers occurs somewhat selectively, but this selectivity is not as complete as for **13**-G_1a. The outer triazole rings bear a ferrocenyl ring that carries more steric bulk than the inner triazole rings that are connected to the tethers by two methylene groups, and this steric effect alone could account for the observed selectivity.

For complexation of the triazole unit to palladium, the presence of methanol is required, since no interaction is observed in CH_2Cl_2 or $CHCl_3$ (Figure 30 of the Supporting Information). It is known that methanol (as well as water) readily breaks the trimeric species $[\{Pd(OAc)_2\}_3]$ upon dechelating one or more acetate ligands.[26] After one of the acetate ligands is dechelated, the triazole ligand binds the metal, thereby accelerating the reduction of Pd^{II} to Pd^0, (see NMR data, Figures 26–32 of the Supporting Information). Indeed, a few minutes after addition of $Pd(OAc)_2$ to the dendrimer in methanol, the UV/Vis spectra of the dendrimers show a new band at 278 nm that corresponds to the start of the PdNP formation and stabilization by the triazole interaction (Figure 8 of the Supporting Information). This band remains after the formation of the PdNPs (either using $NaBH_4$ or methanol as reducing agent). The UV/Vis spectrum of $Pd(OAc)_2$ also shows the complete disappearance of the initial band at 399 nm and the appearance of a large band at 300 nm after 30 min, indicating the initial formation of the PdNPs. After 16 h, evolution of the UV/Vis spectrum to a monotonic typical PdNP spectrum is observed; a similar spectrum is obtained upon PdNP reduction with $NaBH_4$ (see Figure 2). The ^1H NMR data also show the rapid reduction of Pd^{II} to Pd^0 in the presence of methanol

Table 1. Cyclic voltammetry results of the recognition of the $Pd(OAc)_2$ by the poly-1,2,3-triazolylferrocenyl dendrimers.

	No. triazole[a]	$E_{1/2}$[b] ($E_{pa}-E_{pc}$) [V]	Recognition of $Pd(OAc)_2$ $E_{1/2}$ ($E_{pa}-E_{pc}$) [V]	 $\Delta E_{1/2}$[c] [V]	 $K_{(0)}/K_{(+)}$[d]
12-G_0	9	0.540 (0.050)	0.640 (0.030)	−0.100	53
13-G_1a	36	0.540 (0.030)	0.625 (0.020)	−0.085	29
14-G_2a	117	0.540 (0.030)	0.595 (0.020)	−0.055	9

[a] Number of triazole units (interior + exterior). [b] $E_{1/2}=(E_{pa}+E_{pc})/2$ versus $FeCp_2$*, Cp* = η^5-C_5Me_5 (in V). Electrolyte: $[nBu_4N][PF_6]$ 0.1 M; solvent: chloroform/methanol (2:1); working and counter electrodes: Pt; quasi-reference electrode: Ag; internal reference: $FeCp_2$*; scan rate: 0.200 $V s^{-1}$; 20 °C. [c] Difference between values of $E_{1/2}$ before (3rd column) and after (4th column) titration. [d] Ratios of apparent association constants; error = 10 %; $\Delta E_{1/2} = 0.058 \log(K_{(0)}/K_{(+)})$ at 20 °C.[25]

and triazole: after 10 min of reaction, a decrease of the intensity of the dendrimer NMR signals is observed, showing only small broad peaks (Figure 32 of the Supporting Information). However, the presence of NPs (in the absence of $NaBH_4$) is only observed after 16 h, indicating that the formation of NPs under these conditions is slowed by the partial stabilization of Pd^0 by the triazole ligands. The TEM data confirm the formation of the NPs using either methanol or $NaBH_4$ as a reducing agent.

Synthesis and characterization of PdNPs stabilized by the 1,2,3-triazolyl dendrimers: All the seven poly-1,2,3-triazolyl dendrimers reported here were used to stabilize PdNPs in $CHCl_3$/MeOH (2:1) with two different reducing agents: $NaBH_4$ (method 1) and methanol (method 2). In method 1, the dendrimer was mixed with $Pd(OAc)_2$ (1 equiv per triazole unit) in $CHCl_3$/MeOH (2:1), followed by addition of $NaBH_4$ (10 equiv per Pd). Since methanol is able to reduce

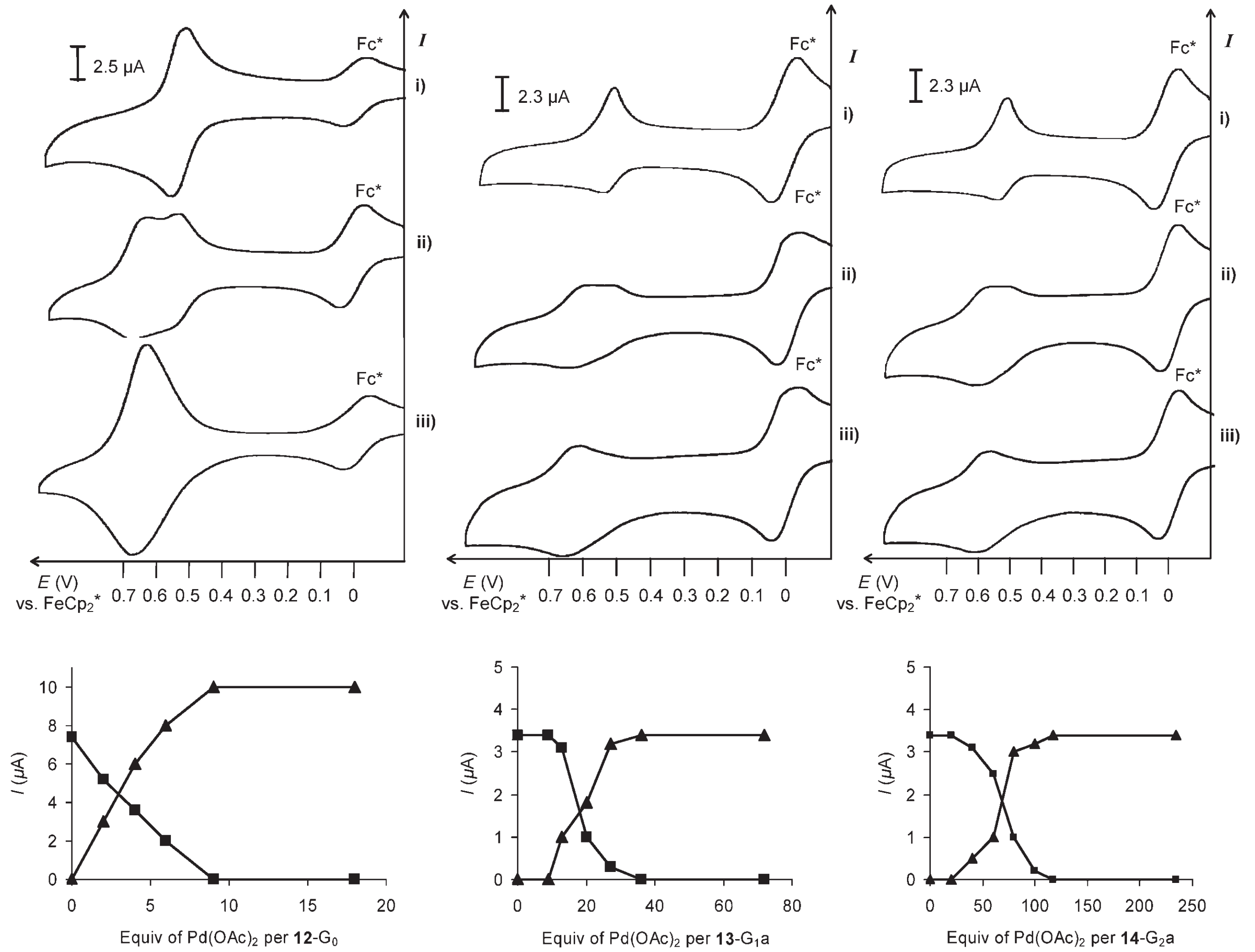


Figure 1. Top: Titration of $Pd(OAc)_2$ with **12**-G_0 ($c = 1.47 \times 10^{-4}$ M; left), **13**-G_1a ($c = 4.89 \times 10^{-4}$ M; middle), and **14**-G_2a ($c = 1.63 \times 10^{-5}$ M; right) by cyclic voltammetry. The CVs were obtained i) before addition $Pd(OAc)_2$; ii) during titration of $Pd(OAc)_2$ (**12**-G_0: 0.5 equiv; **13**-G_1a: 0.6 equiv; and **14**-G_2a: 0.65 equiv per triazole); and iii) at the end of titration of $Pd(OAc)_2$ (1 equiv per triazole). Bottom: Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) versus the number of equiv of $Pd(OAc)_2$ added per dendrimer **12**-G_0 (left), **13**-G_1a (middle), and **14**-G_2a (right).

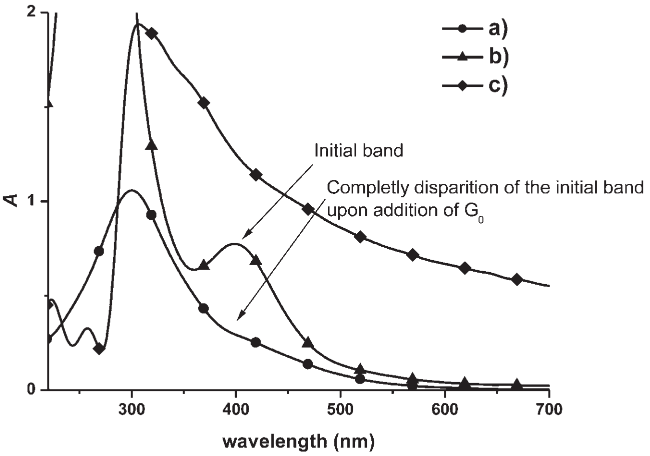
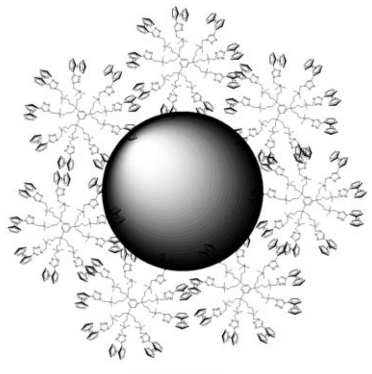
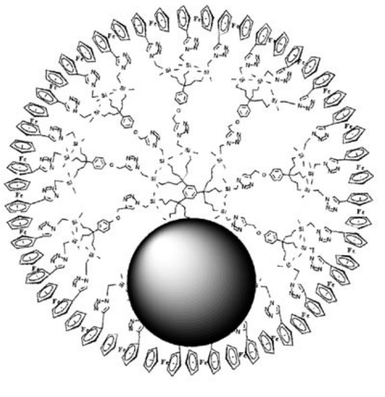


Figure 2. a) UV/Vis spectrum of a freshly prepared solution of $Pd(OAc)_2$ (2.97×10^{-3} M) in $CHCl_3$/MeOH (2:1); b) UV/Vis spectrum of a solution of **12**-G_0 ($9.78x10^{-5}$ M) and 9 equiv of $Pd(OAc)_2$ (8.80×10^{-4} M) in $CHCl_3$/MeOH (2:1) after 30 min [using a solution of dendrimer (9.78×10^{-5} M) in $CHCl_3$/MeOH (2:1) as blank]; c) UV/Vis spectrum of the PdNPs obtained by reduction with $NaBH_4$ (a similar spectrum was obtained using MeOH as the reductant).



DSN-**12**-G_0



DEN-**13**-G_1a

Table 2. Size of the PdNPs stabilized by the triazolyl dendrimers obtained by TEM.

PdNP	No. Pd atoms[a]	Calculated diameter[b] [nm]	Diameter method 1[c] [nm]	Diameter method 2[c] [nm]
DSN-**12**-G_0	9	–	1.2 ± 0.2	2.8 ± 0.3
DEN-**13**-G_1a	36	1.0	1.1 ± 0.2	1.3 ± 0.2
DEN-**14**-G_2a	117	1.5	1.6 ± 0.3	1.6 ± 0.3
DEN-**14**-G_2a-36	36	1.0	1.1 ± 0.2	1.3 ± 0.3
DEN-**17**-G_1b	27	0.9	1.0 ± 0.3	1.1 ± 0.3
DEN-**18**-G_2b	81	1.3	1.3 ± 0.3	1.4 ± 0.3
DEN-**21**-G_1c	27	0.9	1.0 ± 0.3	1.1 ± 0.3
DSN-**22**-G_1d	27	–	2.0 ± 0.4	2.5 ± 0.3
DEN-PAMAM	40	1.0	1.1 ± 0.2	–

[a] Number of Pd atoms per dendrimer. [b] Calculated using the equation $n=4\pi r^3/3\ V_g$, in which 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 $Å^3$).[28] [c] Diameter obtained by TEM.

$Pd(OAc)_2$ to Pd^0,[27] PdNPs were also prepared by stirring the mixture of dendrimer and $Pd(OAc)_2$ in $CHCl_3$/MeOH (2:1) without adding $NaBH_4$. Reduction of Pd^{II} using only methanol is much slower, and it required 16 h of stirring (method 2). The formation of the NPs was observed by the color change of the solution from yellow to golden brown and confirmed by UV/Vis spectroscopy. The size of all the NPs was obtained by transmition electron microscopy (TEM).

Due to its small size with an open structure, **12**-G_0 cannot encapsulate a PdNP. Thus, **12**-G_0 forms interdendrimer-stabilized PdNPs (DSN-**12**-G_0) in which the NP surface is stabilized by several dendrimers. The TEM data show that, in this case, the PdNPs obtained by reduction with only methanol are larger with **12**-G_0 than with **13**-G_1a or **14**-G_2a. Also, the nature of the reductant has a crucial influence on the size of the NPs formed. Upon reduction with methanol, **12**-G_0 forms DSNs with a diameter of 2.8 ± 0.3 nm (766 Pd atoms stabilized by 85 dendrimers), whereas reduction with $NaBH_4$ affords **12**-G_0-DSN with a diameter of 1.2 ± 0.2 nm (60 Pd atoms stabilised by seven dendrimers).[28] This size difference can be taken into account, as in polymer chemistry, by the stronger reducing power of $NaBH_4$ than methanol, because no encapsulation of the DSNs drives the size control for **12**-G_0. On the other hand, as expected, **13**-G_1a and **14**-G_2a form very small intradendrimer-encapsulated PdNPs (DENs). Their sizes (measured by TEM) correspond to the calculated sizes[28] for the number of Pd atoms inside the dendrimer, that is, the same as that of triazole ligands for **13**-G_1a (36) and **14**-G_2a (117; see Table 2). In constrast to the DSN-**12**-G_0, we find that for DEN-**13**-G_1a and DEN-**14**-G_2a, the size of the PdNPs is about the same regardless of whether $NaBH_4$ or methanol is used (Table 2). This result is well taken in account by the fact that in DENs the size of the PdNPs is governed by the number Pd atoms inserted in the dendrimers before reduction, not by the reducing power of the reductant. The dramatic influence of the nature of the reductant on the size of DSN-**12**-G_0 also confirms the different type of stabilization, DSN versus DENs, when comparing **12**-G_0 with **13**-G_1a and **14**-G_2a.

To compare DENs formed from **13**-G_1a and **14**-G_2a with the same number of Pd atoms in the PdNPs (i.e. 36), another DEN was synthesized, setting only 36 Pd equivalents in the dendrimer **14**-G_2a (DEN-**14**-G_2a-36). This experiment should help us to understand the role of the dendritic structure in the NP formation, stabilization, and catalytic activity. According to the TEM data, these DENs have a size that is similar to that of DEN-**13**-G_1a (1.1 ± 0.2 nm), confirming that these NPs contain about 36 Pd atoms.

For the dendrimers that do not contain triazole units in the interior, **17**-G_1b and **18**-G_2b, the TEM data show that they are also able to form DENs, and the sizes obtained are close to those calculated for the number of triazole ligands in the dendrimers (see Table 2).

According to TEM data, G_1 and G_2 of both classes of ferrocenyl dendrimers (G_na and G_nb, $n=1$ and 2) form DENs. Thus, after the complexation of ferrocenyltriazolyl unit to Pd^{II}, the ferrocenyl group plays an important role. It blocks the periphery, which retains the Pd^0 atoms inside the dendrimer, and consequently leads to the formation of very small PdNPs. This demonstrates that the functionalization of dendrimers with triazolylferrocenyl groups has two major advantages: 1) they can sense the binding of the metal to the triazole fragment in the dendrimer and 2) they block the periphery by stabilizing the nanoparticles inside the dendrimers.

The non-ferrocenyltriazolyl dendrimers **21**-G_1c and **22**-G_1d are also able to stabilize the PdNPs. As expected, and according to the TEM data, the bulky **21**-G_1c forms DENs and the non-bulky **22**-G_1d forms DSNs, because the phenyl terminal groups are not bulky enough to encapsulate the NPs (see Figure 3 and Table 2).

To compare the catalytic activity of the new PdNPs with those of Pd-DENs derived from the PAMAM dendrimers studied by Crooks' group, under the same conditions, we used a known hydrophobic PAMAM-modified dendrimer ($PAMAM-NH_2-G_4$ modified with 1,2-epoxydodecane)[19a] to form Pd-DENs. The DEN-Pd-PAMAM was mixed with 40 equivalents of $Pd(OAc)_2$ per dendrimer in $CHCl_3/MeOH$ (2:1), and $NaBH_4$ was added.

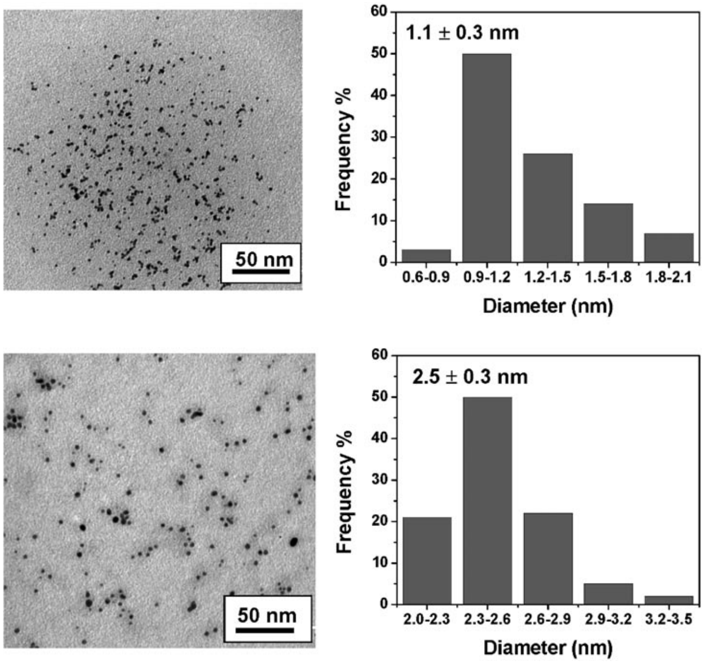


Figure 3. TEM image (left) and size distribution (right) of DEN-**21**-G_1c (top) and DSN-**22**-G_1d (bottom) (both were prepared by method 2—reduction of Pd^{II} using methanol).

Catalytic efficiency and stability of the DSNs and DENs based on the 1,2,3-triazolyl dendrimers: The DSNs and DENs formed with the new poly-1,2,3-triazolyl-ferrocenyl dendrimers prove to be efficient catalysts for hydrogenation of styrene at 0.1 % mol Pd. By using $NaBH_4$ as the reducing agent (method 1), the new DSNs and DENs can be compared to DENs based on the commercial dendrimers more often used as catalysts under the same conditions.

The turn over frequencies (TOF) obtained for styrene hydrogenation at 0.1 % mol Pd with DEN-**13**-G_1a are about six times larger (310 $mol\,H_2\,(mol\,Pd)^{-1}\,h^{-1}$) than the DENs based on PAMAM (56 $mol\,H_2\,(mol\,Pd)^{-1}\,h^{-1}$) (see Table 3).

Table 3. Catalytic efficiency (TOF values) and stability (TON values) obtained for all the new catalysts for styrene hydrogenation at 0.1 % mol Pd.

PdNP	TOF[a] [$mol\,H_2\,(mol\,Pd)^{-1}\,h^{-1}$]		TON	
	Method 1	Method 2	Method 1	Method 2
DSN-**12**-G_0	200	1200	30000	31500
DEN-**13**-G_1a	310	1620	10000	9300
DEN-**14**-G_2a	200	1280	20000	16650
DEN-**14**-G_2a-36	280	1380	7400	10000
DEN-**17**-G_1b	330	1670	9800	9400
DEN-**18**-G_2b	210	1200	20400	21150
DEN-**21**-G_1c	1780	3390	78420	76170
DSN-**22**-G_1d	995	1160	38580	35000
DEN-PAMAM	56	–	7500	–

[a] The catalytic activity of the PdNPs was investigated for the hydrogenation of styrene at 0.1 % Pd, in $CHCl_3/MeOH$ (2:1), 25 °C and 1 atm H_2. Reactions were followed by GPC, and TOF values were determined based on the yield of ethylbenzene formation.

Other known DENs based on the PPI-modified-dendrimers were reported to be very unstable under hydrogenation conditions in organic solvents (turn over number, TON of only 40).[14] On the other hand, the new "click" DENs are very stable under catalytic conditions: they can be re-used in ten catalytic cycles (TON ≈ 10000) for DEN-**13**-G_1a and 20 catalytic cycles for DEN-**14**-G_2a (TON ≈ 20000). The largest TONs are obtained with DSN-**12**-G_0 (TON ≈ 30000), although the TOF is lower than that found with DEN-**13**-G_1a (Table 3).

The catalytic activity of the DSNs and DENs synthesized by method 2 (methanol as reducing agent) is much higher than that of DENs synthesized by method 1, with TOF values of 1620 $mol\,H_2\,(mol\,Pd)^{-1}\,h^{-1}$ (**13**-G_1a) (Table 3), whereas the opposite was known with polymers.[16]

The large increase of catalytic activity found with these "click" DENs compared to DENs prepared from the commercial dendrimers PAMAM and PPI is shown to be due to both the type of dendrimer and nature of the reductant, but we can also assign the contribution of each of these two parameters influencing the increase of catalytic activity. On one hand, the newly designed dendritic framework with triazole ligands is responsible for a large increase of catalytic activity, by comparison with commercial dendrimers under the same conditions. On the other hand, the nature of the reductant, methanol, is also responsible for another large increase of catalytic activity, as shown in Table 3. All the previous literature data with DENs had been recorded with $NaBH_4$, possibly because $NaBH_4$ had provided better catalytic results than methanol in the cases of studies with polymer-stabilized NPs.[16] The better results obtained with $NaBH_4$ relative to methanol as a reducing agent in polymer-stabilized NPs were due to the fact that $NaBH_4$, being a stronger reductant than methanol, produced smaller NPs that were more active in hydrogenation catalysis than the larger polymer-stabilized NPs produced with methanol. In contrast, we find that, with the "click" DENs, the size of the PdNPs obtained from TEM data is about the same regardless of whether $NaBH_4$ or methanol is used (Table 2). This result is taken in account by the fact that the size of the PdNPs is governed only by the number Pd atoms in the DENs, which is the same as that of triazole ligands for G_1 and G_2 species. Methanol does not leave inhibiting residues on the PdNPs surface subsequent to reduction, whereas $NaBH_4$ does ($B(OCH_3)_3$ and Na^+).[29] Also note that, if the nature of the reductant has a strong influence on the catalysis kinetics, it has no significant influence on the stabilities of the "click" DENs as shown by the high TON values found with both reductants. The catalytic efficiency of DEN-G_1 and DEN-G_2 species confirm the trend according 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. We also examined the influence of the dendrimer size on the catalytic activity of "click" DENs. The comparison of the catalytic activity of DEN-**14**-G_2a-36 with those of DEN-**13**-G_1a (36 Pd) and DEN-**14**-G_2a (117 Pd) shows that DEN-**14**-G_2a-36 is more efficient than DEN-**14**-G_2, but less efficient than DEN-**13**-G_1. This allows us to state that the catalytic efficiency of the DENs depends not only on the number of Pd atoms of each NP, but also on the dendrimer structure that encapsulates it. The steric factor is indeed of great importance, the larger dendrimer G_2 species slowing the catalysis kinetics due to steric effects of the large dendrimer framework.[7] We can conclude that, with this family of click dendrimers, the G_1 species is the optimal generation to form DEN catalysts. It is large enough to encapsulate NPs, and it is able to form very small NPs that are very active in catalysis.

There is no significant difference between the catalytic efficiency of both classes of triazolylferrocenyl dendrimers (with and without interior triazole units), **17**-G_1b and **18**-G_2b being slightly more efficient than **13**-G_1a and **14**-G_1a respectively, probably due to the small difference of the number of palladium atoms by NP (36 in **13**-G_1a and 27 in **17**-G_1b; 117 in **14**-G_2a and 81 in **18**-G_2b). This feature shows the importance of a bulky periphery provided by ferrocenyl group in the encapsulation of NPs by dendrimers.

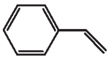
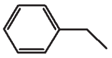
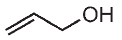
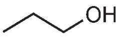
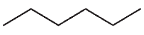
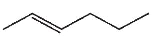
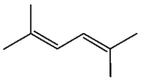
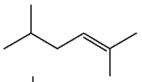
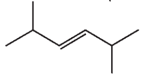
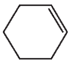
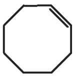
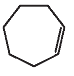
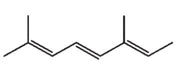
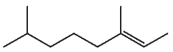
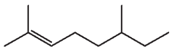
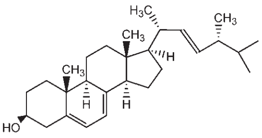
Using method 1, the catalytic activity of the DENs that do not contain ferrocenyl groups (DEN-**21**-G_1c and DEN-**22**-G_1d) is much higher than that of the ferrocenyl-containing DENs (this difference is small when method 2 is used, however). The rationalization of this point is not straightforward, but the interaction between BH_3 (a Lewis acid) and ferrocenyl (a Lewis base) could possibly play a role, particularly a steric one. Indeed, the increase of steric bulk that results from this interaction may slow down the introduction of the olefin substrate into the dendritic framework.

The DEN-**21**-G_1c appears to be the most efficient catalyst ($TOF = 3390\,mol\,H_2\,(mol\,Pd)^{-1}\,h^{-1}$), because it is bulky enough to encapsulate the PdNPs, forming very small NPs. However, the size and mobility of its periphery groups makes the PdNP surface more accessible to substrates for catalysis, relative to DENs containing rigid ferrocenyl groups. These DENs exhibit a very high stability with impressive TON values. Indeed, they can be re-used for 80 catalytic cycles ($TON \approx 80000$). The catalytic efficiency and stability obtained for all the DSNs and DENs based on 1,2,3-triazolyl dendrimers are gathered in Table 3.

After catalysis, the poly-1,2,3-triazolylferrocenyl dendrimers used to stabilize or/and encapsulate the PdNPs can be easily recovered from the reaction media by simple extraction with dichloromethane and precipitation in methanol. We found that the dendritic structures do not suffer any significant structural change (confirmed by ^1H NMR spectroscopy) and they can be re-used as catalyst supports.

Catalytic selectivity with DEN-G_1a for the hydrogenation of various olefin substrates including conjugated dienes and trienes: The DEN-**13**-G_1a/method 2 was tested in the hydrogenation of various olefin substrates under ambient conditions, including conjugated dienes and trienes, to study the selectivity properties of this catalyst. The TOF values obtained are gathered in Table 4. With this new catalyst, styrene and allyl alcohol were converted (100 %) to ethylbenzene and 1-propanol, respectively, with high selectivity of the catalyst for substituted olefins. During the hydrogenation of 1-hexene, the conversion to hexane is 43 %, because the 2-hexene isomer is also produced.[30] The hydrogenation of internal conjugated dienes and trienes using the DEN-**13**-G_1a catalyst was 100 % selective for the formation of monoenes, showing the selectivity of the partial hydrogenation of cyclic and linear internal conjugated dienes. Finally, size selectivity of DEN-**13**-G_1a was investigated by comparing its catalytic activity on hydrogenation of cyclohexadiene and ergosterol (that contains a cyclohexadiene cycle in its structure). We found that DEN-**13**-G_1a catalyzes the partial hydrogenation of cyclohexadiene to cyclohexene, but no hydrogenation is observed in the case of ergosterol. Moreover, only cyclohexadiene is semihydrogenated upon reaction of a mixture of cyclohexadiene and ergosterol. This clearly shows the size selectivity performed by the DEN-**13**-G_1a catalyst; ergosterol is not able to enter into the dendrimer structure so as to locate its double bonds onto the NP surface (see Figure 4).

Table 4. Hydrogenation of olefins catalyzed by DEN-**13**-G_1a/method 2.

Substrate	Products[a]	Yield [%]	TOF[b]
		100	1620
		100	1160
	 	43 57	1800 2400
	 	78 22	810 230
		100	1150
		100	530
		100	130
	 		480[c]
 Ergosterol[d]	no hydrogenation	–	

[a] Reactions are performed at 25°C/1 atm H_2; followed by GPC in the case of styrene and by NMR spectroscopy in all other cases. [b] TOF values are determined on basis of the yield of formation of the final product. [c] The NMR data do not allow to determinate the relative quantities of the two isomers formed. [d] Ergosterol was left under hydrogenation conditions during four days.

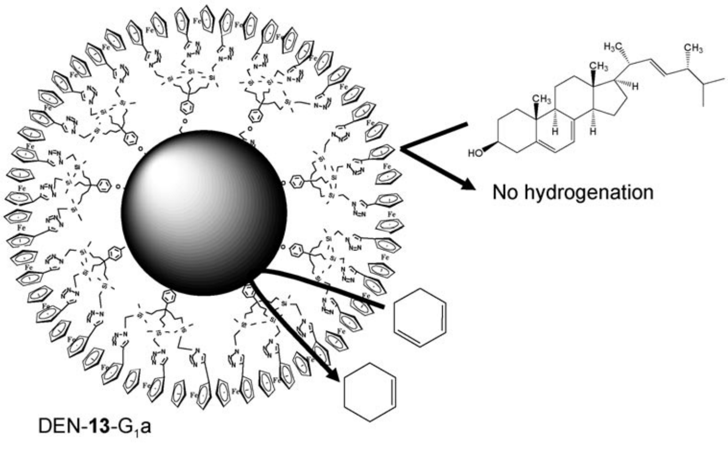


Figure 4. Schematic representation of the size selectivity of DEN-**13**-G_1a.

Conclusion

A full account of the synthesis and characterization of a variety of novel click dendrimers is provided in this article. The engineering of these novel ligand-containing dendrimers and precise redox sensing of Pd^{II} coordinated to the triazole ligands, leads to the production of various dendrimer-encapsulated PdNPs (DENs) with a pre-organized number of Pd atoms that is confirmed by TEM data for first- and second-gernation dendrimers (G_1 and G_2). The TEM data also confirm that **12**-G_0 is too small to encapsulate PdNPs, and the PdNPs are stabilized by several dendrimers around the PdNPs (DSNs) in this case.

This study provides precise DENs and DSNs that are highly efficient, stable, and size-selective hydrogenation catalysts, and the various structural influences on the catalytic performances are rationalized. The dramatic and specific structure-dependent role of the reductant is clearly elucidated, which leads to a significant improvement in our understanding of the catalytic reactions with PdNPs. The results will be useful for comparison with other types of catalysis, and the parameters obtained here should serve further for the design of highly selective heterobimetallic hydrogenation catalysts of industrial relevance.

Experimental Section

General data: Reagent-grade diethyl ether (used in hydrosilylation reactions) was predried over Na foil and distilled from sodium/benzophenone under nitrogen immediately prior to use. Syntheses of the NP's were carried out by using Schlenk techniques with degased solvents. PAMAM-NH_2-G_4 was purchased from Sigma-Aldrich and modified with 1,2-epoxydodecane according to reference [29]. Ethynylferrocene, phenylacetylene, and all the olefinic substrates were purchased from Sigma-Aldrich. Ergosterol was purchased from Alfa Aesar.

Cyclic voltammetry measurements: All electrochemical measurements were recorded under nitrogen atmosphere. Conditions: solvent: $CHCl_3$/MeOH; temperature: 20°C; Supporting electrolyte: $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{PF}_6]$ 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: $FeCp_2^*$ ($Cp^* = \eta^5$-C_5Me_5); scan rate: 0.200 Vs^{-1}.

Transmission electron microscopy (TEM): Samples were prepared placing a drop of a 4.41×10^{-4} M solution ($CHCl_3$/MeOH 2:1) of PdNP (concentration in mol Pd) on a holey-carbon-coated Cu TEM grid. The size of the nanoparticles was measured using the software *sigmascanpro* (for each sample, about 100 nanoparticles were measured).

General procedure for the hydrosilylation reactions: The polyolefin dendrimer, diethyl ether, dimethylchloromethylsilane (2 equiv per branch) and Kartsted catalyst (0.1%) were successively introduced into a Schlenck flask under a nitrogen atmosphere. The reaction solution was stirred at 25°C for 16 h. For dendrimers containing triazole units, several additions of catalyst and longer time reactions were needed to complete reactions (due to possible partial complexation of Pt^0 of the catalyst by the triazole units). The reaction was followed by ^1H NMR spectroscopy; at the end of the reaction, the solvent was removed under vacuum, the catalyst residue was removed by flash chromatography, and the dendrimer was precipitated using dichloromethane/pentane.

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 sulfate, and filtered over paper; and the solvent was removed under vacuum. The dendrimer was precipitated with dichloromethane/methanol.

General procedure for the "click" reactions: The azido dendrimer (1 equiv) and the alkyne (1.5 equiv per branch) were dissolved in tetrahydrofuran (THF) and water was added (1:1 THF/water). At 20 °C, $CuSO_4$ was added (1 equiv per branch, 1 M aqueous solution), followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (2 equiv per branch, 1 M aqueous solution). The solution was allowed to stir for 30 min at room temperature. After removing THF under vacuum, dichloromethane and an aqueous ammonia solution were added. The mixture was allowed to stir for 10 min in order to remove all the Cu^I trapped inside the dendrimer as $Cu(NH_3)_6{}^+$. The organic phase was washed twice with water, dried with sodium sulphate, and filtered, and the solvent was removed under vacuum. The product was washed with pentane in order to remove the excess of alkyne and precipitated using dichloromethane/pentane.

Synthesis of 4: The 9-azido dendrimer **4** was synthesized from **3** (0.190 g, 0.130 mmol) by using the general procedure for azido dendrimers. The product **4** was obtained as a colorless waxy product in 99 % yield (0.196 g, 0.129 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.94$ (s, 3 H; arom C*H*), 2.72 (s, 18 H; CH_2N_3), 1.62 (s, 18 H; $SiCH_2CH_2CH_2$), 1.07 (s, 18 H; $SiCH_2CH_2CH_2$), 0.58 (s, 18 H; $SiCH_2CH_2CH_2$), 0.042 ppm ($Si(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 145.7$ (arom C_q), 121.5 (arom *C*H), 43.9 ($SiCH_2CH_2CH_2$), 41.9 (*C*q), 41.1 (CH_2N_3), 17.7 ($SiCH_2CH_2CH_2$), 15.0 ($SiCH_2CH_2CH_2$), −4.04 ppm ($Si(CH_3)_2$); ^{29}Si NMR ($CDCl_3$, 59.62 MHz): $\delta = 3.33$ ($Si(CH_3)_2CH_2N_3$); elemental analysis calcd (%) for $C_{63}H_{129}N_{27}Si_9$: C 49.86, H 8.57; found: C 49.31, H 8.30. IR: $\tilde{\nu} = 2093$ cm^{-1} (N_3).

Synthesis of 5: The phenoltriallyl dendronic brick p-$HOC_4H_4C(CH_2CH{=}CH_2)_3$ (1.02 g, 4.46 mmol) and Cs_2CO_3 (2.18 g, 6.69 mmol) were introduced in a Schlenck flask and acetone (30 mL) and propargyl bromide (0.58 mL of a 80 % solution in toluene, 5.36 mmol) were added. The mixture was refluxed at 65 °C for 16 h. The solvent was removed under vacuum, the crude product was dissolved with dichloromethane and washed with water. The organic layer was dried with sodium sulfate, filtrated, and the solvent was removed under vacuum. The product was purified by silica column chromatography using pentane as eluent. A colorless oil was obtained (1.178 g, 99 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.27$, 6.98 (2 d, $J = 11$ Hz, 4 H; p-C_6H_4), 5.60 (m, 3 H; $HC{=}CH_2$), 5.05 (m, 6 H; $HC{=}CH_2$), 4.69 (s, 2 H; CH_2CCH), 2.54 (s, 1 H; CCH), 2.46 ppm (d, $J = 10$ Hz, 2 H; $CH_2HC{=}CH_2$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 154.2$ (OC_q), 137.3 (arom C_q), 133.2 ($HC{=}CH_2$), 126.3, 113.0 (arom CH), 116.3 ($HC{=}CH_2$), 77.5 (CH_2CCH), 74.1 (CH_2CCH), 54.4 (CH_2CCH), 41.4 ($C(CH_2HC{=}CH_2)_3$), 40.6 ppm ($CH_2HC{=}CH_2$); elemental analysis calcd (%) for $C_{19}H_{22}O$: C 85.67, H 8.32; found: C 85.82, H 8.62.

Synthesis of 6: The 27-allyl dendrimer **6** was synthesized from **4** (0.127 g, 0.0835 mmol) and **5** (0.334 g, 1.25 mmol) by using the general procedure for "click" reactions. The product **6** was obtained as a colorless waxy product obtained in 92 % yield (0.300 g, 0.0768 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.50$ (s, 9 H; triazole C*H*), 7.20, 6.91 (2 d, $J = 11$ Hz, 36 H; p-C_6H_4), 5.53 (m, 27 H; $CH{=}CH_2$), 5.10 (s, 18 H; CH_2O), 4.97 (m, 54 H; $CH{=}CH_2$), 3.86 (s, 18 H; $SiCH_2N$), 2.40 (d, $J = 10$ Hz, 54 H; $CH_2CH{=}CH_2$), 1.64 (s, 18 H; $CH_2CH_2CH_2Si$), 1.10 (s, 18 H; $CH_2CH_2CH_2Si$), 0.64 (s, 18 H; $CH_2CH_2CH_2Si$), 0.039 ppm (s, 54 H; $Si(CH_3)_2$); ^{3}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 156.2$ (OC_{Ar}), 143.9 (C_q of triazole), 138.3 (substituted arene core *C*), 136.9 (arom C_q of the dendron), 134.6 (inner $C{=}C$), 127.7, 114.2 (unsubstituted arene *C* of the dendron), 123.7 (*C*H of triazole), 117.5 (outer $C{=}C$), 62.0 (CH_2O), 43.9 ($CH_2CH_2CH_2Si$), 42.7 ($SiCH_2N$), 41.9 (CH_2-$CH{=}CH_2$), 41.0, 40.4 (benzylic C_q of the core and dendron), 17.7 ($CH_2CH_2CH_2Si$), 14.9 ($CH_2CH_2CH_2Si$), −3.83 ppm ($Si(CH_3)_2$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta = 2.81$ ($Si(CH_3)_2CH_2N$); MALDI-TOF: m/z calcd for $C_{234}H_{327}N_{27}O_9Si_9$: 3915.05; found: 3937.42 $[M+Na]^+$; elemental analysis calcd (%) for $C_{234}H_{327}N_{27}O_9Si_9$: C 71.79, H 8.42; found: C 71.03, H 8.28.

Synthesis of 7: The 27-chloro dendrimer **7** was synthesized from **6** (0.180 g, 0.0460 mmol) by using the general procedure for hydrosilylation reactions. The product **7** was obtained as a colorless waxy product in 71 % yield (0.192 g, 0.0327 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.51$ (s, 9 H; triazole C*H*), 7.15, 6.89 (2 d, $J = 10$ Hz, 36 H; p-C_6H_4), 5.11 (s, 18 H; CH_2O), 3.86 (s, 18 H; $SiCH_2N$), 2.71 (s, 54 H; CH_2Cl), 1.59 (s, 72 H; $CH_2CH_2CH_2Si$), 1.06 (s, 72 H; $CH_2CH_2CH_2Si$), 0.57 (s, 72 H; $CH_2CH_2CH_2Si$), 0.041 ppm (s, 216 H; $Si(CH_3)_2CH_2Cl$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 156.0$ (OC_{Ar}), 143.9 (C_q of triazole), 140.1 (substituted arene core *C*), 136.9 (arom C_q of the dendron), 127.4, 114.1 (unsubstituted arene *C* of the dendron), 123.6 (*C*H of triazole), 62.1 (CH_2O), 44.0 ($CH_2CH_2CH_2Si$), 41.8 ($SiCH_2N$), 41.0 (benzylic quaternary *C* of the core and dendron), 17.5 ($CH_2CH_2CH_2Si$), 14.4 ($CH_2CH_2CH_2Si$), −3.81 ($Si(CH_3)_2CH_2N$), −4.46 ppm ($Si(CH_3)_2CH_2Cl$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta = 3.54$ ($SiCH_2Cl$), 2.80 ppm ($SiCH_2N$).

Synthesis of 8: The 27-azido dendrimer **8** was synthesized from **7** (0.120 g, 0.0204 mmol) by using the general procedure for azido dendrimers. The product **8** was obtained as a colorless waxy product in 92 % yield (0.132 g, 0.0188 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.51$ (s, 9 H; triazole C*H*), 7.16, 6.89 (2 d, $J = 11$ Hz, 36 H; p-C_6H_4), 5.11 (s, 18 H; CH_2O), 3.86 (s, 18 H; $SiCH_2N$), 2.71 (s, 54 H; CH_2Cl), 1.61 (s, 72 H; $CH_2CH_2CH_2Si$), 1.07 (s, 72 H; $CH_2CH_2CH_2Si$), 0.55 (s, 72 H; $CH_2CH_2CH_2Si$), 0.023 ppm (s, 216 H; $Si(CH_3)_2CH_2Cl$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 156.0$ (OC_{Ar}), 143.9 (C_q of triazole), 140.1 (substituted arene core *C*), 136.9 (arom C_q of the dendron), 127.4, 114.1 (unsubstituted arene *C* of the dendron), 123.6 (*C*H of triazole), 60.3 ($SiCH_2O$), 43.1 ($CH_2CH_2CH_2Si$), 41.8 ($SiCH_2N$), 41.0 (benzylic quaternary *C* of the core and dendron), 17.5 ($CH_2CH_2CH_2Si$), 14.9 ($CH_2CH_2CH_2Si$), −3.86 ($Si(CH_3)_2CH_2N$), −4.41 ppm ($Si(CH_3)_2CH_2N_3$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta = 3.33$ ($SiCH_2N_3$), 2.80 ppm ($SiCH_2N$); elemental analysis calcd (%) for $C_{315}H_{570}N_{108}O_9Si_{36}$: C 53.85, H 8.18; found: C 53.25, H 8.00; IR: $\tilde{\nu} = 2093$ cm^{-1} (N_3).

Synthesis of 9: The 81-allyl dendrimer **9** was synthesized from **8** (0.050 g, 0.00712 mmol) and **5** (0.230 g, 0.865 mmol) by using the general procedure for "click" reactions. The product **9** was obtained as a colorless waxy product in 67 % yield (0.069 g, 0.00477 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41$ (s, 81 H; triazole C*H*), 7.18, 6.90 (brs, 144 H; p-C_6H_4), 5.52 (m, 81 H; $CH{=}CH_2$), 5.13 (s, 72 H; CH_2O), 4.96 (brs, 162 H; $CH{=}CH_2$), 3.84 (s, 72 H; $SiCH_2N$), 2.41 (brs, 162 H; $CH_2CH{=}CH_2$), 1.59 (s, 72 H; $CH_2CH_2CH_2Si$), 1.07 (s, 72 H; $CH_2CH_2CH_2Si$), 0.57 (s, 72 H; $CH_2CH_2CH_2Si$), 0.029 ppm (s, 54 H; $Si(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 156.2$ (OC_{Ar}), 143.8 (C_q of triazole), 138.2 (substituted arene core *C*), 136.6 (arom C_q of the dendron), 134.6 (inner $C{=}C$), 127.7, 114.2 (unsubstituted arene *C* of the dendron), 123.8 (*C*H of triazole), 117.6 (outer $C{=}C$), 62.1 (CH_2O), 43.8 ($CH_2CH_2CH_2Si$), 42.7 ($SiCH_2N$), 41.9 ($CH_2{-}CH{=}CH_2$), 41.1, 40.3 (benzylic C_q of the core and dendron), 17.5 ($CH_2CH_2CH_2Si$), 14.7 ($CH_2CH_2CH_2Si$), −3.99 ppm ($Si(CH_3)_2$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta = 2.86$ ppm ($Si(CH_3)_2CH_2N$); elemental analysis calcd (%) for $C_{828}H_{1164}N_{108}O_{36}Si_{36}$: C 69.95, H 8.25; found: C 69.06, H 8.12.

Synthesis of 10: The 81-chloro dendrimer **10** was synthesized from **9** (0.050 g, 0.00345 mmol) by using the general procedure for hydrosilylation reactions. The product **10** was obtained as a colorless waxy product in 59 % yield (0.047 g, 0.00203 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.50$ (s, 81 H; triazole C*H*), 7.15, 6.89 (2 d, $J = 11$ Hz, 144 H; p-C_6H_4), 5.11 (s, 72 H; CH_2O), 3.86 (s, 72 H; $SiCH_2N$), 2.71 (s, 162 H; CH_2Cl), 1.59 (s, 234 H; $CH_2CH_2CH_2Si$), 1.06 (s, 234 H; $CH_2CH_2CH_2Si$), 0.57 (s, 234 H; $CH_2CH_2CH_2Si$), 0.041 ppm (s, 702 H; $Si(CH_3)_2CH_2Cl$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 156.1$ (OC_{Ar}), 143.8 (C_q of triazole), 140.4 (substituted arene core *C*), 137.1 (arom C_q of the dendron), 127.3, 114.1 (unsubstituted arene *C* of the dendron), 123.3 (*C*H of triazole), 62.0 (CH_2O), 44.1 ($CH_2CH_2CH_2Si$), 41.7 ($SiCH_2N$), 41.0 (benzylic C_q of the core and dendron), 17.6 ($CH_2CH_2CH_2Si$), 14.5 ($CH_2CH_2CH_2Si$), −3.84 ($Si(CH_3)_2CH_2N$), −4.51 ppm ($Si(CH_3)_2CH_2Cl$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta = 3.57$ ($SiCH_2Cl$), 2.83 ppm ($SiCH_2N$).

Synthesis of 11: The 81-azido dendrimer **11** was synthesized from **10** (0.047 g, 0.00203 mmol) by using the general procedure for azido dendrimers. The product **11** was obtained as a colorless waxy product with 91 % yield (0.043 g, 0.00185 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.42$ (s, 81 H; triazole C*H*), 7.16, 6.90 (2 d, $J = 11$ Hz, 144 H; p-C_6H_4), 5.11 (s, 72 H; CH_2O), 3.86 (s, 72 H; $SiCH_2N$), 2.71 (s, 162 H; CH_2Cl), 1.61 (s, 234 H; $CH_2CH_2CH_2Si$), 1.07 (s, 234 H; $CH_2CH_2CH_2Si$), 0.55 (s, 234 H; $CH_2CH_2CH_2Si$), 0.023 ppm (s, 702 H; $Si(CH_3)_2CH_2Cl$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta=156.1$ ($\mathrm{O\mathit{C}_{Ar}}$), 143.7 ($\mathrm{C_q}$ of triazole), 140.2 (substituted arene core *C*), 136.7 (arom $\mathrm{C_q}$ of the dendron), 127.3, 114.2 (unsubstituted arene *C* of the dendron), 123.6 (*C*H of triazole), 62.0 ($\mathrm{\mathit{C}H_2O}$), 43.1 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 41.6 ($\mathrm{Si\mathit{C}H_2N}$), 41.1 (benzylic quaternary *C* of the core and dendron), 17.5 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 14.6 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), −3.90 ($\mathrm{Si(\mathit{C}H_3)_2CH_2N}$), −4.39 ppm ($\mathrm{Si(\mathit{C}H_3)_2CH_2N_3}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=3.33$ ($\mathrm{\mathit{Si}CH_2N_3}$), 2.81 ppm ($\mathrm{\mathit{Si}CH_2N}$); elemental analysis calcd (%) for $\mathrm{C_{1071}H_{1893}N_{351}O_{36}Si_{117}}$: C 54.62, H 8.10; found: C 53.67, H 8.01; IR: $\tilde{\nu}=2093\ \mathrm{cm^{-1}}$ ($\mathrm{N_3}$).

Synthesis of 12-G$_0$: The 9-ferrocenyltriazole dendrimer **12**-G$_0$ was synthesized from **4** (0.100 g, 0.0659 mmol) and ethynylferrocene (0.187 g, 0.890 mmol) by using the general procedure for "click" reactions. The product **12**-G$_0$ was obtained as an orange powder in 94% yield (0.211 g, 0.0619 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.38$ (s, 9H; triazole C*H*), 6.91 (s, 3H; A$_r$ core), 4.70, 4.27, 4.04 (s, 81H; Cp), 3.83 (s, 18H; $\mathrm{SiC\mathit{H}_2N}$), 1.59 (s, 18H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.06 (s, 18H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.59 (s, 18H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.045 ppm (s, 54H; $\mathrm{Si(C\mathit{H}_3)_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): $\delta=146.1$ ($\mathrm{C_q}$ of triazole), 120.0 (*C*H of triazole), 75.7 ($\mathrm{C_q}$ of Cp), 69.5, 68.6, 66.5 (*C*H of Cp), 43.8 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 41.7 (benzylic $\mathrm{\mathit{C}_q}$ of the core), 40.8 ($\mathrm{\mathit{C}H_2N}$), 17.6 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 14.8 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), −3.74 ppm ($\mathrm{Si(\mathit{C}H_3)_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=2.90$ ppm ($\mathrm{\mathit{Si}(CH_3)_2CH_2N}$); MS (MALDI-TOF): *m*/*z* calcd for $\mathrm{C_{171}H_{219}N_{27}Si_9Fe_9}$: 3408.12; found: 3408.18 $[M]^+$; elemental analysis calcd (%) for $\mathrm{C_{171}H_{219}N_{27}Si_9Fe_9}$: C 60.26, H 6.48; found: C 59.47, H 6.67; polydispersity obtained by SEC <1.02.

Synthesis of 13-G$_1$a: The 27-ferrocenyltriazole dendrimer **13**-G$_1$a was synthesized from **8** (0.040 g, 0.00569 mmol) and ethynylferrocene (0.048 g, 0.230 mmol) by using the general procedure for "click" reactions. The product **13**-G$_1$a was obtained as an orange waxy product in 71% yield (0.051 g, 0.00404 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.50$ (s, 9H; inner triazole C*H*), 7.29 (s, 27H; outer triazole C*H*), 7.14, 6.87 (brs, 36H; p-$\mathrm{C_6\mathit{H}_4}$), 5.08 (s, 18H; $\mathrm{C\mathit{H}_2O}$), 4.70, 4.26, 4.03 (s, 243H; Cp), 3.82 (s, 54H; $\mathrm{SiC\mathit{H}_2N}$), 1.56 (s, 72H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.04 (s, 72H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.57 (s, 18H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.053 ppm (s, 54H; $\mathrm{Si(C\mathit{H}_3)_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): $\delta=156.1$ ($\mathrm{O\mathit{C}_{Ar}}$), 146.2 ($\mathrm{C_q}$ of outer triazole), 143.7 ($\mathrm{C_q}$ of inner triazole), 139.8 (aromatic $\mathrm{C_q}$ of the dendron), 127.4, 114.2 (unsubstituted arene *C* of the dendron), 123.7 (*C*H of inner triazole), 119.7 (*C*H of outer triazole), 75.7 ($\mathrm{C_q}$ of Cp), 69.5, 68.6, 66.5 (*C*H of Cp), 62.1 ($\mathrm{\mathit{C}H_2O}$), 43.1 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 41.8, 40.9 (benzylic quaternary *C* of the core and dendron), 40.8 ($\mathrm{Si\mathit{C}H_2N}$), 17.4 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 14.8 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), −3.86 ppm ($\mathrm{Si(\mathit{C}H_3)_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=2.97$ ppm ($\mathrm{\mathit{Si}(CH_3)_2CH_2N}$); polydispersity obtained by SEC <1.02.

Synthesis of 14-G$_2$a: The 81-ferrocenyltriazole dendrimer **14**-G$_2$a was synthesized from **11** (0.030 g, 0.00128 mmol) and ethynylferrocene (0.033 g, 0.156 mmol) by using the general procedure for "click" reactions. The product **14**-G$_2$a was obtained as an orange waxy product in 56% yield (0.029 g, 0.000715 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.59$ (s, 36H; inner triazole C*H*), 7.29 (s, 81H; outer triazole C*H*), 7.13, 6.89 (brs, 144H; p-$\mathrm{C_6\mathit{H}_4}$), 5.12 (s, 72H; $\mathrm{C\mathit{H}_2O}$), 4.69, 4.26, 4.03 (s, 729H; Cp), 3.82 (s, 162H; $\mathrm{SiC\mathit{H}_2N}$), 1.57 (s, 234H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.04 (s, 234H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.57 (s, 234H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.056 ppm (s, 54H; $\mathrm{Si(C\mathit{H}_3)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): $\delta=156.1$ ($\mathrm{O\mathit{C}_{Ar}}$), 146.5 ($\mathrm{C_q}$ of outer triazole), 143.1 ($\mathrm{C_q}$ of inner triazole), 138.3 (aromatic $\mathrm{C_q}$ of the dendron), 127.4, 114.2 (unsubstituted arene *C* of the dendron), 123.7 (*C*H of inner triazole), 120.0 (*C*H of outer triazole), 76.1 ($\mathrm{C_q}$ of Cp), 69.9, 68.9, 66.7 (*C*H of Cp), 62.1 ($\mathrm{\mathit{C}H_2O}$), 43.1 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 40.4 (benzylic $\mathrm{\mathit{C}_q}$ of the dendron), 40.6 ($\mathrm{Si\mathit{C}H_2N}$), 17.4 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 14.8 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), −3.82 ppm ($\mathrm{Si(\mathit{C}H_3)_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=2.97$ ppm ($\mathrm{\mathit{Si}(CH_3)_2CH_2N}$); polydispersity obtained by SEC <1.02; hydrodynamic diameter obtained by DLS: 12 ± 0.5 nm.

Synthesis of 15: The 27-azido dendrimer **15** was synthesized from 27-chloro-dendrimer (0.100 g, 0.0163 mmol) by using the general procedure for azido dendrimers. The product was obtained as a colorless waxy product in 99% yield (0.101 g, 0.0161 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.16$, 6.89 (2d, $J=11$ Hz, 36H; p-$\mathrm{C_6\mathit{H}_4}$), 3.53 (s, 18H; $\mathrm{SiC\mathit{H}_2O}$), 2.71 (s, 54H; $\mathrm{C\mathit{H}_2N_3}$), 1.62 (s, 72H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.09 (s, 72H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.55 (s, 72H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.0061 (s, 54H; $\mathrm{Si(C\mathit{H}_3)_2CH_2O}$), 0.043 ppm (s, 162H; $\mathrm{Si(C\mathit{H}_3)_2CH_2N_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): $\delta=159.2$ ($\mathrm{O\mathit{C}_{Ar}}$), 139.1 (arom $\mathrm{C_q}$ of the dendron), 127.2, 113.6 (unsubstituted arene *C* of the dendron), 60.3 ($\mathrm{Si\mathit{C}H_2O}$), 43.1 (benzylic quaternary *C* of the core and dendron), 41.1 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 29.8 ($\mathrm{Si\mathit{C}H_2N_3}$), 17.6 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 15.0 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), 0.0023 ($\mathrm{Si(\mathit{C}H_3)_2CH_2O}$), −3.99 ppm ($\mathrm{Si(\mathit{C}H_3)_2CH_2N_3}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=3.33$ ($\mathrm{\mathit{Si}CH_2N_3}$), 0.52 ppm ($\mathrm{\mathit{Si}CH_2O}$); IR: $\tilde{\nu}=2093\ \mathrm{cm^{-1}}$ ($\mathrm{N_3}$).

Synthesis of 16: The 81-azido dendrimer **16** was synthesized from the 81-chloro dendrimer (0.100 g, 0.0050 mmol) by using the general procedure for azido dendrimers. The product was obtained as a colorless waxy product in 99% yield (0.102 g, 0.0049 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.16$, 6.86 (2d, $J=11$ Hz, 144H; p-$\mathrm{C_6\mathit{H}_4}$), 3.53 (s, 72H; $\mathrm{SiC\mathit{H}_2O}$), 2.71 (s, 162H; $\mathrm{C\mathit{H}_2N_3}$), 1.62 (s, 234H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.09 (s, 234H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.55 (s, 234H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.0062 (s, 216H; $\mathrm{Si(C\mathit{H}_3)_2CH_2O}$), 0.039 ppm (s, 486H; $\mathrm{Si(C\mathit{H}_3)_2CH_2N_3}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): $\delta=159.5$ ($\mathrm{O\mathit{C}_{Ar}}$), 139.0 (aromatic $\mathrm{C_q}$ of the dendron), 127.4, 113.9 (unsubstituted arene *C* of the dendron), 60.6 ($\mathrm{Si\mathit{C}H_2O}$), 43.4 (benzylic $\mathrm{\mathit{C}_q}$ of the core and dendron), 41.4 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 30.1 ($\mathrm{Si\mathit{C}H_2N_3}$), 17.9 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 15.6 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), 0.0027 ($\mathrm{Si(\mathit{C}H_3)_2CH_2O}$), −3.74 ppm ($\mathrm{Si(\mathit{C}H_3)_2CH_2N_3}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=3.32$ ($\mathrm{\mathit{Si}CH_2N_3}$), 0.51 ppm ($\mathrm{\mathit{Si}CH_2O}$); IR: $\tilde{\nu}=2093\ \mathrm{cm^{-1}}$ ($\mathrm{N_3}$).

Synthesis of 17-G$_1$b: The 27-ferrocenyltriazole dendrimer **17**-G$_1$b was synthesized from 15 (0.050 g, 0.0079 mmol) and ethynylferrocene using the general procedure for "click" reactions. The product was obtained as an orange waxy product in 89% yield (0.084 g, 0.0070 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.30$ (s, 27H; triazole C*H*), 7.13, 6.86 (2d, $J=11$ Hz, 36H; p-$\mathrm{C_6\mathit{H}_4}$), 4.70, 4.26, 4.04 (s, 243H; Cp), 3.50 (s, 18H; $\mathrm{SiC\mathit{H}_2O}$), 3.82 (s, 54H; $\mathrm{SiC\mathit{H}_2N}$), 1.58 (s, 72H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.10 (s, 72H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.57 (s, 18H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.050 ppm (s, 54H; $\mathrm{Si(C\mathit{H}_3)_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): $\delta=159.0$ ($\mathrm{O\mathit{C}_{Ar}}$), 146.2 ($\mathrm{C_q}$ of triazole), 139.1 (aromatic $\mathrm{C_q}$ of the dendron), 127.2, 113.6 (unsubstituted arene *C* of the dendron), 119.8 (*C*H of outer triazole), 76.1 ($\mathrm{C_q}$ of Cp), 69.6, 68.6, 66.5 (*C*H of Cp), 60.3 ($\mathrm{Si\mathit{C}H_2O}$), 43.1 (benzylic $\mathrm{\mathit{C}_q}$ of the core and dendron), 40.8 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 30.3 ($\mathrm{Si\mathit{C}H_2N}$), 17.4 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 15.3 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), 0.0023 ($\mathrm{Si(\mathit{C}H_3)_2CH_2O}$), −3.8, −4.4 ppm ($\mathrm{Si(\mathit{C}H_3)_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=2.97$ ($\mathrm{\mathit{Si}CH_2N}$), 0.54 ppm ($\mathrm{\mathit{Si}CH_2O}$); elemental analysis calcd (%) for $\mathrm{C_{612}H_{840}O_9N_{81}Si_{36}Fe_{27}}$: C 61.28, H 7.06; found: C 61.70, H 7.16.

Synthesis of 18-G$_2$b: The 81-ferrocenyltriazole dendrimer **18**-G$_2$b was synthesized from **16** (0.060 g, 0.0029 mmol) and ethynylferrocene by using the general procedure for "click" reactions. The product was obtained as an orange waxy product in 86% yield (0.095 g, 0.0025 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.30$ (s, 27H; triazole C*H*), 7.13, 6.86 (brs, 36H; p-$\mathrm{C_6\mathit{H}_4}$), 4.70, 4.26, 4.04 (s, 243H; Cp), 3.50 (s, 18H; $\mathrm{SiC\mathit{H}_2O}$), 3.82 (s, 54H; $\mathrm{SiC\mathit{H}_2N}$), 1.58 (s, 72H; $\mathrm{C\mathit{H}_2CH_2CH_2Si}$), 1.10 (s, 72H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.57 (s, 18H; $\mathrm{CH_2CH_2C\mathit{H}_2Si}$), 0.050 ppm (s, 54H; $\mathrm{Si(C\mathit{H}_3)_2}$); ^{13}C NMR ($\mathrm{CDCl_3}$, 75.0 MHz): 159.0 ($\mathrm{O\mathit{C}_{Ar}}$), 146.2 ($\mathrm{C_q}$ of triazole), 139.1 (aromatic $\mathrm{C_q}$ of the dendron), 127.2, 113.6 (unsubstituted arene *C* of the dendron), 119.8 (*C*H of outer triazole), 76.1 ($\mathrm{C_q}$ of Cp), 69.6, 68.6, 66.5 (*C*H of Cp), 60.3 ($\mathrm{Si\mathit{C}H_2O}$), 43.1 (benzylic quaternary *C* of the core and dendron), 40.8 ($\mathrm{\mathit{C}H_2CH_2CH_2Si}$), 30.3 ($\mathrm{Si\mathit{C}H_2N}$), 17.4 ($\mathrm{CH_2\mathit{C}H_2CH_2Si}$), 15.3 ($\mathrm{CH_2CH_2\mathit{C}H_2Si}$), 0.0023 ($\mathrm{Si(\mathit{C}H_3)_2CH_2O}$), −3.8, −4.4 ppm ($\mathrm{Si(\mathit{C}H_3)_2}$); ^{29}Si NMR ($\mathrm{CDCl_3}$, 59.6 MHz): $\delta=2.97$ ($\mathrm{\mathit{Si}CH_2N}$), 0.54 ppm ($\mathrm{\mathit{Si}CH_2O}$); elemental analysis calcd (%) for $\mathrm{C_{612}H_{840}O_9N_{81}Si_{36}Fe_{27}}$: C 61.28, H 7.06; found: C 61.70, H 7.16.

Synthesis of 19: The phenoltriallyl dendron **3** (0.194 g, 0.851 mmol), dry diethyl ether, tripropylsilane (0.808 g, 5.11 mmol, 2 equiv per branch) and the Kartsted catalyst (0.1%) were successively introduced into a Schlenck flask under a nitrogen atmosphere. The reaction solution was stirred at 25 °C for 15 days (several additions of catalyst were necessary to complete the reaction). The solvent was removed under vacuum, and the product was purified by silica chromatography by using pentane/diethyl ether (95.5) as eluent. The product was obtained as a colorless oil (0.238 g, 0.338 mmol) with 40% yield. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta=7.13$, 6.76 (d, $J=11$ Hz, 4H; aromatic C*H*), 4.90 (s, 1H; O*H*), 1.59 (m, 6H; $\mathrm{C_qC\mathit{H}_2}$), 1.29 (m, 18H; $\mathrm{SiCH_2C\mathit{H}_2CH_3}$), 1.03 (m, 6H; $\mathrm{CH_2C\mathit{H}_2CH_2Si}$), 0.93 (m, 27H; $\mathrm{SiCH_2CH_2C\mathit{H}_3}$), 0.48 ppm (m, 18H;

$CH_2SiCH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): 152.8 (C-OH), 140.3 (aromatic C_q), 127.6, 114.5 (aromatic CH), 43.2 (Cq), 42.4 ($CH_2CH_2CH_2Si$), 18.6 ($SiCH_2CH_2CH_3$), 17.8 ($SiCH_2CH_2CH_2$), 17.4 ($SiCH_2CH_2CH_3$), 15.4 ($SiCH_2CH_2CH_3$), 13.5 ppm ($SiCH_2CH_2CH_2$); ^{29}Si NMR ($CDCl_3$, 59.62 MHz): $\delta = 2.16$ ppm ($SiCH_2CH_2CH_3$); elemental analysis calcd (%) for $C_{43}H_{86}OSi_3$: C 73.42, H 12.32; found: C 73.50, H 12.02.

Synthesis of 20: The dendron **19** (0.230 g, 0.327 mmol) and Cs_2CO_3 (0.160 g, 0.490 mmol) were introduced in a Schlenck flask and acetone (30 mL) and propargyl bromide (0.05 mL of a 80% solution in toluene, 0.399 mmol) were added. The mixture was refluxed at 65 °C for 16 h. The solvent was removed under vacuum, the crude product was dissolved with dichloromethane and washed with water. The organic layer was dried with sodium sulfate and filtered over paper; the solvent was removed under vacuum. The product was purified by silica column chromatography with pentane as eluent. A colorless oil was obtained (0.237 g, 98% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.20$, 6.90 (d, $J = 10$ Hz, 4H; aromatic CH), 4.67 (s, 2H; CH_2CCH), 2.49 (CH_2CCH), 1.61 (m, 6H; C_qCH_2), 1.26 (m, 18H; $SiCH_2CH_2CH_3$), 1.04 (m, 6H; $CH_2CH_2CH_2Si$), 0.93 (m, 27H; $SiCH_2CH_2CH_3$), 0.45 ppm (m, 18H; $CH_2SiCH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 155.0$ (arom C–O), 141.0 (arom C_q), 127.3, 113.9 (aromatic CH), 78.8 (CH_2CCH), 75.0 (CH_2CCH), 55.7 (CH_2CCH), 43.1 (Cq), 42.3 ($CH_2CH_2CH_2Si$), 18.5 ($SiCH_2CH_2CH_3$), 17.8 ($SiCH_2CH_2CH_2$), 17.3 ($SiCH_2CH_2CH_3$), 15.3 ($SiCH_2CH_2CH_3$), 13.4 ppm ($SiCH_2CH_2CH_2$); ^{29}Si NMR ($CDCl_3$, 59.62 MHz): $\delta = 4.34$ ($SiCH_2CH_2CH_3$); elemental analysis calcd (%) for $C_{46}H_{88}OSi_3$: C 74.52, H 11.96; found: C 74.67, H 11.82.

Synthesis of 21-G$_1$c: The dendrimer **21**-G$_1$c was synthesized from **16** (0.030 g, 0.0048 mmol) and the dendron **20** (0.141 g, 0.190 mmol) by using the general procedure for "click" reactions. The product **21**-G$_1$c was purified by precipitation in dichloromethane/methanol, and was obtained as a colorless waxy product in 97% yield (0.123 g, 0.0046 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.46$ (s, 27H; triazole CH), 7.18, 6.89 (brs, 144H; arom CH), 5.13 (s, 54H; triazole-CH_2O), 3.86 (s, 54H; $SiCH_2N$), 3.54 (s, 18H; inner-CH_2O), 1.59 (m, 234H; $CH_2CH_2CH_2Si$), 1.26 (m, 486H; $SiCH_2CH_2CH_3$), 1.04 (m, 234H; $CH_2CH_2CH_2Si$), 0.91 (m, 729H; $SiCH_2CH_2CH_3$), 0.65 (m, 234H; $CH_2CH_2CH_2Si$), 0.45 (m, 486H; $SiCH_2CH_2CH_3$), 0.070 ppm (s, 216H; $Si(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 156.2$ (OC_{Ar}), 141.1 (C_q of triazole), 139.8 (arom C_q of the dendron), 127.8, 114.3 (arom CH of the outer dendron), 125.9, 113.8 (arom CH of the inner dendrons), 123.7 (CH of triazole), 75.5 (triazole-CHO), 62.6 (inner CH_2O), 43.6 ($CH_2CH_2CH_2Si$), 42.8 (benzylic quaternary C of the dendrons), 38.5 ($SiCH_2N$), 19.0 ($SiCH_2CH_2CH_3$), 17.8 ($SiCH_2CH_2CH_3$), 17.4 ($CH_2CH_2CH_2Si$), 14.2 ($CH_2CH_2CH_2Si$), 13.9 ($SiCH_2CH_2CH_3$), −3.58 ppm ($Si(CH_3)_2$); elemental analysis calcd (%) for $C_{1530}H_{2919}O_{36}Si_{117}N_{81}$: C 69.83, H 11.18; found: C 69.11, H. 11.16.

Synthesis of 22-G$_1$d: The dendrimer **22**-G$_1$d was synthesized from **16** (0.050 g, 0.0079 mmol) and phenylacetylene (0.033 g, 0.321 mmol) by using the general procedure for "Click" reactions. The product **22**-G$_1$d was obtained as a colorless waxy product in 95% yield (0.068 g, 0.0075 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.79$, 7.37 (m, 135H; arom CH of phenyl), 7.53 (s, 27H; triazole CH), 7.12, 6.83 (brs, 36H; arom CH), 3.85 (s, 54H; $SiCH_2N$), 3.50 (s, 18H; inner-CH_2O), 1.58 (m, 72H; $CH_2CH_2CH_2Si$), 1.08 (m, 72H; $CH_2CH_2CH_2Si$), 0.56 (m, 72H; $CH_2CH_2CH_2Si$), 0.050 ppm (s, 216H; $Si(CH_3)_2$); ^{13}C NMR ($CDCl_3$, 75.0 MHz): $\delta = 159.1$ (Cq of phenyl), 135.7, 130.8, 125.5 (CH of phenyl), 151.5 (OC_{Ar}), 147.3 (C_q of triazole), 139.8 (aromatic C_q of the dendron), 127.8, 113.5 (arom CH of dendron), 125.5 (CH of triazole), 60.3 (CH_2O), 43.9 ($CH_2CH_2CH_2Si$), 42.9 (benzylic quaternary C of the dendrons), 34.2 ($SiCH_2N$), 17.4 ($CH_2CH_2CH_2Si$), 14.2 ($CH_2CH_2CH_2Si$), −3.88 ppm ($Si(CH_3)_2$); ^{29}Si NMR ($CDCl_3$, 59.6 MHz): $\delta = 2.97$ ppm ($Si(CH_3)_2$); elemental analysis calcd (%) for$C_{504}H_{705}N_{81}Si_{36}O_9$: C 66.86, H 7.85; found: C 66.17, H 7.81.

General procedure for the preparation of the PdNP's (the procedure is described using preparation of DSN-12-G$_0$ as an example)

Method 1: A solution of dendrimer **12**-G$_0$ (2.0 mg, 5.87×10^{-4} mmol) in chloroform (2 mL) was placed in a Schlenk flask under nitrogen. A solution of $Pd(OAc)_2$ (1.2 mg, 5.28×10^{-3} mmol, 1 equiv per triazole) in chloroform (1.2 mL) was added. Chloroform (0.8 mL) and methanol (2 mL) were added in order to obtain a solution 8.82×10^{-4} M in Pd, 2:1 ($CHCl_3$/MeOH). The solution was stirred for 5 min, $NaBH_4$ (2 mg, $5.87x10^{-2}$ mmol, 10 equiv per Pd) was added, and the yellow solution turned to golden brown indicating the nanoparticle formation.

Method 2: A solution of dendrimer **12**-G$_0$ (2.0 mg, $5.87x10^{-4}$ mmol) in chloroform (2 mL) was introduced into a Schlenk flask under nitrogen. of a $4.5x10^{-3}$ M A solution of $Pd(OAc)_2$ (1.2 mg, $5.28x10^{-3}$ mmol, 1 equiv per triazole) in chloroform (1.2 mL) was added. Chloroform (0.8 mL) and methanol (2 mL) were added in order to obtain a solution 8.82×10^{-4} M in Pd, 2:1 ($CHCl_3$/MeOH). The solution was stirred for 16 h and turned from yellow to golden brown indicating the nanoparticle formation.

Hydrogenation reactions: The nanoparticles were freshly prepared in a Schlenck flask in order to obtain a solution 8.82×10^{-4} M (in Pd), in $CHCl_3$/MeOH (2:1), and 1000 equiv of the substrate was added. The Schlenck flask was filled with H_2 (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 turn over frequency (TOF) was carried out by using several samples of the solution that were extracted at different reaction times and analyzed. Calculation of the turn over number (TON) was carried out by using the sum of substrate that reacted in all the catalytic cycles, after analyzing the final reaction solution.

Acknowledgements

We are grateful to Dr. Eric Cloutet (LCPO, Bordeaux) for helpful assistance in the SEC and DLS experiments, and to Fundação para a Ciência e a Tecnologia (FCT), Portugal (Ph.D. grant to C.O.), the Institut Universitaire de France (IUF, DA), the CNRS, and the Université Bordeaux I for financial support.

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Received: September 6, 2007