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Water-soluble glycodendrimers: synthesis and stabilization of catalytically active Pd and Pt nanoparticles

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ABSTRACT

A new water-soluble glycodendrimer containing 9 terminal modified xylose branches was prepared from nona-azide terminated dendrimer by 'click' chemistry. The glycodendrimer was analyzed by ^{1}H, ^{13}C NMR and mass spectroscopy and used to stabilize palladium (PdNPs) and platine (PtNPs) nanoparticles. These DSN are stable in water and were characterized by TEM. The platinum NPs showed a remarkable catalytically activity for olefin hydrogenation in water at room temperature.

Cheap molecules such as D-xylose and L-arabinose derived from corn are building blocks of choice for the formation of various compounds with a broad spectrum of applications. Recently, we have chosen to valorize these sugars in glycodendrimer chemistry,[1] an area developed by Roy's group, that we wish to apply to catalysis and vectorization.

Dendrimers[2] can be used in various fields of nanosciences such as nanoreactors,[3] molecular micelles,[4] drug vectors,[5] sensors,[6] green catalysts,[7] supramolecular electronics,[8] and light-harvesting devices,[9] and in these areas water solubility is a key factor.

The contribution of dendrimers in the catalysis field is well established, and many studies have clearly shown that dendrimers have high catalytic activities. Crooks and his group have shown that dendrimers can stabilize transition-metal nanoparticles in solution. The presence of 'hydrophobic areas' within the dendrimer allows the development of highly selective catalytic processes, the dendrimer playing the role of an efficient 'nanofilter'.[3a–c] The function of dendrimers as micelles has been pioneered by Newkome in his seminal publication on 'arborols',[4] and Tomalia, Meijer and Zimmerman have also shown useful dendrimer encapsulation of guest molecules in early reports.[10] Recently, Astruc et al. described the use of recyclable dendritic nanoreactors for the catalysis of olefin metathesis reactions in water using the classical Grubbs catalysts.[11] Amphiphilic glycodendrimers having a chiral surface found potential applications in enantioselective catalysis,[1b–d,12] and the supramolecular interaction between sugars and proteins such as for instance lectins,[13] are involved in nanomedicine.[1f,g,l,2c]

Recently, we reported the syntheses of a series of large glycodendrimers containing 27, 81, and 243 terminal modified xylose branches by 'click' chemistry.[1i] However, the mildly basic conditions (MeONa) used to cleave the acetate group in order to give glycodendrimers with free hydroxyl groups resulted in their decomposition. This led us to envisage a new synthetic route to dendrimers decorated by unprotected sugar entities. We first used the known dendrimer core[14] **1** (Scheme 1) to induce a Huisgen-type 1,3 dipolar 'click' reaction of the azido-terminated dendrimer with 2′-(prop-2-ynyloxy) 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside.[15] After cleavage of acetate groups in basic medium, this reaction yielded a xylose-terminated water-soluble dendrimer containing nine sugar termini (Scheme 1).

The nona-azide core **1** was treated with 2′-(prop-2-ynyloxy) 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside in the presence of $CuSO_4$ (4 equiv per branch) in stoichiometric amount and sodium ascorbate (8 equiv per branch) in aqueous tetrahydrofuran (H_2O/THF 1:1). The excess of Cu salt was removed as $[Cu(NH_3)_2(H_2O)_2][SO_4]$ by washing ten times with an ammonia solution. The desired protected glycodendrimer **2** was purified by precipitation with CH_2Cl_2/Et_2O in order to remove the excess sugar, and the reaction yield was 52%.[16] The presence of signals in the ^{1}H NMR spectrum at 7.40 ppm and the ^{13}C NMR spectrum at 124.1 and 144.2 ppm unambiguously proved

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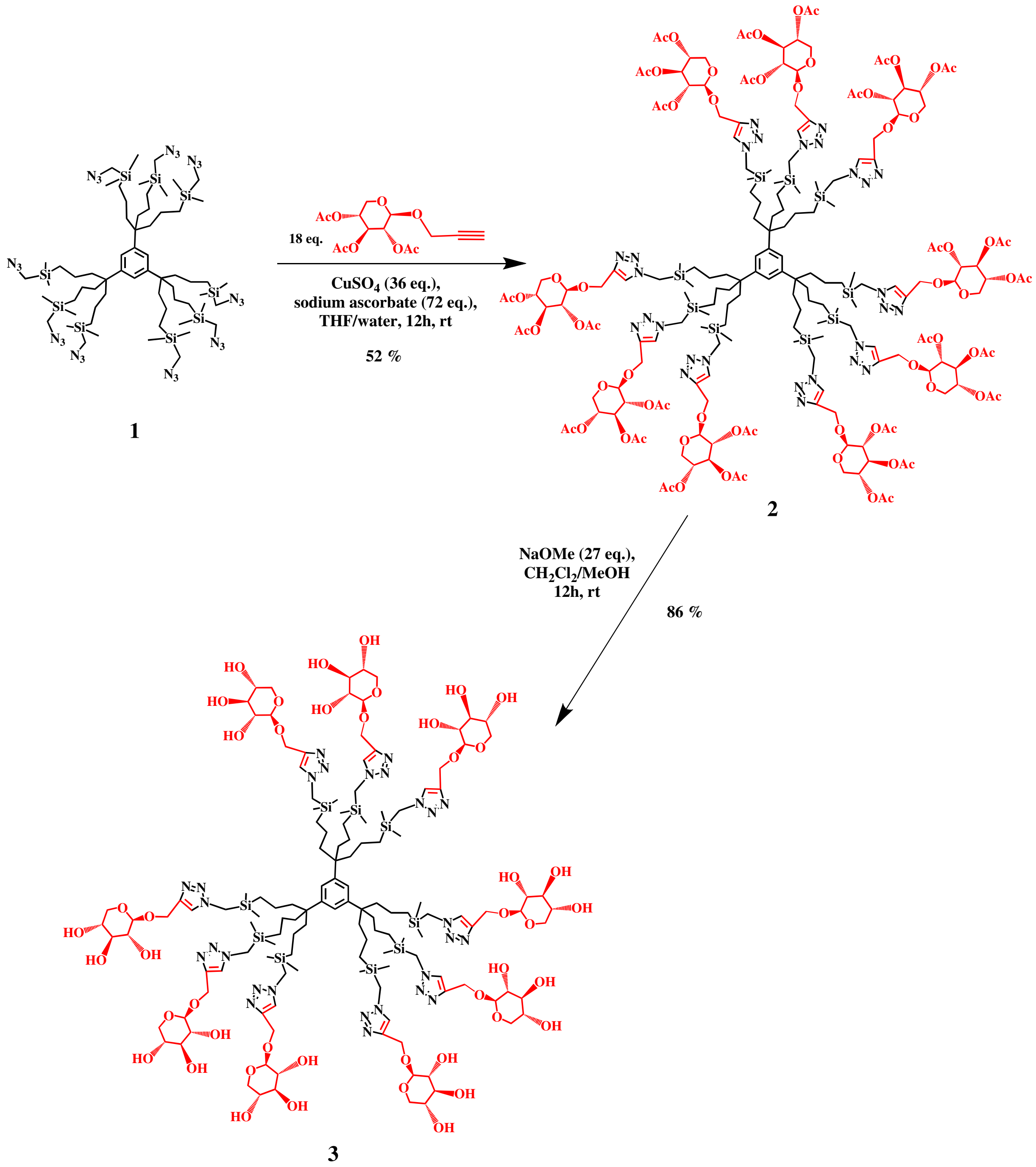


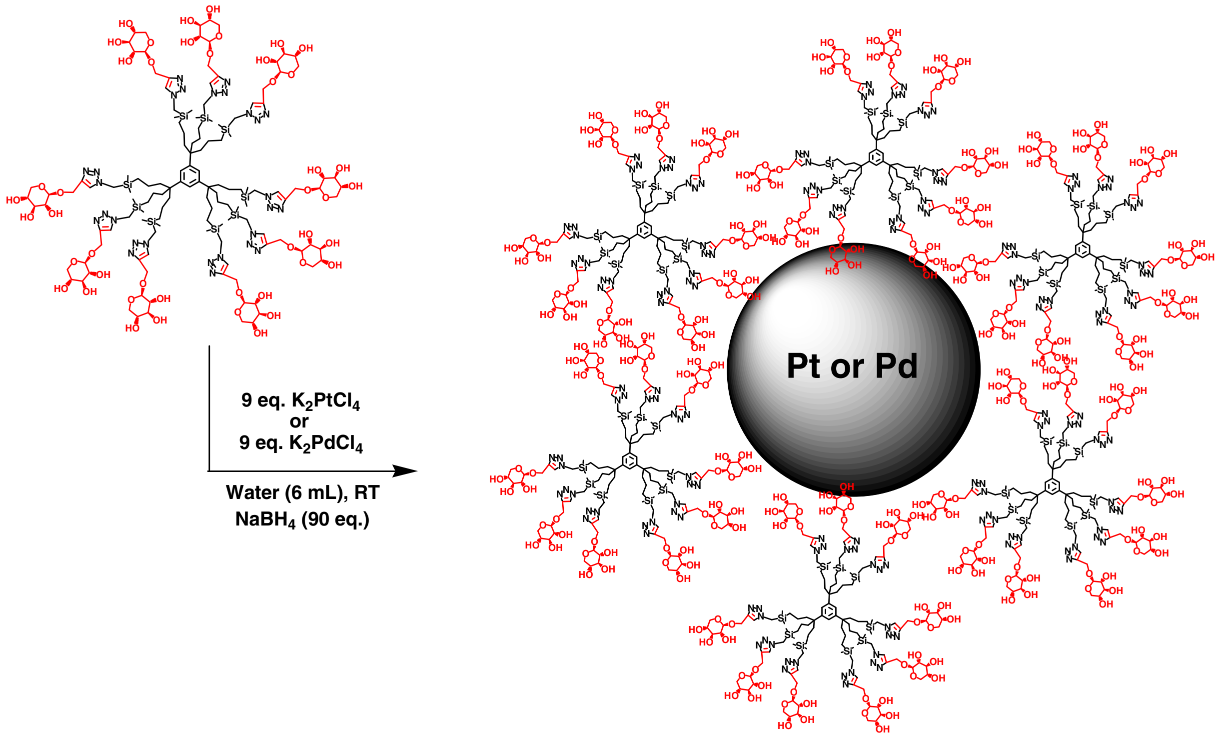
Scheme 1. Synthesis of the glycodendrimer **3** in two steps from the nona-azide core **1**.

the formation of the triazole ring, and the composition of compound **2** was further confirmed by elemental analysis.

The acetylated glycodendrimer **2** was then quantitatively deprotected in the presence of sodium methanolate to give glycodendrimer **3** with free hydroxyl groups. Compound **3** was purified by precipitation with MeOH/Et_2O and characterized by ^1H, ^{13}C NMR spectroscopy and mass spectroscopy.[17] No signals were found for methyl groups or carbonyl carbons in the ^1H and ^{13}C NMR spectra, respectively. The mass spectrum of **3** contained peaks at m/z 3233.4 and m/z 1628.2 corresponding to [M+Na] and [M/2+Na], respectively.

Furthermore, we noticed that a diluted solution of **3** in water showed considerable foaming, which is a good indication for the surfactant properties of this dendrimer. The glycodendrimer **3** was used as a template for the preparation of palladium nanoparticles (PdNPs) and platinum nanoparticles (PtNPs) in water. Reactions between K_2MCl_4 (M = Pd or Pt) and **3** in the presence of $NaBH_4$ as the reducing agent led in less than 10 min. to the formation of nanoparticles stabilized by the dendrimer **3** (Scheme 2).[18] Brown solutions were obtained and the reduction of Pd^{II} to Pd^0 was confirmed by the decrease of the shifts in ^1H NMR of dendrimer **3**, as previously reported.[19]

The TEM data (Figs. 1 and 2) show that DSNs with a diameter of 4.7 ± 0.4 nm for PdNPs (3624 Pd atoms stabilized by 403 dendrimers) and of 14.0 ± 3.0 nm for PtNPs (89795 Pt atoms for 9978 dendrimers) were formed. The TEM data also show that the PtNPs are more monodisperse than the PdNPs and, therefore, appear to be more suitable for careful catalytic studies.[3]



Scheme 2. Formation and stabilization of Pd and Pt nanoparticles in water.

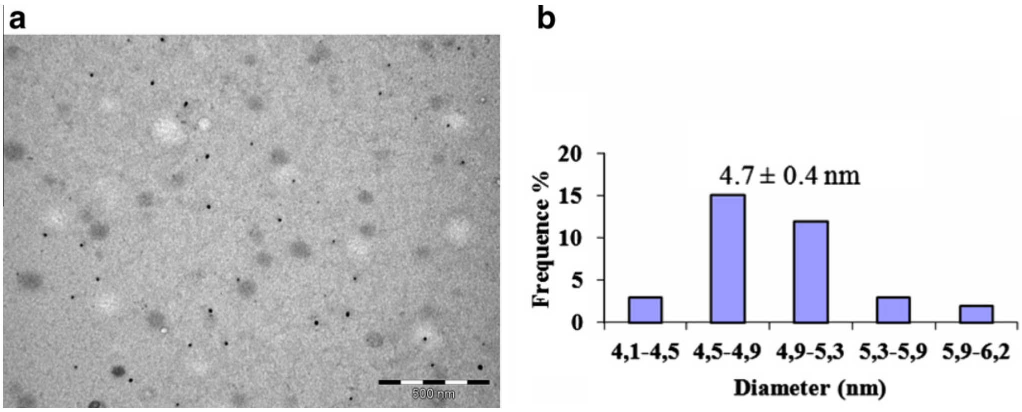


Figure 1. PtNPs: (a) TEM image and (b) size distribution.

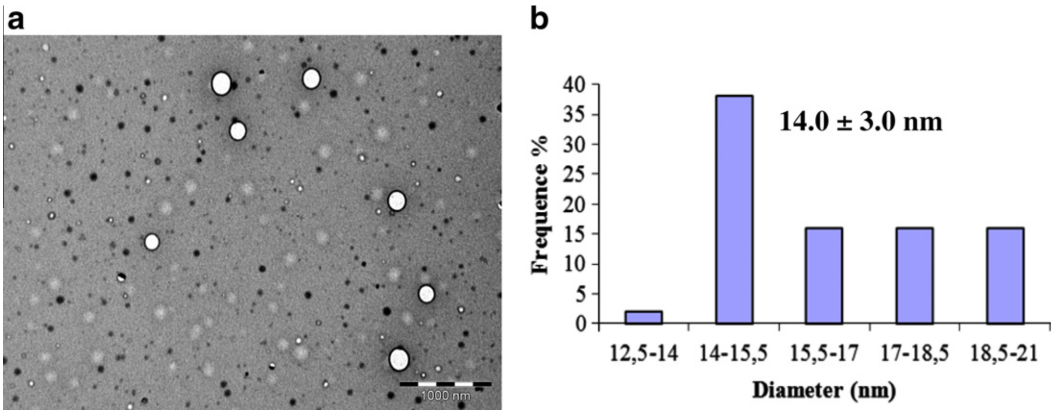
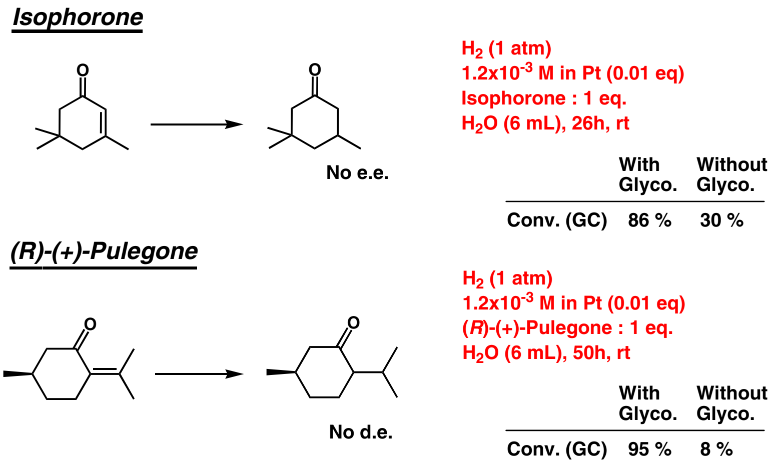


Figure 2. PdNPs: (a) TEM image and (b) size distribution.



	With Glyco.	Without Glyco.
Conv. (GC)	86 %	30 %

	With Glyco.	Without Glyco.
Conv. (GC)	95 %	8 %

Scheme 3. Hydrogenation reactions in the presence of Pt nanoparticles stabilized by the glycodendrimer **3**.

Solutions containing PtNPs were used in hydrogenation reactions with isophorone and (*R*)-(+)-pulegone (Scheme 3). The hydrogenation reactions were conducted under an H_2 atmosphere at room temperature in water.[20] Remarkably, for the isophorone, we found that the conversion of the substrate in the presence of PtNPs stabilized by glycodendrimer **3** proceeded more rapidly than the same reaction performed in the absence of glycodendrimer. Similar observations were made for the hydrogenation of (*R*)-(+)-pulegone for which the influence of glycodendrimer **3** was much more significant (Scheme 3).

Unfortunately, no stereoselectivity was observed even in the presence of the chiral sugar used as the decorating entities. Catalytic experiments are underway in order to tentatively benefit from the chiral character of the glycodendrimer, as well as to recycle the catalyst.

In conclusion, we have described here the preparation of a new Si-based dendrimer decorated with D-xylose groups using click chemistry. This water-soluble dendrimer can be used for the preparation and stabilization of Pd and Pt nanoparticles in water. Preliminary catalytic hydrogenation studies in water in the absence of co-solvent using Pt stabilized nanoparticles showed promising results.

Acknowledgments

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References and notes

1. (a) Roy, R. *Curr. Opin. Struct. Biol.* **1996**, *6*, 692; (b) Schmitzer, A.; Perez, E.; Rico-Lattes, I.; Lattes, A. *Tetrahedron Lett.* **1999**, *40*, 2947; (c) Schmitzer, A.; Perez, E.; Rico-Lattes, I.; Lattes, A.; Rosca, S. *Langmuir* **1999**, *15*, 4397; (d) Schmitzer, A.; Perez, E.; Rico-Lattes, I.; Lattes, A. *Tetrahedron: Asymmetry* **2003**, *14*, 3719; (e) Roy, R. *Trends Glycosi. Glycotechnol.* **2003**, *85*, 291; (f) Touaiba, M.; Wellens, A.; Tze, C. S.; Wang, Q.; Sirois, S.; Bouckaert, J.; Roy, R. *ChemMedChem* **2007**, *2*, 1190; (g) Chabre, Y. M.; Roy, R. *Curr. Top. Med. Chem.* **2008**, *8*, 1237; (h) Rajakumar, P.; Anandhan, R.; Kalpana, V. *Synlett* **2009**, *9*, 1417; (i) Camponovo, J.; Hadad, C.; Ruiz, J.; Cloutet, E.; Gatard, S.; Muzart, J.; Bouquillon, S.; Astruc, D. *J. Org. Chem.* **2009**, *74*, 5071; (j) Hadad, C.; Majoral, J.-P.; Muzart, J.; Caminade, A.-M.; Bouquillon, S. *Tetrahedron Lett.* **2009**, *50*, 1902; (k) Kikkeri, R.; Liu, X.; Adibekian, A.; Tsai, Y.-H.; Seeberger, P. H. *Chem. Commun.* **2010**, *46*, 2197; (l) Chabre, Y. M.; Roy, R. *Adv. Carbohydr. Chem. Biochem.* **2010**, *63*, 165.
2. (a) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74; (b) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *III. Angew. Chem., Int. Ed.* **1990**, *29*, 138; (c) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665; (d) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857; (e) Newkome, G. R.; Shreiner, C. *Chem. Rev.* **2010**, *110*, 6338.
3. (a) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181; (b) Niu, Y.; Crooks, R. M. C. R. *Chimie* **2003**, *6*, 1049; (c) Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. J. *Phys. Chem. B* **2005**, *109*, 692; (d) Krämer, M.; Pérignon, N.; Haag, R.; Marty, J.-D.; Thomann, R.; Lauth-de Viguerie, N.; Mingotaud, C. *Macromolecules* **2005**, *38*, 8308; (e) Astruc, D.; Ornelas, C.; Ruiz, J. *Acc. Chem. Res.* **2008**, *41*, 841.
4. (a) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. J. *Org. Chem.* **1985**, *50*, 2003; (b) Newkome, G. R.; Moorefield, C. N. *Aldrichimica Acta* **1992**, *25*, 31; (c) Newkome, G. R. *Pure Appl. Chem.* **1998**, *70*, 2337; (d) Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Behera, R. K.; Escamillia, G. H.; Saunders, M. J. *Angew. Chem., Int. Ed.* **1992**, *31*, 917.
5. (a) Astruc, D. C. R. *Acad. Sci.* **1996**, *322*, 757; (b) Pistolis, G.; Malliaris, A.; Paleos, C. M.; Tsiourvas, D. *Langmuir* **1997**, *13*, 5870; (c) Jansen, J. F. G. A.; den Berg, E. M. M.; Meijer, E. W. *Science* **1999**, *266*, 1226; (d) Liu, M.; Kono, K.; Fréchet, J. M. J. *J. Controlled Release* **2000**, *65*, 121; (e) Malik, N.; Wiwattanapatapee, R.; Klopsch, R.; Lorenz, K.; Frey, H.; Weener, J. W.; Meijer, E. W.; Paulus, W.; Duncan, R. J. *Controlled Release* **2000**, *65*, 133; (f) Guillot-Nieckowski, M.; Eisler, S.; Diederich, F. *New J. Chem.* **2007**, *31*, 1111; (g) Caminade, A.-M.; Turrin, C.-O.; Majoral, J.-P. *Chem. Eur. J.* **2008**, *14*, 7422; (h) Boisselier, E.; Astruc, D. *Chem. Soc. Rev.* **2009**, *38*, 1759.
6. (a) Daniel, M.-C.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **2003**, *125*, 1150; (b) Daniel, M.-C.; Ruiz, J.; Nlate, S.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **2003**, *125*, 2617; (c) Astruc, D. *Pure Appl. Chem.* **2003**, *75*, 461; (d) Astruc, D.; Daniel, M.-C.; Ruiz, J. *Chem. Commun.* **2004**, 2637; (e) Ashton, P. R.; Balzani, V.; Clemente-Leon, M.; Colonna, B.; Credi, A.; Jayaraman, N.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *Chem. Eur. J.* **2002**, *8*, 673.
7. (a) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828; (b) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991; (c) Kleij, A. W.; Ford, A.; Jastrzebski, J. T. B. H.; van Koten, G. In *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; Wiley: New York, 2002; p 185; (d) Chase, P. A.; Klein Gebbink, R. J. M.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 4016; (e) Astruc, D.; Heuze, K.; Gatard, S.; Méry, D.; Nlate, S.; Plault, L. *Adv. Synth. Catal.* **2005**, *347*, 329; (f) Méry, D.; Astruc, D. *Coord. Chem. Rev.* **2006**, *250*, 1965; (g) Helms, B.; Fréchet, J. M. J. *Adv. Synth. Catal.* **2006**, *348*, 1125; (h) Andrés, R.; de Jesus, E.; Flores, J. C. *New J. Chem.* **2007**, *31*, 1161.
8. (a) Wang, P.-W.; Liu, Y.-J.; Devadoss, C.; Bharati, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237; (b) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978; (c) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286; (d) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219–221*, 545; (e) Daniel, M.-C.; Sakamoto, A.; Ruiz, J.; Astruc, D.; Nishihara, H. *Chem. Lett.* **2006**, *35*, 38.
9. (a) Juris, A.; Balzani, V.; Barrigelletti, F.; Campagna, S.; Denti, G.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26; (b) Andronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701.
10. (a) Naylor, A. M.; Goddart, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339; (b) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.
11. Diallo, A. K.; Boisselier, E.; Liang, L.; Ruiz, J.; Astruc, D. *Chem. Eur. J.* **2010**, *16*, 11832.
12. Schmitzer, A. R.; Franceschi, S.; Perez, E.; Rico-Lattes, I.; Lattes, A.; Thion, L.; Erard, M.; Vidal, C. *J. Am. Chem. Soc.* **2001**, *123*, 5956.
13. Lis, H.; Sharon, N. *Chem. Rev.* **1998**, *98*, 637.
14. Dendrimer **1** was prepared by $CpFe^+$-induced nona-allylation of mesitylene in $[CpFe(\eta^6\text{-mesitylene})][PF_6]$,[14a] followed by decomplexation using visible-light,[14b,c] hydrosilylation with $HSiMe_2CH_2Cl$ and reaction with NaN_3 as

already reported. For a recent application, see ref.[14d]. (a) Moulines, F.; Astruc, D. *Angew. Chem., Int. Ed., 1988*, *27*, 1347. (b) Catheline, D.; Astruc, D. *J. Organomet. Chem*. **1983**, *248*, C9. (c) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417. (d) Boisselier, E.; Diallo, A. K.; Salmon, L.; Ornelas, C.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **2010**, *132*, 2729.

15. Ding, H.; Yang, R.; Song, Y.; Xiao, Q.; Wu, J. *Nucleosides, Nucleotides and Nucleic Acids* **2008**, *27*, 368.
16. *Preparation of glycodendrimer **2**:* To a solution of dendrimer **1** (1.0 equiv) in a THF/water 1:1 (v:v) mixture were added 2′-(prop-2-ynyloxy) 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (2.0 equiv per branch), $CuSO_4.5H_2O$ (4.0 equiv per branch), and sodium ascorbate (8.0 equiv per branch). The mixture was stirred at room temperature under an argon atmosphere for 12 h. The mixture was concentrated and CH_2Cl_2 was added. The organic layer was washed with aqueous ammonium hydroxide until a colorless aqueous layer was obtained and then with water to neutrality. The organic phase was concentrated to dryness in vacuo. The crude product was dissolved in a minimum of CH_2Cl_2 and precipitated with excess of diethylether. The glycodendrimer **2** was obtained as a colorless oil in 52% yield. Data for glycodendrimer **2** $C_{189}H_{291}N_{27}O_{72}Si_9$: MW 4346.27 g mol^{-1}; yield 52%; NMR ^1H (250 MHz, $CDCl_3$, 25 °C, TMS) 0.05 (s, 54 H, $Si(CH_3)_2$), 0.63 (s, 18H, $CH_2CH_2CH_2Si$), 1.09 (s, 18H, $CH_2CH_2CH_2Si$), 1.62 (s, 18H, $CH_2CH_2CH_2Si$), 1.97–2.03 (m, 81 H, CH_3 sugar), 3.36 (m, 9H, H_{5a} sugar), 3.83 (s, 18H, Si-CH_2–$N_{triazole}$), 4.10 (dd, $J = 5$ Hz, $J = 12.5$ Hz, 9H, H_{5e} sugar), 4.60 (d, $J = 7.5$ Hz, 9H, H_1sugar), 4.66-4.93 (m, 18H+9H+9H, $H_{1'}+H_3+H_4$ sugar), 5.13 (m, 9H, H_2 sugar), 6.93 (s, 3H, H_{Ar}), 7.40 (s, 9H, $H_{triazole}$). NMR $^{13}C\{^1H\}$ (250 MHz, $CDCl_3$, 25 °C, TMS) −3.44 (CH_3), 15.4 (CH_2), 18.1 (CH_2), 21.2 (CH_3), 41.4 (CH_2), 42.2 (CH_2), 44.3 (C), 62.6 (CH_2), 63.1 (CH_2), 69.3 (CH), 71.2 (CH), 71.9 (CH), 100.4 (CH), 121.6 (CH), 124.1 (CH), 144.2 (C), 146.2 (C), 169.9 (C), 170.3 (C), 170.4 (C). Anal. Found (Calcd) for $C_{189}H_{291}N_{27}O_{72}Si_9 + 5H_2O$: C 51.17 (51.17), H 6.59 (6.84), N 8.35 (8.52).
17. *Preparation of glycodendrimer **3**:* The acetylated dendrimer **2** (168 mg, 38.7 mmol) was dissolved in 1/1 MeOH-CH_2Cl_2 and a 0.5 M solution of NaOMe (1.5 equiv per branch, 2.08 mL) was then added. After stirring for 24 h at room temperature, the mixture was neutralized with Amberlite IR120 and filtered. The organic phase was concentrated to dryness in vacuo, and the crude product was dissolved in a minimum of MeOH and precipitated with an excess of diethylether. The glycodendrimer **3** was obtained as a white solid in 86% yield ($m = 107$ mg). Data for glycodendrimer **3** $C_{135}H_{237}N_{27}O_{45}Si_9$: MW 3211.27 g mol^{-1}; NMR ^1H (250 MHz, CD_3OD, 25 °C): 0.00 (s, 54 H, $Si(CH_3)_2$), 0.59 (s, 18H, $CH_2CH_2CH_2Si$), 1.11 (s, 18H, $CH_2CH_2CH_2Si$), 1.64 (s, 18H, $CH_2CH_2CH_2Si$), 3.14–3.35 (m, 9H+9H+9H, $H_{5a}+H_2+H_3$ sugar), 3.47 (m, 9H, H_4), 3.86 (dd, $J = 5$ Hz, $J = 12.5$ Hz, H_{5e}), 3.94 (s, Si-CH_2-$N_{triazole}$), 4.31 (d, $J = 7.5$ Hz, 9H, H_1), 4.76 (m, 18H, $H_{1'}$ sugar), 4.93 (s, 18H, -OH), 7.03 (s, 3H, H_{Ar}), 7.81 (s, 9H, $H_{triazole}$). NMR $^{13}C\{^1H\}$ (250 MHz, CD_3OD, 25 °C): −3.03 (s, CH_3), 16.3 (CH_2), 19.4 (CH_2), 42.4 (CH_2), 43.4 (CH_2), 45.6 (C), 63.6 (CH_2), 67.4 (CH_2), 71.5 (CH), 75.2 (CH), 78.1 (CH), 104.7 (CH), 123.5 (CH), 126.4 (CH), 145.8 (CH_2), 147.7 (C). MS m/z for $C_{135}H_{237}N_{27}O_{45}Si_9Na$ found (calcd): 3233.4 (3234.3) and for $C_{67.5}H_{118.5}N_{13.5}O_{22.5}Si_{4.5}Na$ found (calcd) 1628.2 (1628.7).
18. *General procedure for the preparation of PtNPs and PdNPs*: A solution of glycodendrimer **3** (2.6 mg, $8.02.10^{-7}$ mol) in water (2 mL) was placed in a Schlenk flask under argon. A solution of K_2PtCl_4 (3 mg, $7.22.10^{-6}$ mol, 1 equiv per triazole) or K_2PdCl_4 (2.3 mg, $7.22.10^{-6}$ mol, 1 equiv per triazole) in water (2 mL) was added. The solution was stirred for 5 min, $NaBH_4$ (2.7 mg, $7.22.10^{-5}$ mol, 10 equiv per Pt) in solution in water (2 mL) was added, and the solution turned a little bit brown indicating the nanoparticle formation.
19. Ornelas, C.; Salmon, L.; Ruiz, J.; Astruc, D. *Chem. Commun.* **2007**, 4946.
20. *General procedure for hydrogenation reactions with PtNPs:* PtNPs were freshly prepared in a Schlenk flask in an aqueous solution ($1.2.10^{-3}$ M in Pt), and 100 equiv of the substrate were added. The Schlenk flask was filled with H_2 and the solution was allowed to stir at 25 °C. After respectively, for the isophorone and the (*R*)-(+)-pulegone, 26 and 50 h, the mixture is analyzed by gas chromatography (injector temperature, 250 °C; split injection mode; carrier gas, nitrogen at 1 mL min^{-1}; initial oven temperature, 60 °C, 1 min; rate, 10 °C min^{-1}; final temperature, 250 °C, 2 min; detector, 300 °C; solvent, diethyl ether). The retention times were found to be approx. 8 min for the isophorone and 7 min for the corresponding hydrogenated product.